

An Investigation of the Formation of Active Sites in Fe-N-C Electrocatalysts for the Oxygen Reduction Reaction

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Reduction Reaction

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An Investigation of the Formation of Active Sites in Fe-N-C Electrocatalysts for the Oxygen Reduction Reaction

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i. Abstract

Polymer electrolyte membrane fuel cells (PEFCs) are clean, efficient and sustainable energy conversion devices poised to succeed traditional fossil fuels in power supplies. They have seen a continuous growth in development towards commercialization. However, the cost of platinum hinders their breakthrough. Therefore, research into alternative earth-abundant metal catalysts is of paramount importance. Catalysts consisting of pyrolysed mixtures of iron-, nitrogen- and carbon-containing compounds (Fe-N-C) have shown promising activity towards the oxygen reduction reaction (ORR) in PEFCs. Many groups around the world have used a variety of synthesis methods and precursors, yielding Fe-N-C catalysts with widely varying properties. Their design and optimization is generally based on an empirical approach, rather than rational design. Therefore, the main objective of this thesis was to understand the processes involved in the formation of active sites in Fe-N-C catalysts.

In Chapter 1, the progress and limitations of platinum catalyzed PEFCs were explained. Then, progress in the study of Fe-N-C materials as alternative catalysts to conventional platinum-supported carbons was outlined. The lack of empirical and systematic synthesis methods was highlighted as a major hinderance to understanding the catalytic mechanisms of the produced Fe-N-C catalysts, justifying the need to study formation mechanisms of Fe-N-C catalysts. In order to achieve this objective, a two-step method was used to synthesize model Fe-N-C catalysts. The first step involved the synthesis and optimisation of template-free nitrogen-doped carbon foams as model supports and the second step focused on iron-decoration onto the support.

In Chapter 2, the different experimental methods used in this thesis were explained in detail.

In Chapter 3, template-free nitrogen-doped carbon foams were synthesized as model electrocatalyst supports. The purpose of this was to reduce the number of possible variables during

Fe-N-C catalyst synthesis, due to their relatively stable surface area, porosity and nitrogen content. These foams were first optimized and screened for their electrochemical activity before moving to the next synthesis step.

In Chapter 4, the iron decoration synthesis step was investigated. Different iron precursors, namely iron acetate (FeAc), iron chloride (FeCl₃), and iron phthalocyanine (FePc), were adsorbed onto the surface of the support, heat-treated at 900 °C in ammonia, and acid washed in 1 M H₂SO₄. The resulting properties were compared, whilst their ORR activity was determined using rotating ring disk electrode voltammetry. Catalysts synthesized using FeCl₃ precursors showed the best ORR performance, followed by those synthesized using FeAc and FePc. A combination of different properties were concluded to be effective towards the creation of ORR sites, namely: (i) large micropore surface area for hosting active sites; (ii) wide pore diameter and high mesopore/micropore volume ratio for enhanced mass diffusion; and (iii) a high proportion of Fe-N bonds to act as ORR active centers.

In Chapter 5, in situ techniques were used to investigate the changes that occurred during heat treatment and subsequent exposure to oxygen. Quadrupole mass spectrometry (QMS) was used to determine the decomposition mechanisms during synthesis, providing new evidence for the formation of carbon-encapsulated iron nanoparticles in Fe-N-C catalysts (i.e. via iron-catalyzed growth of graphitic carbon), and the increase in pore diameter and pore volume in FeAc and FeCl₃-based catalysts (i.e. via iron catalyzed steam gasification of the carbon support). High temperature X-ray photoelectron spectroscopy (HT-XPS) was used to confirm that Fe-N bonds are retained in significant amounts during pyrolysis, and that these correlate with the ORR activity. Near ambient pressure XPS (NAP-XPS) was used to investigate the adsorption of oxygen on the surface of electrocatalysts. However, no new bonds were detected, and it was thus inferred that O₂ and/or

H₂O mainly bind to Fe atoms in the electrocatalysts, or that the application of a potential is required to observed significant changes.

In Chapter 6, in-situ electrochemical X-ray adsorption spectroscopy (XAS) was used to probe specific changes in the oxidation state of iron during the ORR. A correlation between the proportion of Fe-N bonds and the amount of oxygen adsorption during the ORR also corresponded with the increasing ORR activity. As such, oxygen adsorption was concluded to occur on the iron atoms coordinated to nitrogen.

In Chapter 7, the findings of the previous chapters were summarized. Overall, these results provided significant new insights into the formation mechanisms of Fe-N-C electrocatalysts. The use of thermally-stable nitrogen-doped carbon foams as a support for different iron precursor allowed changes in the nature of the adsorbed iron precursor to be systematically investigated. It was concluded that a combination of large microporous surface area, high mesoporous to microporous volume ratio, and a high proportion of accessible Fe-N sites residing in the micropores is essential in creating highly active Fe-N-C electrocatalysts. In particular it was newly concluded that: i) wide micropores generated by iron-catalyzed steam gasification during decomposition of the iron precursor contribute significantly to enhanced ORR activity by increasing the active site density; ii) iron-catalyzed growth of graphitic carbon results in the formation of iron-encapsulated iron nanoparticles (however, these do not correlate with the ORR activity); and iii) that the ORR activity correlates with the abundance of accessible Fe-N sites. This study provides clues for the development of new Fe-N-C catalysts with enhanced ORR activity in the future.

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iii. Peer Reviewed Publications

1. *Insights into the Formation of Fe-N-C Foam Electrocatalysts via In-situ High-Temperature X-ray Photoelectron Spectroscopy (HT-XAFS) Measurements*, A. Mufundirwa, T. Sugiyama, S. Yoshioka, K. Ogi, G. F. Harrington, M. Nishihara, K. Sasaki, A. Hayashi, S. M. Lyth, In preparation (2020).
2. *Hydrogen Sorption Characteristics of a High Surface Area Graphenic Foam Derived from Sodium Ethoxide Decomposition*, B. V. Cunning, B. Smid, A. Mufundirwa, H. Shao, E. Akiba, S. M. Lyth, In preparation (2020).
3. *Comparing the Roles of Different Iron Precursors on Formation of ORR Active Sites in Fe-N-C Electrocatalysts*, A. Mufundirwa, C. Gell, T. Sugiyama, S. Yoshioka, G. F. Harrington, K. Sasaki, A. Hayashi, S. M. Lyth, In preparation (2020).
4. *False Positives: Platinum Dissolution from the Counter Electrode Enhances the Activity of Non-PGM Electrocatalysts During Voltammetry Measurements*, A. Eldiven, A. Mufundirwa, G. F. Harrington, K. Sasaki, A. Hayashi, Hubert A. Gasteiger S. M. Lyth, In preparation (2020).
5. *Gram-scale Synthesis of Alkoxide-derived Nitrogen-doped Carbon Foam Supports as a Support for Fe-N-C Electrocatalysts*, A. Mufundirwa, Y. Shundo, G. F. Harrington B. Smid, B. V. Cunning, M. Ismail, M. Pourkashanian, K. Sasaki, A. Hayashi, S.M. Lyth. IOP Nanotechnology, **31**, 225401, 2020.
6. *Durability of Template-free Fe-N-C foams for the Electrochemical Oxygen Reduction in Alkaline Solution*, A. Mufundirwa, G. Harrington, B. Smid, B. V. Cunning, K. Sasaki, S.M. Lyth. Journal of Power Sources, **375**, 244-254, 2018.
7. *Nitrogen-Doped Carbon Foam as a Highly Durable Metal-Free Electrocatalyst for the Oxygen Reduction Reaction in Alkaline Solution*, Jianfeng Liu, B. V. Cunning, Takeshi Daio, A. Mufundirwa, K. Sasaki, S.M. Lyth. Electrochimica Acta, 220, 554-561, October 2016.

iv. Book Chapters

1. *Electrocatalysts in Polymer Electrolyte Membrane Fuel Cells*, S. M. Lyth, A. Mufundirwa. Heterogeneous Catalysts: Emerging Techniques for Design, Characterization and Applications, Wiley-VCH (2020, In Press)

v. Conference Proceedings

1. *Gram-Scale Synthesis of High Surface Area Metal-Free Nitrogen-Doped Carbon Foams for the Oxygen Reduction Reaction*, A. Mufundirwa, Y. Shundo, J. Liu, B. Smid, B. V. Cuning, K. Sasaki, S. M. Lyth, ECS Meeting Abstracts, October 2016.
2. *Gram-Scale Synthesis of Nitrogen-Doped Carbon Foams as Template-Free, Metal-Free, Non-Precious Electrocatalysts for Oxygen Reduction and CO₂ Conversion*, S. M. Lyth, J. Liu, A. Mufundirwa, B. Smid, S. Ma, P.J.A. Kenis, K. Sasaki, 230th ECS Meeting Abstracts, 2770, 2016.
3. *Doped and Decorated Graphene Foam Electrocatalysts*, S. M. Lyth, J. Liu, A. Mufundirwa, K. Sasaki, T. Daio, 226th ECS Meeting Abstracts, 1383, 2014.

vi. Awards

1. *Toshiba and Cataler Company Best Poster Award*, Next-Generation Fuel Cell Research Center (NEXT-FC) Seminar for Industry, Kyushu University, 2020.
2. *Q-PIT Research Support Program for Young Researchers and Doctoral Students* (200,000 JPY), Kyushu University, 2019.
3. *Best Oral Presentation Award*, 4th International Conference on Environment and Renewable Energy (ICERE 2018), Cape Town, South Africa, 2018.
4. *President's Excellence Award*, Kyushu University Energy Week, Japan (2018)
5. *Runner Up Prize for Best Presentation (2nd Place)*, Falling Walls Lab, Tokyo (2017).
6. *Best Poster Award (1st Place)*, PRiME2016 / 230th ECS Meeting (PEFC16 Session), Honolulu, USA (2016).

vii. Oral and Poster Presentations

1. Next-Generation Fuel Cell Research Center (NEXT-FC) Seminar for Industry, Kyushu University, 2020 January (Poster).
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4. Next-Generation Fuel Cell Research Center (NEXT-FC) Seminar for Industry, Kyushu University, 2019 January (Poster).
5. 4th Sheffield-Kyushu Workshop on Electrochemical Energy Conversion (SKWEEK-4), co-sponsored by Royal Society and Japanese Society for the Promotion of Science (JSPS) and Energy, 2019 August (Oral).
6. Carbon-Foam Supported Electrocatalysts for Polymer Electrolyte Membrane Fuel Cells, A. Mufundirwa, T. Sugiyama, S. Yoshioka, K. Ogi, G. F. Harrington, B. Smidt, B. Cuning, K. Sasaki, A. Hayashi, S. M. Lyth, ICERE 2018 (Oral).
7. International Symposium on Novel Energy Nanomaterials, Catalysts and Surfaces for Future Earth (2017), University of Electro-Communications, Tokyo, Japan (Poster).
8. Oxygen-Reduction Electrochemical Measurements of Fe-N-C Electrocatalysts, A. Mufundirwa, G. F. Harrington, K. Sasaki, A. Hayashi, S. M. Lyth, NENCS 2017.
9. Next-Generation Fuel Cell (NEXT-FC) Symposium (poster), Kyushu University, Japan, June 2017.
10. XAS Measurements of Fe-N-C Electrocatalysts, A. Mufundirwa, T. Sugiyama, S. Yoshioka, K. Sasaki, A. Hayashi, S. M. Lyth, NENCS 2017.
11. Germany Innovation Award (Gottfried Wagener Prize 2017), Grant Hyatt, Tokyo, Japan (Poster).
12. Falling Walls Lab Tokyo, Germany Research and Innovation Forum (DWIH Tokyo) 2017 edition (oral), A. Mufundirwa, Miraikan, Tokyo, Japan, May 2017.

13. Kyushu University Energy Week (abstract and poster), A. Mufundirwa, Kyushu University, Japan, January 2017.
14. Next-Generation Fuel Cell (NEXT-FC) Symposium (poster), A. Mufundirwa, Kyushu University, Japan, December 2016.
15. PRiME2016/230th, ECS Meeting (poster), A. Mufundirwa, Y. Shundo, J. Liu, B. Smid, B. V. Cuning, K. Sasaki, S. M. Lyth, USA, October 2016.
16. Next-Generation Fuel Cell (NEXT-FC) Symposium (poster), A. Mufundirwa, Kyushu University, Japan, April 2016.

viii. Invited Seminars

1. Faculty of Mathematics and Physics, Professor Matolin's Group, Charles University, Prague, Czech Republic (2019).
2. School of Physics, Professor Bhattacharyya's Group, University of the Witwatersrand, Johannesburg, South Africa (2018).
3. Institute for Basic Science, Center for Multidimensional Carbon Materials, Professor Ruoff's Group, Ulsan National Institute of Science and Technology, Ulsan, South Korea (2018).

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Chapter 1 Introduction

1.1 Issues with Traditional Energy Technologies

Energy provision is increasingly becoming a key issue for global society as the human population continues to grow. The main energy sources of this era are fossil fuels such as coal, petroleum and natural gas. However, there are many issues coupled with energy production. The combustion of fossil fuels produces pollutants such as NO_x and SO_x which cause smog and acid rain, $\text{PM}_{2.5}$ which causes serious health problems, and CO_2 which is a greenhouse gas. The concentration of atmospheric CO_2 is rapidly increasing, which is resulting in global heating and climate change.¹ Thus, developing a clean and sustainable form of energy is extremely important to the future of society.

The hydrogen economy is an alternative system that can contribute to the replacement of the current fossil fuel-based system for energy production. The hydrogen economy will liberate energy from hydrogen gas via an electrochemical process, without the requirement for combustion. Hydrogen can provide clean energy with low or zero carbon emissions, as long as hydrogen is generated using renewables. Fuel cells are at the heart of the hydrogen economy, converting chemical energy into electrical energy using electrochemistry. Their maximum efficiency is not limited by the Carnot cycle, and

therefore they can have a high energy conversion efficiencies reaching 40 to 60 %. Fuel cells are an alternative energy conversion technology to supplement batteries and hydrocarbon fuels burned in combustion engines. However, there are many areas to improve on for fuel cells to be able to penetrate the fossil fuel and battery dominated market.

1.2 Polymer Electrolyte Fuels Cells (PEFCs)

Fuel cells are devices that generate electricity from electrochemical reactions between a fuel and an oxidant at the anode and cathode, respectively. These electrodes are physically separated by an electrolyte. There are many different types of fuel cells, but here we focus specifically on polymer electrolyte fuel cells (PEFCs). By using hydrogen as a fuel, these have the potential to enable the replacement of fossil fuels. They are an extremely promising technology due to their high power density, efficient operation, and versatility for different applications.²

The operation principle of a PEFC is represented in Figure 1.1. At the anode, the hydrogen oxidation reaction (HOR) occurs on the surface of a platinum electrocatalyst, releasing protons and electrons (Eq. 1). At the cathode, the oxygen reduction reaction (ORR) occurs also requiring a platinum catalyst - oxygen from air combines with protons and electrons

and is reduced to form water (Eq. 2). These two half-reactions generate a potential difference across the cell, driving protons through the electrolyte and electrons around the external circuit. Completing the circuit sustains the reaction indefinitely until the fuel or oxidant supply stops. The overall reaction is shown in Eq. 3. This reaction is identical to burning hydrogen in oxygen, but in a PEFC most of the energy released can be captured as useful electricity and heat.

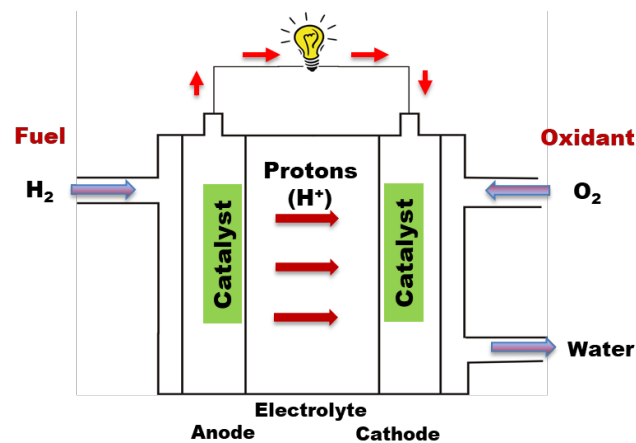
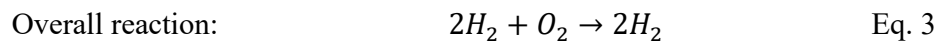
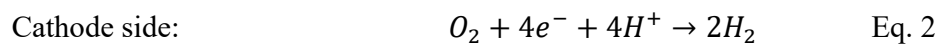
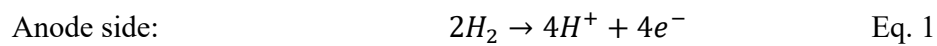


Figure 1.1: Principle of operation of PEFCs.

1.3 Practical Applications of PEFCs

Grove first discovered the principle of the hydrogen fuel cell in 1839.^{3,4} Since then, there has been huge amount of research and development into PEFCs and many landmark developments to get to the point of modern practical applications. The first practically applicable hydrogen fuel cells were developed by Bacon in 1952, and a few years later his 5 kW alkaline fuel cell was successfully demonstrated in powering a 2 ton fork lift truck.⁵ This work led to the development of the Gemini Fuel Cell System, a 1 kW acid electrolyte fuel cell, which was used to provide power on the Apollo space missions in 1965.⁶ Much more recently, fuel cell electric vehicles (FCEVs) have been released commercially e.g. the Toyota MIRAI, and the Honda Clarity (Figure 1.2).^{7,8} Residential combined heat and power systems based on PEFCs with outputs from 0.3 to 1.0 kW are currently available on the market in Japan under the trade name ENE-FARM.⁹ These work by extracting hydrogen from liquified petroleum gas, generating electricity in the PEFC, whilst simultaneously capturing the thermal energy to heat up water. Elsewhere, ultralightweight PEFC systems have been developed to power drones, under the brand name HYCOPTER (Figure 1.3).¹⁰ In 2018, France-based rail manufacturer Alstom launched the world's first passenger hydrogen fuel cell train.¹¹ Recently, on 8 April 2020, it was reported that a memorandum of understanding (MOU) was signed between leading

technology producers and hydrogen specialist Hydrogène de France (HDF) to develop fuel cells of megawatt-scale for merchant ships.¹² It had taken a long time, but PEFCs are finally on the verge of becoming a mainstream technology.



Figure 1.2: Fuel Cell Vehicle – Honda Clarity.⁸



Figure 1.3: Hycopter with ultralightweight PEFC.¹⁰

1.4 Platinum Electrocatalysts

A key limitation of PEFCs is the sluggish nature of the ORR kinetics at the cathode. This necessitates the use of a platinum catalyst to improve the efficiency. Conventionally, platinum nanoparticles dispersed on a carbon black support are used (Pt/C), in order to increase the surface area.¹³ Whilst platinum is an efficient catalyst, the main drawback is that it is expensive. One method to reduce cost is to improve the mass- and area-specific activities in order to reduce the amount of platinum required to obtain the same performance. Intensive research has been performed to this end over the decades in the areas of e.g. alloying platinum with cheaper metals such as Co or Ni,¹⁴ the design of platinum nanoparticles with advanced geometry;¹⁵ strain engineering of platinum via the use of metal oxide supports;¹⁶ or confinement of Pt nanoparticles in the pores of mesoporous carbons.¹⁷ However, these techniques tend to add expensive processing steps, offsetting the benefits of using less platinum. In addition, the price of platinum will inevitably rise significantly if FCEV and residential PEFC co-generation systems are rolled out across the world at scale.

Besides cost, the durability of platinum electrocatalysts is also an issue of concern.

Platinum nanoparticles undergo degradation during PEFC operation due to several

different mechanisms. Firstly, the binding energy between Pt and the carbon black support is weak, so the nanoparticles can move around on the surface of the support. When one particle meets another, they stick together, leading to agglomeration. This decreases the triple phase boundary by reducing the accessible surface area of the Pt nanoparticles. Similarly, the nanoparticles can detach from the carbon surface, decreasing the triple phase boundary by disrupting the electron pathway from the carbon to the platinum. Another mode of catalyst degradation is platinum dissolution within certain potential ranges. A related process is Ostwald ripening, where small nanoparticles dissolve during potential cycling, reprecipitating onto larger and more thermodynamically stable nanoparticles, decreasing the surface area. The final major mode of Pt degradation is carbon corrosion. During start-up and shut-down operation (e.g. turning an FCV on and off) the cell potential can reach 1.5 V, causing the carbon support to react with oxygen or water, forming surface oxides, carbon monoxide, or carbon dioxide gas. This increases the electronic conductivity and leads to particle detachment.

1.5 Limitations of PEFCs

Despite impressive progress in the development of practical, commercial devices, the market penetration of PEFC systems is still very low compared to conventional energy conversion systems, such as the internal combustion engine, or lithium ion batteries. Most commercial applications are high-end, or niche oriented. This is largely due to cost. According to a Department of Energy cost analysis based on an 80 kW automotive PEFC system, the fuel cell stack accounts for 66 or 43 % of the total system cost at a production capacity of 1,000 and 500,000 systems per year, respectively.¹⁸ A cost breakdown of the stack components shows that the combined cost of the platinum-based electrocatalyst materials and their application constituted the highest proportion of system cost, and that this percentage only increases with increasing production volume.

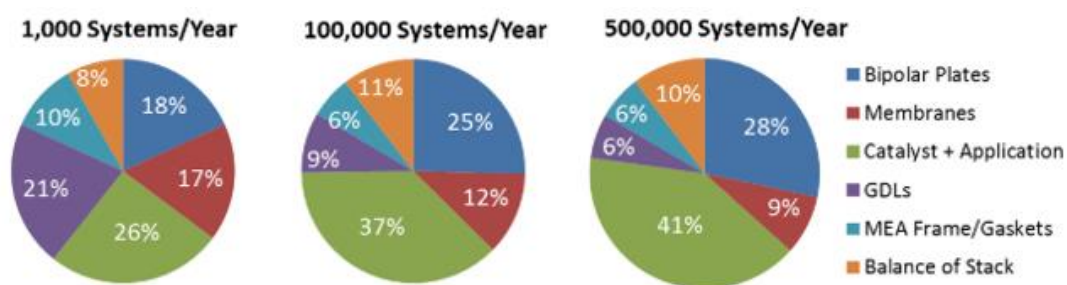


Figure 1.4: Breakdown of the 2017 projected fuel cell stack cost at 1,000, 100,000, and 500,000 systems per year. Credit: U.S. Department of Energy, 2017.¹⁸

1.6 Platinum-free Electrocatalysts

Due to the above issues, much effort has been expended on replacing platinum with alternative platinum-free electrocatalysts. These are generally known as non-platinum group metal (non-PGM) electrocatalysts. Iron-carbon-nitrogen (Fe-N-C) based electrocatalysts have been the most-studied group of non-PGMs, showing promising performance as a substitute for platinum in PEFCs. Research into Fe-N-C electrocatalysts for the ORR began in 1964,¹⁹ when Jasinski et al. investigated the use of phthalocyanine molecules as electrocatalysts in fuel cells, inspired by the use of such materials as catalysts in nature. It was later determined by Jahnke et al in 1976 that the performance of these transition-metal containing organic molecules could be dramatically improved by thermal treatment,²⁰ despite the decomposition of the supposedly catalytically active molecular structure. Eventually it was realized that almost any combination of iron, nitrogen and carbon resulted in the production of active electrocatalysts after heat treatment.

Today, a wide range of Fe-N-C electrocatalyst synthesis methods and precursors are used worldwide, with every group having their own special “recipe”. These different methods yield Fe-N-C materials with highly differing morphology, porosity, surface area and

chemical structure. These protocols are generally based on an empirical approach, using optimization and observation in deciding the best precursors and synthesis conditions, rather than rational design.

For instance, Zitolo et. al. made highly active Fe-N-C catalysts by combining iron (II) acetate, 1,10-phenanthroline, and a zeolitic imidazole framework (ZIF-8), in ethanol/water solution. The solvents were evaporated and ball milled. Pyrolysis was performed in argon gas at 1050 °C for 1h, followed by acid-washing in H₂SO₄.²¹ Chen et. al performed in-situ polymerization of amino-pyridines on a silica template, followed by pyrolysis at 950 °C and etching of the template in HF and HNO₃, followed by a second heat treatment step in ammonia.²² Fei et. al. prepared an aqueous suspension of graphene oxide, FeCl₃ and H₂O₂, which they then subjected to hydrothermal treatment at 180 °C to form a self-assembled hydrogel. This was freeze dried and then heat treated at 900 °C in NH₃.²³ Meanwhile, Li et al. infiltrated Fe(NO₃)₃ into an anodic aluminum oxide template, followed by chemical vapor deposition of acetonitrile, under flowing NH₃ at 800 °C. Acid washing in a mixture of HF/HCl was used to remove the template and residual Fe nanoparticles, followed by a second heat treatment step in NH₃ at 850 °C. These are just a small cross section of the hundreds of different methods used to synthesize Fe-N-C electrocatalysts. Despite the completely different methodologies, the final catalytic

activities are surprisingly comparable, leading to a lack of understanding of the active site chemistry and the ORR mechanisms, and hindering their further improvement and development.^{24,25} Therefore, a well-planned methodical approach is still needed to provide more insight than the empirical approaches generally used to date.

1.7 Significance of the Processing Steps

A highly generalized methodology for generating highly active catalysts seems to be: i) combine a carbon, nitrogen, and iron source; ii) carbonization; iii) acid washing; and iv) heat treatment in ammonia gas. The inclusion of both nitrogen and iron have a direct impact on the catalytic activity, because the ORR active sites are reportedly made up of Fe-N₄ catalytic centers.^{26,27,28} The presence of carbon, and the carbonisation step are of importance in providing a support for the catalytic active centres, with suitable porosity for mass transport, and electronic conductivity, all factors affecting the final catalytic activity.^{23,29–35} Acid washing is an important step for the removal of exposed metallic iron and iron oxides,^{36,37} which are reported to reduce the long-term stability of the catalysts. Exposed metallic iron is known to catalyse O₂ reduction to H₂O₂, which can attack the active sites and/or membrane in PEFCs.³⁸ The second heat treatment step in ammonia is

reported to increase the initial ORR activity by inducing basicity on the support surface.^{28,39} This improves the intrinsic activity of Fe-N sites towards ORR by modifying the chemical and electronic structures.²⁷ However, this step may be detrimental to the long-term stability.^{28,40}

1.7.1 Nature of Active Sites in Fe-N-C Electrocatalysts

This profusion of different varieties of Fe-N-C catalysts has fueled an ongoing debate into the catalytic mechanism. There are three prominent hypotheses, shown in Figure 1.5: (i) that the active sites are porphyrin-like atomically-dispersed Fe atoms coordinated to nitrogen atoms embedded in the carbon lattice (i.e. Fe-N_{2/4} sites);^{21,41–43} (ii) that superparamagnetic iron nanoparticles encapsulated in graphitic carbon shells are ORR active;^{44,45} or (iii) that Fe generates nitrogen-doped carbon active sites without taking part directly in the reaction.^{46–48} Meanwhile, the dual site hypothesis suggests that different sites are required for different steps of the ORR.⁴⁹

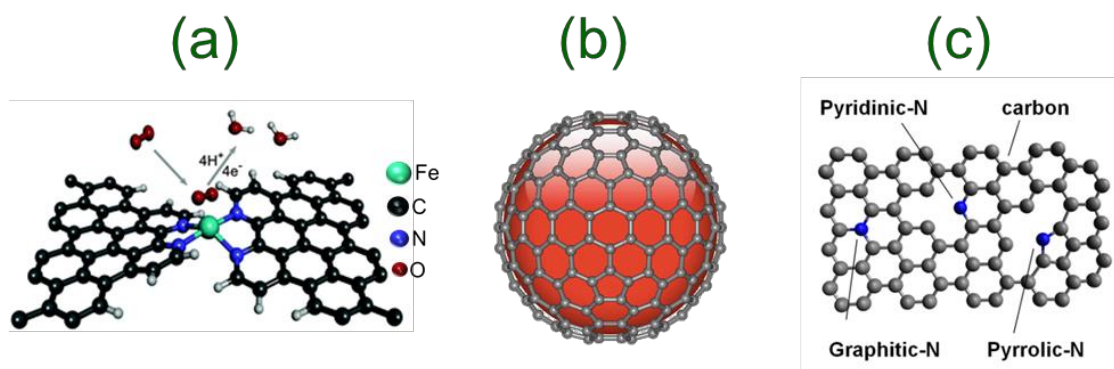


Figure 1.5: The three prominent active sites in Fe-N-Cs: (a) Fe-N_{2/4} sites, reproduced by permission from the Royal Society of Chemistry;⁵⁰ (b) carbon encapsulated iron nanoparticles; and nitrogen functional groups on the surface of carbon, reproduced by permission from Aix Marseille Universit'.⁵¹

Designing simplified Fe-N-C catalysts has helped to narrow down the active site structure and mechanism by discounting some contributions from the different factors mentioned above. To this end, several groups have reported advanced Fe-N-C catalysts with only a single type of iron coordination. For example, catalysts containing only atomically dispersed porphyrin-like Fe environments have been reported, without the presence of any metallic phases,^{42,52,28} and the Fe-N₄ sites within have recently been directly visualized using aberration-corrected scanning transmission electron microscopy.^{53,54,55} Conversely, ORR active catalysts free from any Fe-N coordination and containing only carbon-encapsulated iron nanoparticles have also been reported.^{44,37,56,57} Most groups

have reached a consensus that all three types of active sites are active toward ORR to different extents in acidic conditions, with Fe-N₄ sites being the most likely to contribute to significant ORR activity in Fe-N-C electrocatalysts.⁵⁸ Assuming that the main active site is Fe-N₄ type, the ORR mechanism goes through a 4-electron pathway as illustrated in the schematic below, Figure 1.6.³⁸ In brief, an O₂ molecule chemisorbs directly on the Fe²⁺ active site, proceeding to a “ferric-superoxo” species (Fe³⁺ oxidation state) as it forms a bond with the surface. This is then converted to a “ferric-hydroperoxyl” species (Fe³⁺ oxidation state) by accepting an electron and a water molecule, and then “ferrous-hydroperoxyl” species (Fe²⁺ oxidation state) by accepting another electron. Accepting another electron and a water molecule produces a “ferric-hydroxyl” species (Fe³⁺ oxidation state). Finally, this site accepts another electron, completing the ORR, and leaving the active site with an adsorbed OH⁻ species (Fe²⁺ oxidation state). Although this mechanism cycle is for alkaline conditions, the idea can be inferred to work in a similar way in acid medium, except that OH⁻ species will block O₂ chemisorption.⁵⁹

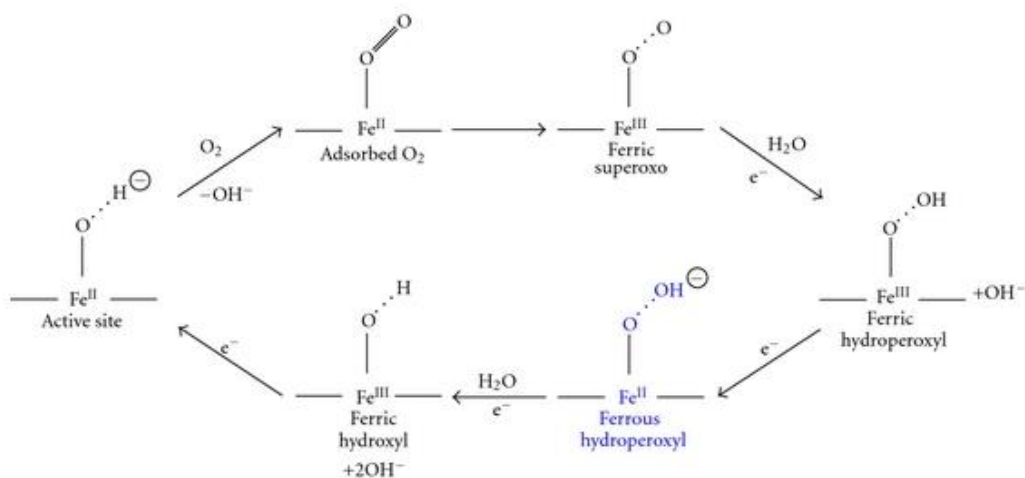


Figure 1.6: Proposed ORR mechanism. Catalyst cycle showing the redox mechanism involved in ORR on pyrolyzed Fe-N_x/C active sites in dilute alkaline medium, modified from the original by Ramaswamy et.al.³⁸

Meanwhile, Tylus et. al proposed a different dual active site, comprising Fe-N₄ sites accompanied by carbon encapsulated Fe nanoparticles, where in acid medium the Fe²⁺-N₄ site is involved in the ORR initiation step of O₂ adsorption, in a 2-electron reduction to peroxide intermediate. The peroxide needs a secondary active site, in this case the carbon-encapsulated iron nanoparticle, to proceed the reduction to the 4-electron water product. Otherwise the peroxide desorbs into electrolyte, resulting in a 2-electron transfer mechanism.⁶⁰ Elsewhere, it has been reported that graphitic-N and pyridinic-N in nitrogen-doped carbons are active functional groups and support ORR.^{61,62} Overall, the ORR mechanism on Fe-N-C is still a matter of debate.

1.8 Nitrogen-doped Carbon Foams

Nanostructured carbon materials are commonly used as supports for electrocatalysts in general, and especially as a basis for Fe-N-C electrocatalysts. Carbon has a wide variety of bonding configurations, leading to a huge variety of different structures. Carbon materials can be synthesized to have very large surface area, and controllable porosity, potentially providing suitable passageways for diffusion of reactants and products in PEFC electrodes.^{63,64} Carbon is also relatively chemically inert, making it resistant to many reactive species, and ensuring it has reasonable durability in electrochemical devices.⁶⁵ It has high electrical conductivity, helping to minimize electrode resistance and thus minimizing ohmic losses for fuel cell applications.⁶⁶ An enhanced understanding of the fundamental principles behind the synthesis process of carbon-based catalysts will enable development of better synthesis protocols and improved ability to scale-up production.

Previous work from our lab employed a specific type of carbon foam derived from the decomposition of metal alkoxide powders as a basis for Fe-N-C catalysts. The advantage of this class of carbon foam is that it can be synthesized without the need for a sacrificial template; it has very large surface area (up to 3000 m²/g); it has relatively large primary

pore-size ($>1\ \mu\text{m}$) as well as being highly microporous; it can be produced at multi-gram scale; and as a “bottom-up” technique the chemical structure can be routinely modified.⁶⁷ This type of carbon foam was first synthesized by Choucair et al., by solvothermal reaction between sodium and ethanol, followed by pyrolysis.⁶⁸ A study by Chandran et.al. on the decomposition of sodium ethoxide, using TGA-MS data, reported that the decomposed solid residues contain carbon with sodium carbonate and sodium hydroxide,⁶⁹ whereas the gaseous products had methane and ethylene (as major constituents) while ethane, propylene and butylene were minor constituents.⁶⁹ Sodium hydroxide is responsible for the activation and micropore formation of the carbon, and sodium carbonate does not play a major role in this activation process.⁷⁰ Lyth et al. showed that the solvothermal step was not required; that such carbon foams can be formed simply through pyrolysis of sodium ethoxide powder; and that it had applications such as hydrogen storage, due to the large surface area.^{71–73} Superhydrophobic fluorinated carbon foam can be synthesized by replacing ethanol with e.g. trifluoroethanol.⁷⁴

Doping with nitrogen is well-known to modify the intrinsic properties of carbon materials, such as the electronic characteristics, surface properties, and local chemical features. Nitrogen atoms have comparable atomic size to that of carbon, and there are five valence electrons available for bonding with carbon atoms, therefore nitrogen is highly suited as

a dopant for carbon nanomaterials.⁷⁵ Nitrogen atoms can replace carbon atoms at different lattice sites, creating defects in the carbon matrix, whilst the electron donating properties are widely accepted to facilitate the ORR.⁷⁶ As such, nitrogen-doped carbon foams were synthesized in our group by replacing ethanol with e.g. ethanolamine,⁷⁷ and used to gain insight into the ORR in metal-free (or “no metal added”) non-PGM catalysts.^{78–80} The nitrogen content can be controlled by changing the amount and the type of nitrogen-source in the reaction, e.g. by using varying ratios of ethanol with either ethanolamine, diethanolamine, or triethanolamine.

1.9 Objectives and Methodology

As explained above, the empirical synthesis approach makes it difficult to understand the mechanisms taking place during Fe-N-C catalyst synthesis. This results in catalysts with a wide range of different microstructure, surface area, porosity, degrees of graphitization, and elemental environments, and all of these factors influence the catalyst performance.^{23,29–35} Systematic probing of factors that contribute to effective performance of non-PGM catalysts is of paramount importance in terms of designing Pt-free catalysts with better activity, capable of replacing Pt in commercial PEFC systems.

As such, in this thesis a two-step synthesis approach is utilized in the production of Fe-N-C catalysts. First, a nitrogen-doped carbon foam support with well-defined properties was synthesized (i.e. fixed surface area and porosity, fixed nitrogen-content, and fixed crystallinity). Then this model support was decorated with a selection of different iron precursors, followed by heat treatment in ammonia and acid washing. As such, any changes occurring during catalyst synthesis can be attributed mainly to changes in the iron precursor, and not to temperature-induced changes in the underlying carbon support. This is in contrast to conventional techniques, in which the properties of the support will vary considerably during the different stages of synthesis. Therefore, this unique methodology allows to decouple the porosity, microstructure, and conductivity of the support from the ORR activity of the active sites, which can instead be fully attributed to the chemical environment of iron. This entails understanding: i) the carbon support properties; ii) how the catalytically active elements behave on the support; and iii) their combined effect on performance.

In order to work towards this goal, this thesis focuses first on the synthesis and optimization of the nitrogen-doped carbon foam support in order to obtain the best properties for electrochemical activity (Chapter 3). Then, the emphasis shifts to three different precursors (i.e. iron acetate, iron chloride, and iron phthalocyanine) which are

adsorbed onto the nitrogen-doped carbon foam support, pyrolysed, and systematically characterized. The material properties are linked to the ORR activity and PEFC performance (Chapter 4). After this, advanced in situ high temperature and near ambient pressure characterization techniques are employed to investigate in unprecedented detail how these iron precursors change during pyrolysis to form Fe-N-C electrocatalysts, and how the resulting catalysts interact with oxygen (Chapter 5). Finally, advanced electrochemical X-ray absorption spectroscopy is used to investigate how the chemical environment of iron in the precursors changes during decomposition to form active sites (Chapter 6).

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Chapter 2 Experimental Methods

2.1 Synthesis of Nitrogen-doped Carbon Foams

Nitrogen-doped carbon foams were synthesized by the decomposition of a nitrogen-rich sodium alkoxide precursor (the synthesis protocol of which is explained in Chapter 3.2). A two-step pyrolysis protocol was used. The first “structure forming” pyrolysis step at 600 °C was performed in a box furnace (Figure 2.1) to allow for scale-up. The carbonized product (Figure 2.2) was crushed using a mortar, then stirred overnight in deionized water, washed five times using vacuum filtration (to remove sodium-containing impurities), and then dried at 60 °C. The powders were then subjected to second “graphitization” pyrolysis step at 1000 °C for 2 hours (N_2 , 75ml/min, 5 °/min), using a tube furnace.

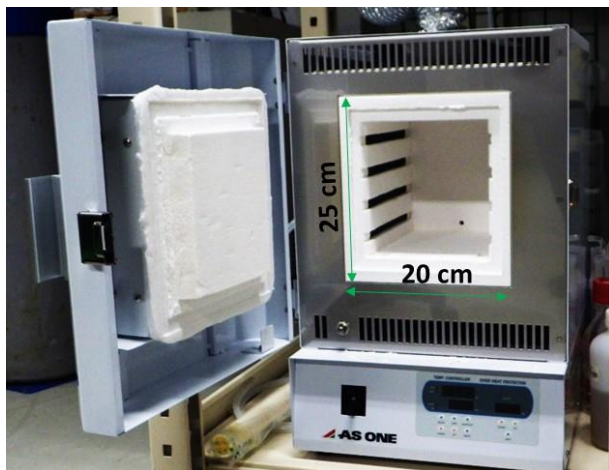


Figure 2.1: Box furnace used for the pyrolysis of metal alkoxide powders (ASONE).

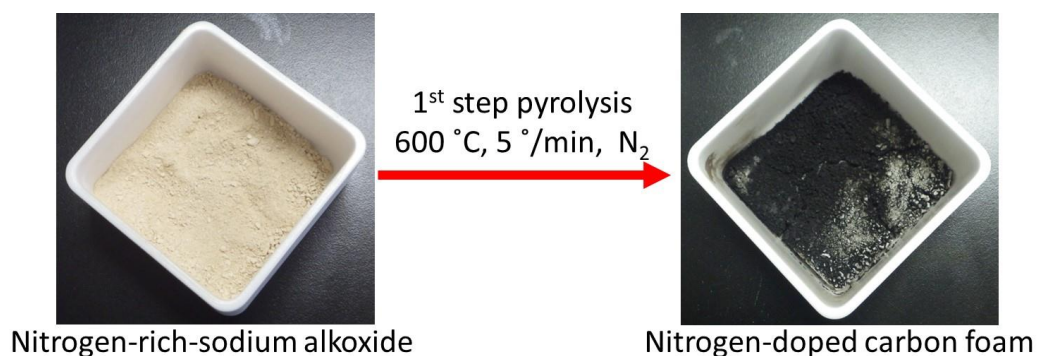


Figure 2.2: Photo of the nitrogen-doped sodium alkoxide powder before and after the “structure forming” pyrolysis step.

2.2 Synthesis of Fe-N-C Electrocatalysts

Iron adsorption onto nitrogen-doped carbon foams was done using a wet impregnation technique. The nitrogen-doped carbon foam was dispersed in ethanol, whilst the iron precursor was dissolved in either water or ethanol depending on its solubility. Two methods were then used in the following stages. In the “*vacuum filtration method*” the nitrogen-doped carbon powder and iron precursor solutions were combined ($\text{Fe} = 0.5 \text{ wt\%}$) and magnetically stirred for 2 hrs. Then, vacuum filtration was used to collect the Fe-adsorbed-N-C mixture (with some inevitable loss of the iron precursor). The sample was then placed in a petri dish and dried at 60°C overnight. This method was used in Chapter 3. Alternatively, in the “*evaporation method*”, the nitrogen-doped carbon foam and the iron precursor solutions were also combined. However, in contrast to the vacuum filtration method, the mixture was magnetically stirred in a beaker at 80°C , until all of the solvent was evaporated. The beaker was then placed in oven at 60°C to dry overnight. This method resulted in all of the iron precursor remaining in the sample, making it easier to calculate the iron content of the resulting catalysts.

The dried nitrogen-doped carbon powders with iron precursors adsorbed on the surface were then pyrolyzed in a tube furnace according to (Figure 2.3). During heating at 5 °/min the carrier gas was N₂ (100 ml/min). When the temperature reached 900 °C, NH₃ gas was introduced in the ratio N₂:NH₃ = 3:1 and the sample was pyrolysed for 1h. Then the sample was cooled, and the NH₃ supply was switched off when the furnace cooled down to <100 °C.¹

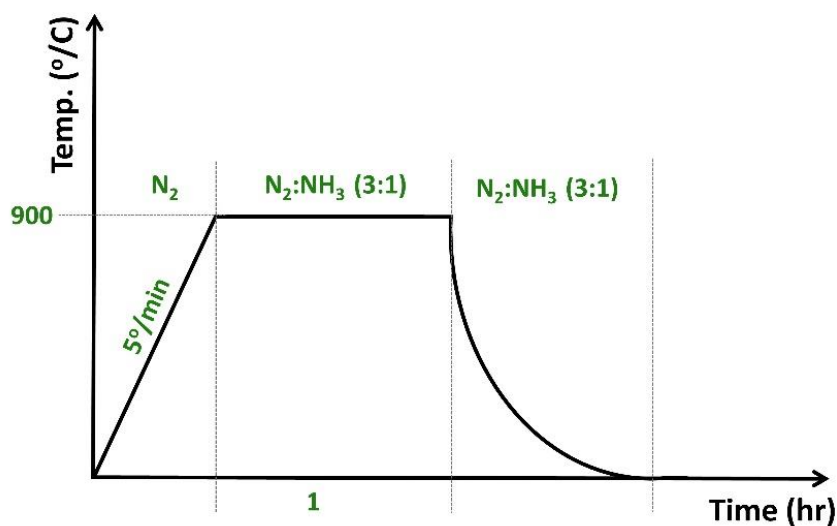


Figure 2.3: A schematic showing the pyrolysis conditions and temperature for heat-treatment of the iron-adsorbed nitrogen-doped carbon foam samples.

The NH₃ heat-treated samples were then acid washed in 1 M H₂SO₄ (aq.) (for example 200 mg of powder in 100 ml acid solution, in a 200 ml beaker). The mixture was sonicated to disperse the sample and then stirred at 80 °C for at 3h, whilst monitoring the reaction. After 3 h, the mixture was added into pure water to dilute it (a safety measure). Then, the mixture was filtered and washed

in de-ionized water until it reached neutral pH. The sample was then dried in an oven at 60 °C, overnight. After this, the electrochemical properties of the samples could be investigated.

2.3 Characterization Techniques

2.3.1 Surface Area and Pore Size Distribution

Nitrogen gas adsorption takes advantage of the fact that nitrogen gas molecules can physically adsorb on solid surfaces at cryogenic temperatures (77 K), due to van der Waals forces. Here, samples were carefully weighed, and placed inside glass tubes. After attaching the sample tube to the machine, they were degassed using a pretreatment unit at 200 °C under vacuum for 2 hours (Figure 2.4a). Then the sample tubes are transferred and mounted onto the N₂ adsorption/desorption equipment (Belsorp-mini, BEL Japan, Inc, Figure 2.4b), equipped with a liquid nitrogen dewar. The glass cells are then submerged into liquid nitrogen, and the amount of adsorbed gas is measured as the pressure increases. The recorded isotherms can be used to determine the surface area (using Brunauer Emmet and Teller (BET) analysis), and porosity parameters (using MP-plots, T-plots, and Barrett Joyner and Halenda (BJH) analysis).

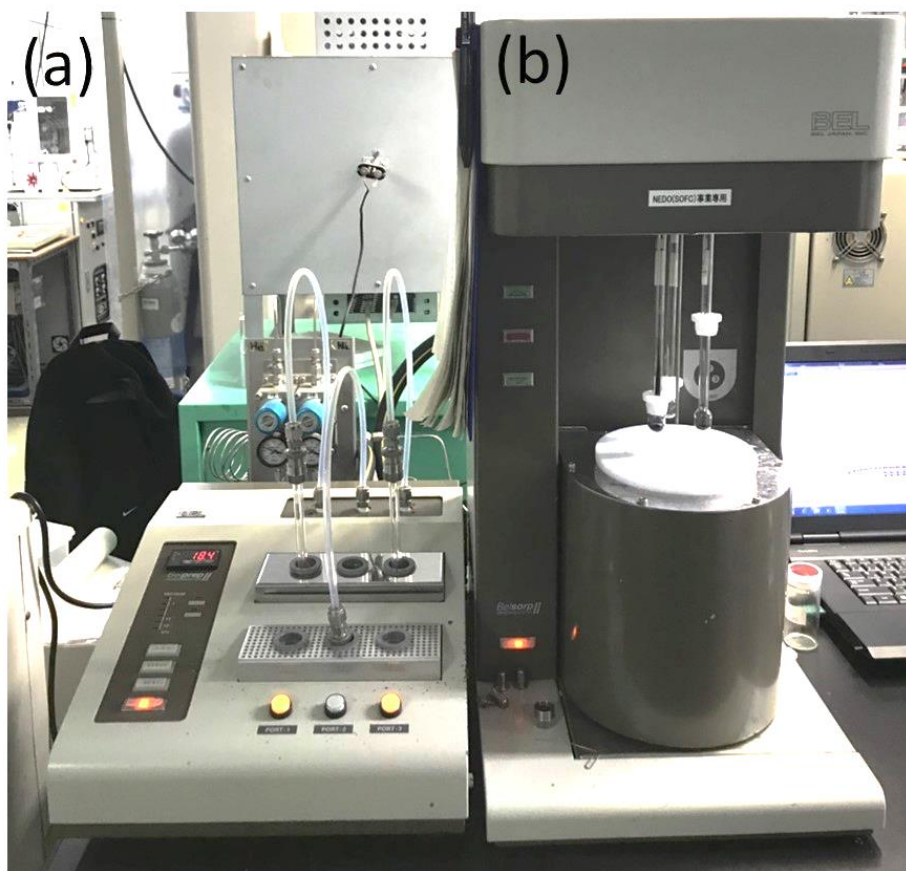


Figure 2.4: Photo of the nitrogen gas adsorption/desorption setup (Belsorp-mini, BEL Japan).

2.3.2 Scanning Electron Microscopy (SEM)

The microstructure of samples was characterized by field emission-scanning electron microscopy (FE-SEM, JEOL JSM-7001F, WDS, EDS, 15 kV). Catalyst powders were sprinkled onto double-sided carbon tape (Nisshin Em Co., Ltd., Tokyo, Japan), which was attached to the sample holder. An air blower was used to remove excess sample powder.

2.3.3 Transmission Electron Microscopy (TEM) & Selected Area Electron Diffraction (SAED)

Transmission electron microscopy (TEM) is a technique in which a thin layer of sample (typically ~100 nm thick) is subjected to a parallel beam of high-energy electrons, which are transmitted through the sample, forming an image because of this interaction. TEM has the ability to image at very high resolution, due to the small de Broglie wavelength of electrons. Selected area electron diffraction (SAED) is a crystallographic technique performed using a TEM. An SAED pattern is obtained in the k-space of lattice planes. SAED images give information about crystallinity. In this work, a conventional TEM (JEM-2100HC, LaB6 emission gun) at an acceleration voltage of 100 kV was used for observing nanostructures in the electrocatalyst (e.g. Fe nanoparticles and carbon nanostructures) and to determine the lattice spacing of graphitic shells. Samples were prepared by dispersing 100 µg of catalyst powder in 1 ml ethanol, followed by sonication to make a homogenous dispersion. A few drops were added to a holey-carbon coated Cu TEM grid, and the solvent was allowed to evaporate.

2.3.4 Raman Spectroscopy

Raman spectroscopy is used to study vibrational, rotational and other low-frequency modes in molecular systems, and depends on inelastic scattering (or Raman scattering) of monochromatic laser light with a wavelength in the visible, near-infrared, or near-ultraviolet range.^{2,3} Raman spectra show the intensity of light scattered from a sample that has been irradiated with monochromatic laser light of a specific wavelength. Raman spectroscopy is extremely useful in the characterization of carbon materials, since all the major bands can be observed within the spectral region between 1300 and 2800 cm⁻¹.^{4,5,6} In this study, Raman spectroscopy was carried

out using a Renishaw inVia Raman Microscope DM2500M (Figure 2.5), using an argon-ion laser with a wavelength of 532 nm.



Figure 2.5: Renishaw inVia Raman Microscope

2.3.5 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is a non-destructive X-ray analytical technique, primarily used to characterize the crystallographic structure of materials, including the interatomic and inter-planar spacing, and the crystallite size. X-ray diffraction is based on constructive interference of monochromatic X-rays and crystalline sample.^{7,8} According to Bragg's Equation (Eq. 2.1), the position of atoms in the crystal lattice can be determined by measuring the angles and intensities of the diffracted beams,

$$n\lambda = 2d\sin\theta \qquad \text{Eq. 2.1}$$

using positive integer n , X-ray wavelength λ , interlayer spacing d and angle between incident ray and scattering planes. Figure 2.6a is a schematic showing the principle of XRD. Here, it was used to identify the different phases in the nitrogen-doped carbon foam and the Fe-N-C catalysts.⁹ X-ray diffraction (XRD) was done using a Rigaku Smartlab X-ray Diffractometer (Figure 2.6b) with a Cu K α -radiation source ($\lambda=1.5418$ Å). All samples were prepared by packing the powders onto a glass sample holder, Figure 2.6c).

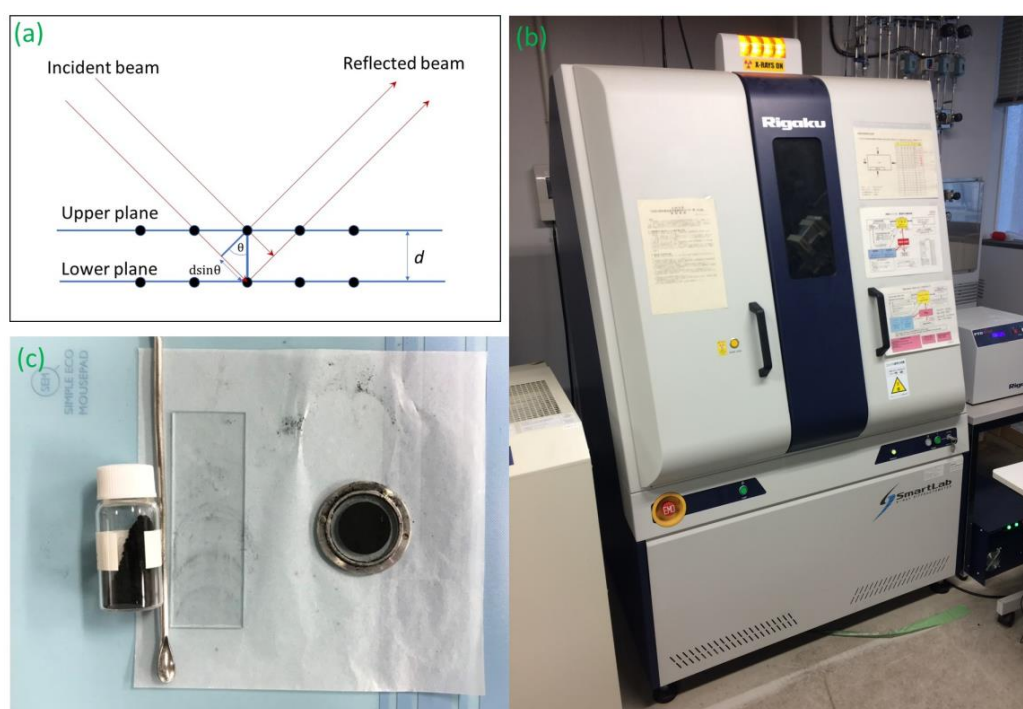


Figure 2.6: (a) Principle of X-ray diffraction (XRD); (b) Rigaku Smartlab X-ray Diffractometer; and (c) powder on glass sample holder.

2.3.6 X-ray Photoelectron Spectroscopy (XPS)

XPS is a non-destructive technique used for investigating the elemental abundance and chemical structure of materials. A surface is irradiated with monochromatic X-rays (commonly Mg K α ,

1253.6 eV or Al K α , 1486.6 eV) in vacuum. This results in the emission of photoelectrons whose energies are characteristic of the elements within the sampling volume (Figure 2.7). Once these photo-ejected electrons are emitted to vacuum, they are collected by an electron analyzer that measures their kinetic energy, producing an energy spectrum of intensity versus binding energy. Different energy peaks on the spectrum correspond to specific elements.

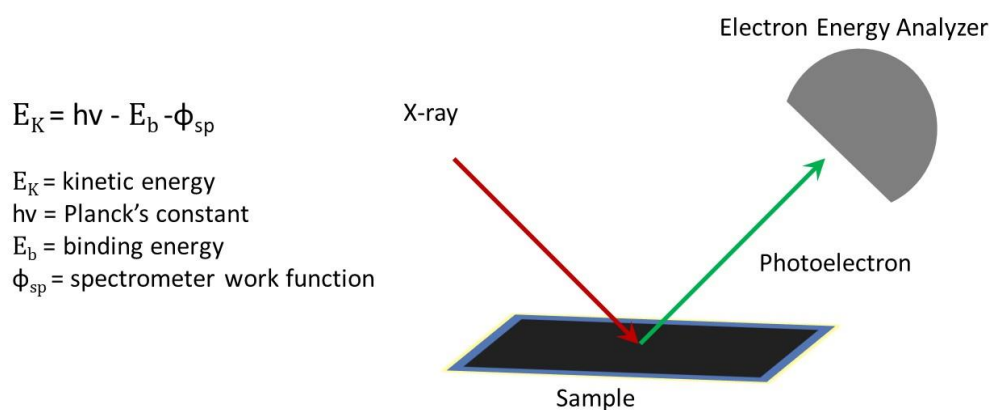


Figure 2.7: Principle of X-ray photoelectron spectroscopy (XPS).

Here, XPS measurements were performed using an ultrahigh vacuum (UHV) setup equipped with a high-resolution analyzer (PHI 5000 Vera Probe II, ULVAC-PHI, INC.). The samples were prepared by pressing the powders on to indium foil, which was fixed to a sample holder. Wide scans and elemental scans were performed on all samples according to the measurement conditions in Table 2.1. The binding energies were calibrated based on the C1s peak at 284.5eV. The resultant spectra were deconvoluted using KolXPD software (Kolibrick.net) using a Gaussian-Lorentz (70:30) function and Shirley background subtraction. The FWHM values were fixed between 1.5 eV~1.6eV for most of the peaks. Table 2.2 shows a summary of chemical bonds with their respective binding energies for C 1s, N 1s and O 1s.

Table 1: XPS measurement conditions

Element	Number of Sweeps	Pass energy (eV)	eV Step
Wide scan	20	187.85	0.2
C 1s	20	46.95	0.1
N 1s	200	46.95	0.1
O 1s	100	46.95	0.1
Na 1s	50	46.95	0.1
Fe 2p	200	46.95	0.1

2.3.7 X-ray Absorption Spectroscopy (XAS)

X-ray absorption spectroscopy (XAS) is a technique for studying (at the atomic and molecular scale) the local geometric and electronic structure of selected elements in a sample. Crystallinity is not a requirement for XAS measurements which makes it possible to probe highly defective materials. XAS experiments are normally conducted using high energy, tunable X-ray beams generated at synchrotron radiation facilities. This makes it possible to probe elements of extremely low concentrations (≤ 1 wt%).¹⁰ XAS spectra can be separated into three regions: (i) the edge region, which is comprised of the pre-edge and rising edge; (ii) the X-ray absorption near-edge structure (XANES) region which is dominated by photoelectrons with kinetic energy of ~ 40 eV from the edge; and (iii) the extended X-ray absorption fine structure (EXAFS) region for high kinetic energy (~ 40 to 1000 eV from the edge), Figure 2.8.¹¹ Normally XANES and EXAFS are combined collectively as X-ray absorption fine structure (XAFS) to define the oscillatory features above the edge. XANES is used to retrieve information on the oxidation state, the electronic

structure and the local symmetry, whilst EXAFS data can be used to obtain information on coordination numbers and bond distances.

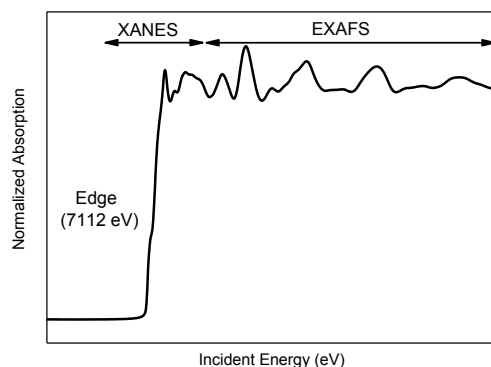


Figure 2.8: Schematic showing the different regions of the XAS spectrum.

Here, XAS measurements were performed in either transmission or fluorescent mode. All XAS experiments were performed using X-rays generated by the synchrotron at Saga Light Source, on the Kyushu University Beamline (BL06). Transmission mode (Figure 2.9a) involves measurement of the incident X-ray flux (I_o) and the transmitted flux (I) after the beam passes the sample. These two fluxes are related by $I/I_o = \exp(-\mu(E)x)$, where $\mu(E)$ is the X-ray absorption coefficient, and x is the thickness of sample. This is normally used for samples whose element of interest has high concentration. The sample is pressed to make a pellet with boron nitride binder (Figure 2.10a), and the thickness of the pellet is adjusted using the relationship; $t = \log(I/I_o)$ and this should correspond to a change in absorption coefficient of $\Delta\mu = 1$.

Fluorescent mode uses the relation that $\mu(E) \propto I_f/I_o$, where I_f is the monitored intensity of absorption process- fluorescence line. This is normally used for lower concentration samples

(down to ppm levels). The samples are prepared simply by placing powders into a plastic sample bag (2.10b). Low concentration samples were used to avoid self-absorption effects. The Fe-atom absorbs X-ray photons and emits fluorescent photons, and a silicon drift detector (SDD) detects $K\alpha$ fluorescence. The SDD detector set at 45° to the sample which is also set at 45° to I_0 . Data output and analysis was done using Athena (XAS data processing) software.

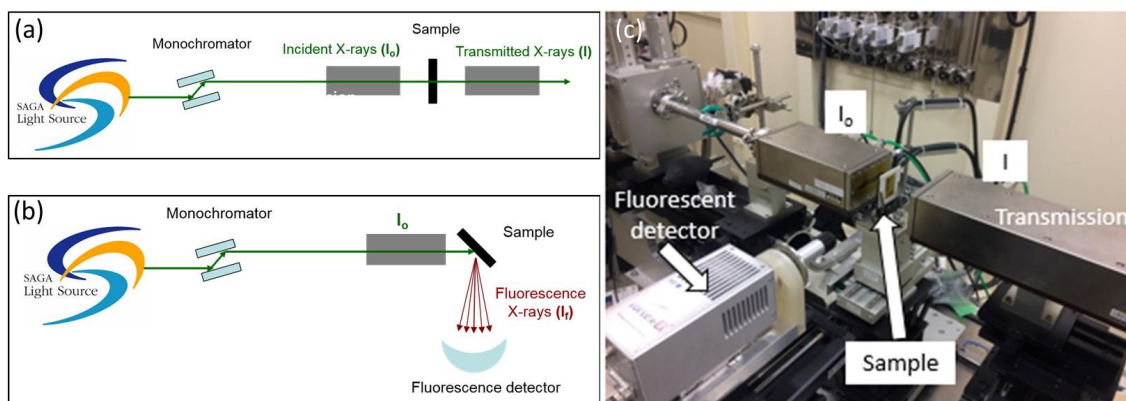


Figure 2.9: A schematic representation of XAS measurements in: (a) transmission mode setup, and (b) fluorescent mode setup. (c) Photo including both setups at Kyushu University beamline (BL06) at SAGA Light Source.

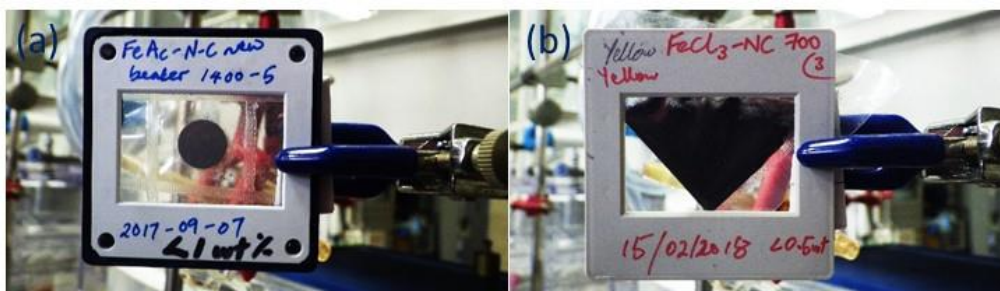


Figure 2.10: XAS sample preparation: (a) powder samples pelletized with boron nitride (transmission mode); and (b) powder samples placed in a plastic sample bag (fluorescence mode).

2.4 Electrochemical Evaluation

2.4.1 Voltammetry

Voltammetry techniques were used to analyze the electrochemical behavior of PEFC catalysts on an electrode, revealing information about the different species involved in redox reactions. These were performed in a *three-electrode cell* with: (1) a *working electrode* where the catalyst of interest is deposited; (2) a *counter electrode* which balances charge transfer; and (3) a *reference electrode* which monitors and controls the potential (Figure 2.11a). Changes in current are recorded as the potential of the working electrode is varied, and the results are plotted in a *voltammogram*. This current corresponds to charge transfer to or from the electrode. Since they describe charge transfer at a single electrode rather than for the whole PEFC, they are known as *half-cell measurements*. The focus was on the oxygen reduction reaction (ORR) at the cathode.

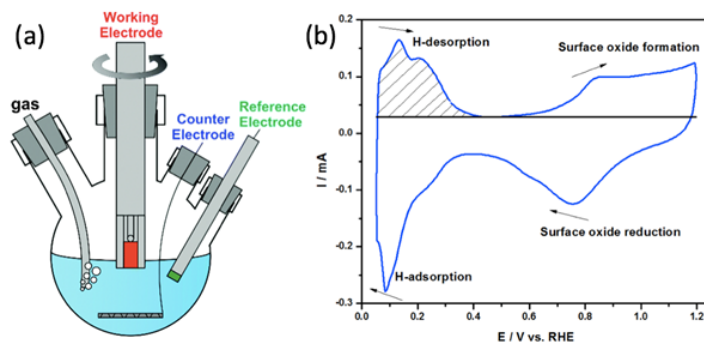


Figure 2.11: (a) Schematic of a three-electrode electrochemical cell, (b) Typical cyclic voltammogram for a Pt/C electrocatalyst, courtesy of Jianfeng Liu, PhD Thesis, © 2014.

Cyclic Voltammetry (CV)

CV measurements were performed in nitrogen-saturated 0.1 M perchloric acid. The electrode potential applied between the reference electrode and the working electrode was swept linearly

versus time at a fixed scan rate of 50 mV/s. Before recording data, the potential was cycled 50 times to remove any possible surface contaminants. The resultant current between the counter electrode and the working electrode was recorded and plotted as current versus potential. The potential was cycled between $E_1 = 0.05 \text{ V}_{\text{RHE}}$ and $E_2 = 0.20 \text{ V}_{\text{RHE}}$.

Linear sweep voltammetry (LSV)

LSV measurements were performed using a rotating ring disk electrode (RRDE). The measurements were performed at a sweep rate of 10 mVs^{-1} , in O_2 -saturated 0.1 M perchloric acid, from 1.20 to 0.07 V_{RHE} (i.e. 0.94 to -0.2 V Ag/AgCl) at 400, 900, 1600, and 2500 rpm. For analysis, LSVs were obtained after subtracting a blank current measured under nitrogen and subsequent normalization to zero where the minimum current density was observed. As with the CV data, the LSV plots are presented after 50 break-in cycles, after the activity stabilized.

2.4.2 Preparation of Working Electrodes

The working electrode was prepared using the sample of interest, using The Fuel Cell Commercialization Conference of Japan (FCCJ) protocols. A rotating ring disk electrode (RRDE) was used (glassy carbon disk and platinum ring) (0.196 cm^2 , Hokuto Denko Corp.). The electrode was first polished using two alumina pastes ($0.3 \text{ }\mu\text{m}$, then $0.05 \text{ }\mu\text{m}$), then washed with deionized water in an ultrasonic bath for 10 min. For the non-PGM catalysts, the powder was dispersed in a mixture of deionized water, ethanol and 5 wt. % Nafion solution, in a volume ratio of 3:3:1. For Pt/C, the ratio was 19:6:0.1. The catalyst ink was sonicated for 30 min. 8 μl of the non-PGM ink

(or 10 μL of Pt/C) was carefully deposited onto the disk of a glassy carbon-disk Pt-ring electrode then dried at 60°C for 15 minutes. The resulting loading of catalyst on the electrode was $580\ \mu\text{g cm}^{-2}$ for the non-PGM catalysts, and $17.3\ \mu\text{g cm}^{-2}$ for Pt/C.

2.4.3 Durability Measurements

Durability measurements were performed using FCCJ protocols for both load-cycling and start-stop tests. Load-cycling durability measurements were carried out between 0.6 and 1.0 V_{RHE} , (Figure 2.12) in 0.1 M HClO_4 in order to simulate potential fluctuations during the operation of fuel cell systems. Cycling was paused, and conventional LSVs were carried out at 0, 5,000 and 10,000 potential cycles.

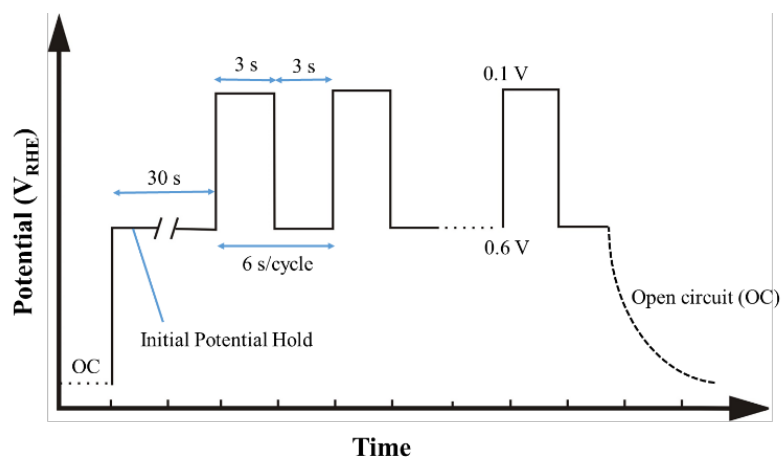


Figure 2.12: FCCJ potential load-cycling durability test program.

Start-stop cycle durability tests were performed to evaluate the electrochemical stability of catalyst supports against oxidation and corrosion in acid. This was performed according to a simulated start-stop 2 s triangular potential cycle between 1.0 and 1.5 V_{RHE} , as shown in Figure 2.13. During potential cycle tests, ORR measurements (CV and LSV curves) were performed before and after

10000, 30000 and 60000 cycles (unless otherwise specified) in order to evaluate catalyst degradation.

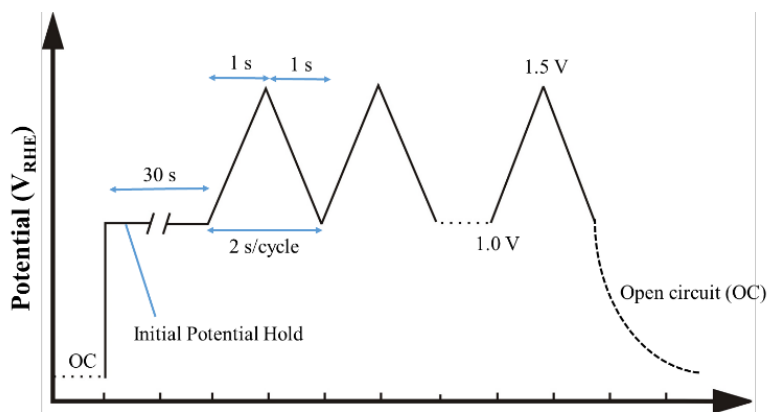


Figure 2.13: FCCJ potential start-stop durability test program.

2.4.4 Membrane Electrode Assembly (MEA) Preparation

MEAs were prepared using Fe-N-C as the cathode catalyst and anode was platinum decorated Ketjen black (Pt/KB Tanaka 45.6%, TKK Corp.). Inks were prepared according to the following protocols. First, 100 mg of Pt/KB 45.6% catalyst was dispersed in a solution of 5% Nafion ionomer, ethanol and H₂O, with a Nafion to Pt/C ratio of 0.28 to 0.72. Then, Fe-N-C catalyst was dispersed in 5 wt% Nafion and 2 ml of ethanol solution, and the Nafion to catalyst ratio was 1 to 2. The ink was sonicated for 30 minutes using an ultrasonic homogenizer (SMT Company, UH-600). The prepared inks were then sprayed onto both sides of Nafion[®] NRE-212 membrane (Dupont), within a circular area of 0.5 cm² using a spray printing machine (Nordson, C-3J). The catalyst loadings were: 0.3 mg/cm² Pt loading (Pt/KB on anode side); and 1 mg/cm² (non-PGM on cathode side). The resulting catalyst-coated membrane (CCM) was hot-pressed at 0.3 KN for 180 seconds.

The fabricated MEAs were then sandwiched between two sheets of hydrophobic carbon paper (Toray, EC-TPI-060T) with same area as the flow field of cell holder and assembled in a 1 cm² flow field NEDO cell holder. The holder was then placed in an oven, heated to 80 °C, and the anode and cathode were purged with N₂ gas (100 ml min⁻¹) prior to the introduction of reactants. Then, 100 %-humidified H₂ gas and air were supplied to the anode and the cathode, respectively, at atmospheric pressure, with a flow rate of 100 sccm, and current-voltage (I-V) measurements were recorded. After the measurement, the gas lines were again purged with N₂ to remove residual hydrogen from the chamber

2.5 In-situ Experiments at Charles University in Prague, Czech Republic

The following experiments were all performed using a specialised system installed at Charles University in Prague (Figure 2.14, SPECS Surface Nano Analysis, GmbH Germany, equipped with a PHOIBOS 150 Hemispherical Energy Analyzer), coupled with a differentially-pumped electrostatic pre-lens system and a quadrupole mass spectrometer.

For sample preparation, a drop of isopropanol was added to a small amount of catalyst powder and this was mixed to a paste using a spatula. The paste was pressed onto a stainless-steel mesh, and the solvent was allowed to evaporate. The mesh was checked carefully to ensure sufficient adhesion, and then spot-welded onto a bespoke sample holder. This was then loaded into the vacuum chamber via an airlock. The sample was positioned under the analyser nozzle (Figure 2.14).

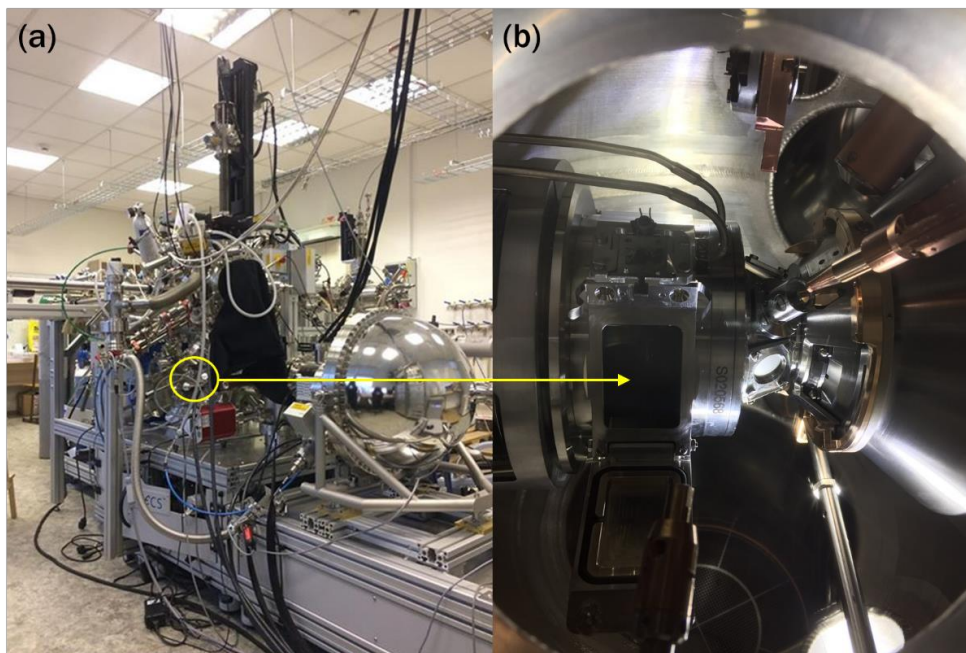


Figure 2.14: Images of (a) the specialised SPECS NAP-XPS system, and (b) the high temperature / near ambient pressure chamber.

2.5.1 High Temperature X-ray Photoelectron Spectroscopy (HT-XPS)

The sample stage in this system has a heating element, which allows heating samples up to 650 °C (Figure 2.15). As such, the XPS spectra of various Fe-N-C samples was measured in situ at high temperature in order to determine changes in the nature of the iron precursors.

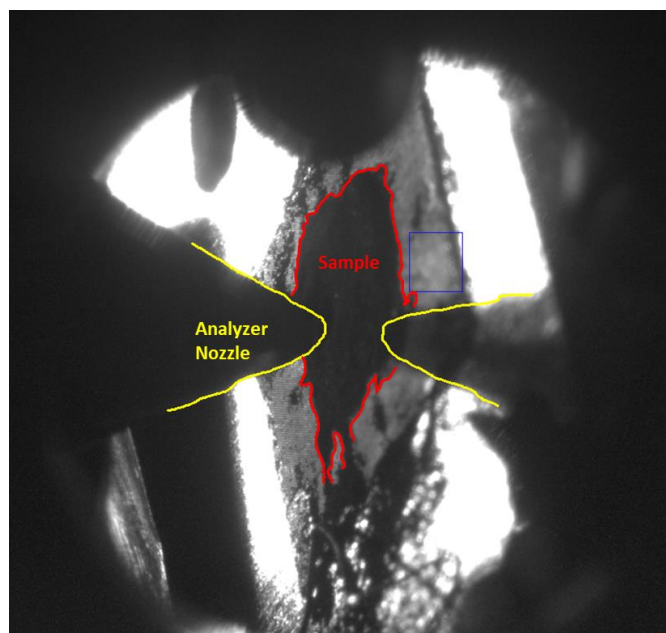


Figure 2.15: Image showing the sample mounted on the heating stage inside the in the NAP-chamber.

2.5.2 Near Ambient Pressure XPS (NAP-XPS)

NAP-XPS allows for the chemical composition characterization of the surface of a material under relatively high pressures (i.e. ≤ 2 kPa) relative to conventional UHV XPS, by using a very small aperture to the analyser. The measurements can be done under different gas flows (e.g. N₂, O₂, H₂, H₂O, CO₂, CO, and NH₃). Detection of the photoelectrons is enhanced by reducing the pressure after the aperture down to vacuum. A series of pumping stages are therefore connected after the aperture in order to achieve the vacuum, thus limiting the distance travelled by the electrons through the near ambient pressure cell. NAP-XPS experiments were performed using a SPECS Surface Nano Analysis, GmbH Germany, Figure 2.14. equipped with a analyzer (a PHOIBOS 150 Hemispherical Energy Analyzer), coupled with a differentially-pumped electrostatic pre-lens system and a quadrupole mass spectrometer.

2.5.3 Quadrupole Mass Spectrometry (QMS)

Mass spectrometry is an analytical method used to accurately determine the mass of atoms and molecules. The technique involves measurements of the mass-to-charge ratios of the ions formed when a sample is ionized.¹² Mass spectrometers include an ion source, a mass analyzer, and a detector. Recently, the quadrupole has become the most widely used mass analyzer for this technique, because it is highly sensitive to the order of hundreds of ppm.¹³ It comprises two radio frequency rods, and two direct current (DC) voltage rods, Figure 2.16. Quadrupole mass spectrometry (QMS) is used here to detect the pyrolysis products of the iron-adsorbed nitrogen-doped carbon supports in situ, as they decompose during heat treatment.

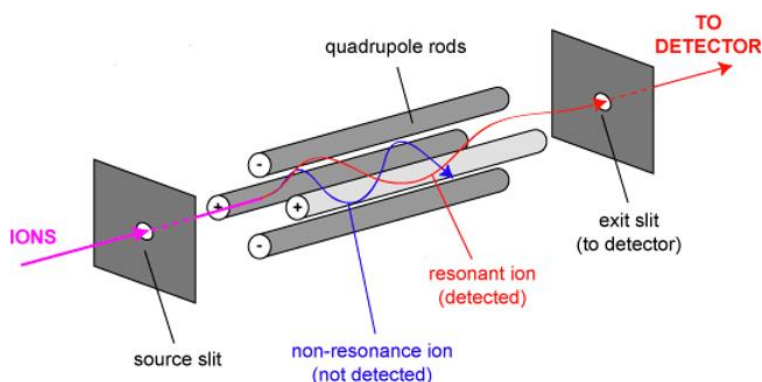


Figure 2.16: Quadrupole mass spectrometry.¹⁴

2.6 In-situ Electrochemical X-ray Absorption Spectroscopy (XAS)

Spectra at the Fe K-edge (7112 eV) were recorded in fluorescence mode using a silicon drift detector (SDD). The electrolyte was 0.1 M HClO₄ and N₂- or O₂-saturation was achieved by

bubbling the respective gases at 5 ml min^{-1} . Chronoamperometry was used to control the voltage at the working electrode. Measurements were performed at potentials of $0.8 \text{ V}_{\text{RHE}}$ (corresponding to the ORR onset region), and $0.2 \text{ V}_{\text{RHE}}$ (corresponding to the mass transfer limited region). Catalysts ink was prepared by mixing 5.23 mg catalyst powder in a solution of ethanol, 5 % Nafion ionomer, H_2O (with a ratio of 3:3:1). The working electrode was prepared by depositing $40 \text{ }\mu\text{l}$ of the ink on a graphite foil ($100 \text{ }\mu\text{m}$ thick) to make a loading of 2 mg/cm^2 , and the ink was left to dry at $60 \text{ }^\circ\text{C}$.

A working electrode with three functions (i) electrochemical function (ii) seal electrolyte in cell (iii) X-ray transparent window was inserted into a PECC-2 cell, then the cell was filled with electrolyte (0.1 M HClO_4), Figure 2.17.¹⁵ The PECC-2 cell was then mounted onto the XAS stage as shown in Figure 2.18. In all cases the cell was saturated with gas of interest for 10 minutes and measurement was done during bubbling. A voltage of interest was then applied, and Fe-K-edge measurement was done after 5 minutes, and in all cases the current measured was constant.

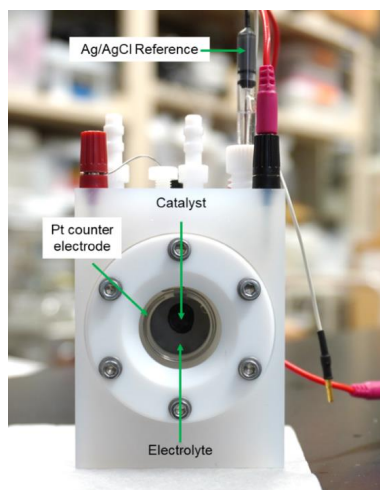


Figure 2.17: X-ray transparent PECC2 cell used in the in-situ electrochemical XAS experiments. The catalyst is deposited on a graphite foil working electrode. The counter electrode is a platinum wire, and the reference electrode is Ag/AgCl. The electrolyte is 0.1 M HClO_4 .

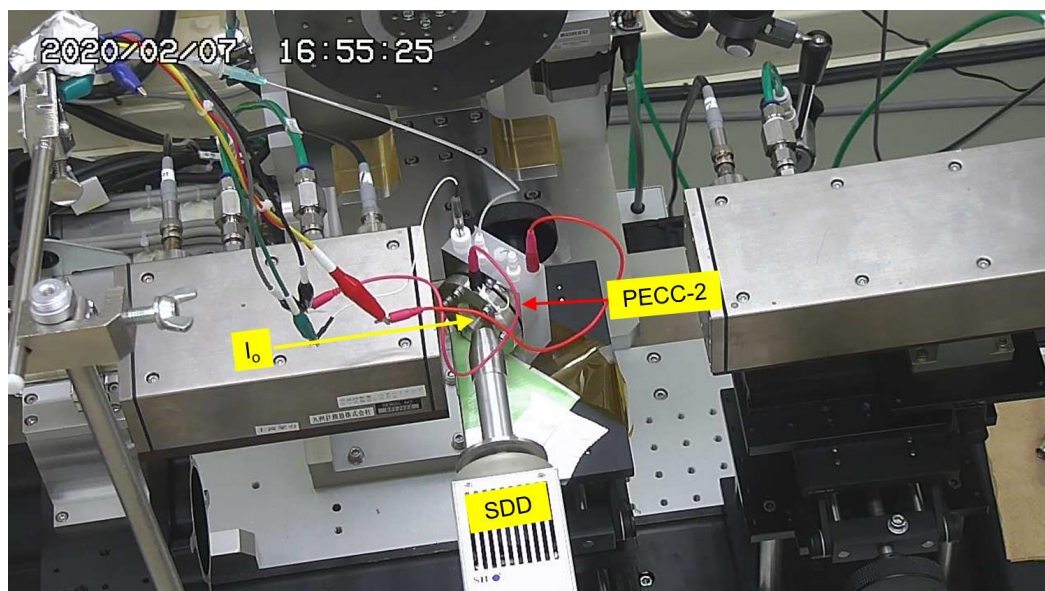


Figure 2.18: PECC2 cell mounted on the XAS stage ready for in-situ electrochemical XAS experiments.

2.7 References

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Chapter 3 Effect of the Properties of the Carbon Support on Fe-N-C Electrocatalyst Performance

3.1 Introduction

Non-precious catalysts are transition metal-containing nitrogen-doped carbon materials, generally synthesized by pyrolysis of various mixtures of iron, nitrogen, and carbon precursors. It is well-established that the final performance of such catalysts is dependent on a wide variety of different factors, including the proportions and ratios of the different elements, the atomic configuration of these elements, and in particular, the chemical environment of nitrogen and transition metal species in the carbon matrix.¹⁻⁹ In addition, other factors such as conductivity and microstructure also play an important role. All of the above factors can vary significantly depending on the type and ratio of precursors used, the pyrolysis temperature, the rate of heating during pyrolysis, the gases used in pyrolysis, and the type of support used.¹⁰⁻¹⁶

Carbon is a commonly used support material for electrocatalysts. It can be synthesized to have very large surface area and controllable porosity, providing suitable passageways for diffusion of reactants and products.^{17,18} Carbon is relatively chemically inert, making it resistant to many reactive species, and improving its durability in electrochemical

devices.¹⁹ Carbon has good electrical conductivity, helping to minimize electrode resistance and increasing the efficiency for fuel cell applications.²⁰ An enhanced understanding of the fundamental principles behind the synthesis process of carbon-based catalysts will enable development of better synthesis protocols and improved ability to scale-up production.

Here a specific type of carbon foam derived from the decomposition of metal alkoxide powders as a support material for Fe-N-C catalysts is employed. The advantage of this class of carbon foam is that it can be synthesized without the need for a sacrificial template, it has very large surface area (up to 3000 m²/g), relatively large pore-size (>1 µm), can be produced at multi-gram scale, and as a “bottom-up” technique the chemical structure can be routinely modified.²¹ This type of carbon foam was first synthesized by Choucair et al., by solvothermal reaction between sodium and ethanol, followed by pyrolysis.²² A study by Chandran et.al. on the decomposition of sodium ethoxide, using TGA-MS data, reported that the decomposed solid residues contain carbon with sodium carbonate and sodium hydroxide,²³ whereas the gaseous products had methane and ethylene (as major constituents) while ethane, propylene and butylene were minor constituents.²³ Sodium hydroxide is responsible for the activation and micropore formation of the carbon.

Sodium carbonate does not play a major role in this activation process.²⁴ Lyth et al. (and other researchers) showed that the solvothermal step was not required, that such carbon foams can be formed simply through pyrolysis of sodium ethoxide powder, and that it had applications such as hydrogen storage, due to the large surface area.^{25–27} Later they showed that superhydrophobic fluorinated carbon foam can be synthesized by replacing ethanol with e.g. trifluoroethanol.²⁸ Similarly, nitrogen-doped carbon foams were synthesized by replacing ethanol with e.g. ethanolamine,¹⁰ and utilized to gain insight into the ORR in metal-free (or “no metal added”) non-platinum group metal (non-PGM) catalysts.^{11,29,30} The nitrogen content can be controlled by changing the amount and the type of nitrogen-source in the reaction, e.g. by using varying ratios of ethanol with either ethanolamine, diethanolamine, or triethanolamine.

In this Chapter, the production of nitrogen-doped carbon foams is simplified and scaled up by switching synthesis of the precursor alkoxide powder from a high temperature and high pressure solvothermal reaction (Method A), to a new ambient temperature and ambient pressure, solution-based reaction protocol (Method B), based on in-house synthesis of a metal alkoxide, involving the use of sodium lumps as a reactant. Furthermore, a third solution-based synthesis route carried out at ambient temperature

and ambient pressure is introduced, which completely avoids the use of metal sodium lumps (Method C). These new protocols mean that scaling up the reaction can be achieved more safely, and the costs of synthesis can be significantly reduced. Several optimization steps are performed with the specific aim of increasing the surface area, increasing the yield, controlling the nitrogen content, finally using these tailored nitrogen-doped carbon foams as supports for effective Fe-N-C catalysts.

3.2 Experimental Methods

The catalyst precursors used in this study were synthesized via three different methods, (Figures 3.1, 3.2 and 3.3), as described below.

3.2.1 Precursor Synthesis

Method A (Solvothermal): The “solvothermal method” previously employed by our group (and others) is here designated **Method A** (Figure 3.1). Anhydrous ethanol (EtOH, Wako) and triethanolamine (TEOA, Aldrich) were added to a polytetrafluoroethylene-lined (PTFE-lined) high-pressure reactor (50 ml, Flon Industry, Japan), followed by an equimolar amount of metal sodium lumps (Aldrich). The reactor was quickly sealed, and then heated to 150 °C for 24 hours. After this, the vessel was cooled to room temperature and opened. Owing to additional safety concerns of high pressure, extra care was given

to the sealing and opening of the reactor. The resulting nitrogen-containing sodium alkoxide powder was removed, dried under vacuum, and crushed in a pestle. Three different types of precursor were synthesized using Method A, by changing the TEOA:EtOH ratio from 1:1 to 1:3 to 1:9, in order to vary the nitrogen content.

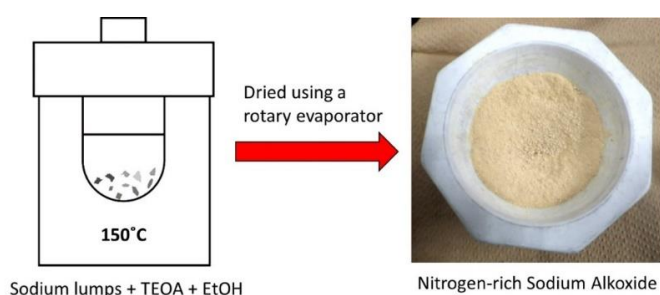
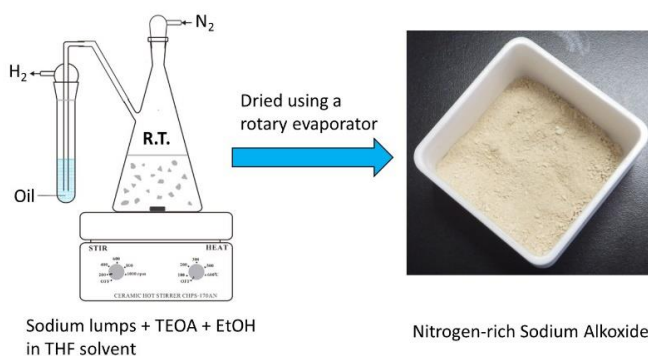


Figure 3.1: Solvothermal synthesis of nitrogen-rich sodium alkoxide at high temperature and pressure (Method A).

Method B (Solution-based): The first “solution-based” synthesis protocol (**Method B**) was designed to be more scalable, lower cost, and safer than Method A, by avoiding high pressure and high temperature operation. Another key difference is the use of the solvent tetrahydrofuran (THF, Wako), slowing down the reaction rate by decreasing the concentration of the reactants. The optimised ratios of TEOA:EtOH determined from Method A were adopted. A two-neck flat-bottom flask (300 ml) was used. First, air was evacuated from the flask using a roughing pump, and then N₂ gas flow was introduced through one of the necks. For safety, the reaction vessel was initially cooled using an ice

bath. THF, EtOH and TEOA were introduced into the flask by pipette, and magnetically stirred, still under flowing N_2 . Finally, sodium lumps were added. The ice bath was removed once the reaction was confirmed to proceed steadily. After 72 hrs the sodium lumps had completely reacted with the EtOH and TEOA, leaving a yellow-brown sodium alkoxide solution. This was dried in a rotary evaporator to recover the THF and obtain a yellow-white alkoxide powder, which was then crushed in a pestle.



*Figure 3.2: Solution-based synthesis of nitrogen-rich sodium alkoxide under flowing nitrogen, at ambient temperature and pressure (**Method B**).*

Method C (Solution-based, Metallic Sodium-Free): The second solution-based synthesis protocol (**Method C**) is designed to avoid the use of metallic sodium lumps, further improving the safety, scalability, and lowering the cost compared to Methods A and B. In Methods A and B sodium was used to deprotonate the alcohol groups in both ethanol (EtOH) and triethanolamine (TEOA) in the process of making a nitrogen-rich sodium alkoxide. Here, commercial sodium ethoxide (EtONa) and TEOA were used as

deprotonating agents instead. Hence, a new mechanism of deprotonation was proposed, based on the acid dissociation constants of EtONa: $pK_a = 15.5$ and TEOA: $pK_a = 7.74$. In solution, EtONa forms Na^+ and EtO^- ion pairs separated by a solvent shell. Since EtONa is a stronger base it is capable of deprotonating the alcohol groups in the TEOA. The ratio between EtONa and TEOA therefore determines where the equilibrium lies, i.e. excess sodium ethoxide deprotonates all of the TEOA molecules. The optimised ratios of TEOA:EtOH determined from Method A and B were adopted. Sodium ethoxide (17.5 g) was added to THF (400 ml) in a sealed round-bottomed flask under N_2 flow, and magnetically stirred for at least 30 minutes, to form a homogeneous dispersion. TEOA (5ml) was then added, the reaction vessel was closed, and solution was stirred under N_2 flow for 24 hours. The THF solvent was then removed by rotary evaporation, leaving the nitrogen-containing sodium alkoxide product.

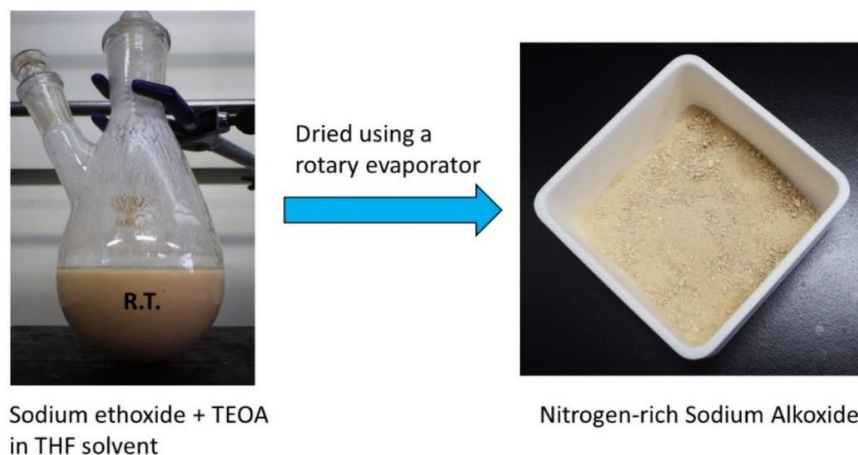


Figure 3.3: Solution-based metallic sodium-free synthesis of nitrogen-rich sodium alkoxide under flowing nitrogen, at standard temperature and pressure (Method C).

3.2.2 Synthesis of Nitrogen-doped Carbon Foam (N-C)

A two-step pyrolysis protocol was selected to provide more control over the carbon product. During the first step, the porous structure of the carbon is formed during decomposition, and therefore this is herein referred to as the “structure forming” step. The second step is performed at higher temperature in order to improve the conductivity and is herein referred to as the “graphitization step”.^{23,31,32} The powdery sodium alkoxide precursors described above were first heat treated in a box furnace at 600 °C for 2 hours under nitrogen flow (75 ml/min), to form a porous carbonaceous product. The heating rate of this first “structure forming” step was either 2, 5, or 10 °C/min. This carbonized product was then stirred overnight in deionized water, washed five times using vacuum filtration (to remove sodium-containing impurities), and then dried at 60 °C in an oven

overnight. The powders were then subjected to a second pyrolysis step under nitrogen, at either 900 or 1000 or 1400 °C for 2 hours (75 ml/min, 5 °C/min). The nitrogen-doped carbon (N-C) derived from the three methods (Method A, Method B and Method C) are labelled N-C-M($x:y$) _{r,T} , where M denotes the method (A, B or C); $x:y$ is the ratio TEOA:EtOH; r is the heating-rate during the first “structure-forming” pyrolysis step (either 2, 5 or 10 °C/min); and T is the temperature of the second pyrolysis step.

Method A was primarily used for the optimization of the TEOA:EtOH ratio. An optimized TEOA:EtOH ratio of 1:3 was then adopted for making the Method B support materials. The Method B supports were employed for the optimization of the 1st step pyrolysis heating-rate. Subsequently, the optimized parameters from Method B were used for the Method C pyrolysis steps. Method C was designed to be simpler, quicker, safer, to improve the yield, and the obtained samples were used for the optimization of the graphitization step.

3.2.3 Synthesis of Fe-N-C Electrocatalysts

The Fe-N-C catalyst was then prepared using iron (II) acetate (FeAc, Tokyo Chemical Industry), adsorbed onto selected nitrogen-doped carbon foam catalyst supports. 100 mg of N-C-B (1:3)_{5,1000} was added to 50 ml of water, 14.3 mg of FeAc was added to 10 ml of water, and then these two solutions were mixed together and magnetically stirred for 2 hrs. This mixture was then vacuum filtered once to remove excess FeAc, dried under vacuum, and then heat-treated in a tube furnace under flowing NH₃:N₂ (1:19, 100 ml/min) at 900 °C, for 2 hours. Table 3.1 summarizes the synthesis conditions heat treatment steps and measured properties for all of the nitrogen-doped carbon samples used in this Chapter.

3.3 Results and Discussion

3.3.1 Product Mass and Yield

Table 3.1 (and Table A3.1 in the Appendix) show the mass and yield of the carbon products synthesized using different methods and conditions. For Method A, the final product mass varies between 160 and 540 mg, whilst the yield varies from 0.8 to 3.1%. The low yield of 1.3 % at low TEOA ratio (1:9) may be attributed to the low concentration and strong basic nature of TEOA (pH = 10) in the precursor reactants, resulting in a slower rate of deprotonation compared to that of ethanol (pH = 7.3). The low yield at high TEOA

ratio of 1:1 could be due to an increase in viscosity of the solution under these conditions, complicating the uniform deprotonation of TEOA and EtOH. The best yield and mass are obtained for the sample with a TEOA:EtOH ratio of 1:3 and therefore this ratio was selected for use in Method B.

Using Method B, the product mass increases to between 440 and 1200 mg, whilst the yield increases to between 2.5 and 7.0 %, compared with Method A. The overall increase in yield for Method B is largely attributed to the use of flowing nitrogen, preventing the formation of side-products through reaction between oxygen or humidity in the air with the sodium, due to temperature and kinetic effects. These results are a clear indication of the advantage of the new synthesis protocol, Method B. Notably, the sample formed with a ramp rate of 5 °/min resulted in the highest yield, a significant improvement compared to heating rates of 2 and 10 °/min. This clearly indicates the importance of optimizing the heating rate for the second heat treatment step.

For Method C, there is a further increase in product mass (to between 1.50 and 1.68 g) and yield (to between 8.6 and 9.6 %) compared with Methods A and B. This increase in yield is attributed to the avoidance of metallic sodium as a reactant. In Methods A and B,

the sodium undergoes side reactions such as the formation of sodium hydroxides, and during pyrolysis, the formation of sodium carbonates. These are then washed out of the sample, significantly reducing the mass yield. In the case of Method C, the sodium ethoxide reacts directly with the TEOA, with fewer side products, significantly improving the yield. These results are a clear indication of the benefit of the sodium metal-free, solution-based synthesis of Method C.

Table 3.1: Summary of the synthesis conditions, product mass, yield, and surface area for the samples from Methods A, B and C. NB: The product mass of the 2nd heat treatment step is inferred from the yield – the real value is approximately half of this, since the samples were divided for different heat treatment conditions.

	TEOA: EtOH	1 st Step Ramp Rate (°/min)	2 nd Step Temperature (°C)	2 nd Step Product Mass (g)*	Final Yield (%)	Final Surface area (m²/g)	Sample Name
Method A	1:9	10	900	0.21	1.3	346	N-C-A(1:9) _{10,900}
	1:3		900	0.54	3.1	400	N-C-A(1:3) _{10,900}
			1000	0.53	3.0	351	N-C-A(1:3) _{10,1000}
	1:1		900	0.16	0.8	100	N-C-A(1:1) _{10,900}
Method B	1:3	10	900	0.61	3.5	1075	N-C-B(1:3) _{10,900}
			1000	0.58	3.3	813	N-C-B(1:3) _{10,1000}
		5	900	1.24	7.0	1500	N-C-B(1:3) _{5,900}
			1000	1.20	6.8	1286	N-C-B(1:3) _{5,1000}
		2	900	0.46	2.7	1866	N-C-B(1:3) _{2,900}
			1000	0.44	2.5	1620	N-C-B(1:3) _{2,1000}
Method C	TEOA: EtONa 1:3	5	1000	1.68	9.6	710	N-C-C(1:3) _{5,1000}
			1400	1.5	8.6	615	N-C-C(1:3) _{5,1400}

3.3.2 Scanning Electron Microscopy (SEM)

Figure 3.4 shows SEM images of nitrogen-doped carbon foams synthesized using Method A with different TEOA:EtOH ratios. The primary particle size is uniform at ~ 1 to $50\ \mu\text{m}$ in all samples, which was achieved by simply grinding in a pestle, without energy intensive milling or sieving. All the samples have similar microstructure, with a 3-D foam-like carbon framework. This framework is highly porous, with large spheroidal voids $\sim 2\ \mu\text{m}$ in diameter in most cases. The walls of these cells are extremely thin, as evidenced by their electron transparency, even under low accelerating voltage SEM electron irradiation.

Exclusively in the case of N-C-A(1:1)_{10,900} (Figure 3.4(e, f)), solid-appearing spheroidal carbon structures are observed instead of the usual pores, but with similar diameter to the pores of the other samples. These are presumed to be hollow and to effectively be partially-formed pores. This provides some indirect evidence that the formation of these porous carbons is due to a foaming process during decomposition (this foaming can also be observed by eye if the samples are burned in air). The size of the “bubbles” formed during the foaming process therefore determines the size of the pores after carbonization. In the specific case of N-C-A(1:1)_{10,900}, the TEOA ratio is relatively high, affecting the melting point and viscosity of the sodium alkoxide precursor. In this case, this seems to

result in sealed hollow carbon nanoparticle bubbles, rather than the open porous structure of the other materials. We previously observed such hollow nanoparticles by transmission electron microscopy (TEM) in similar fluorinated carbon materials.²⁸ This unusual microstructure will probably affect properties such as surface area and mass diffusion, and this sample is therefore unlikely to be suitable for use as a catalyst or catalyst support. This also informed the decision to use an optimized TEOA:EtOH ratio of 1:3 for Method B, to maximize the nitrogen content in the final product whilst retaining the open porous network.

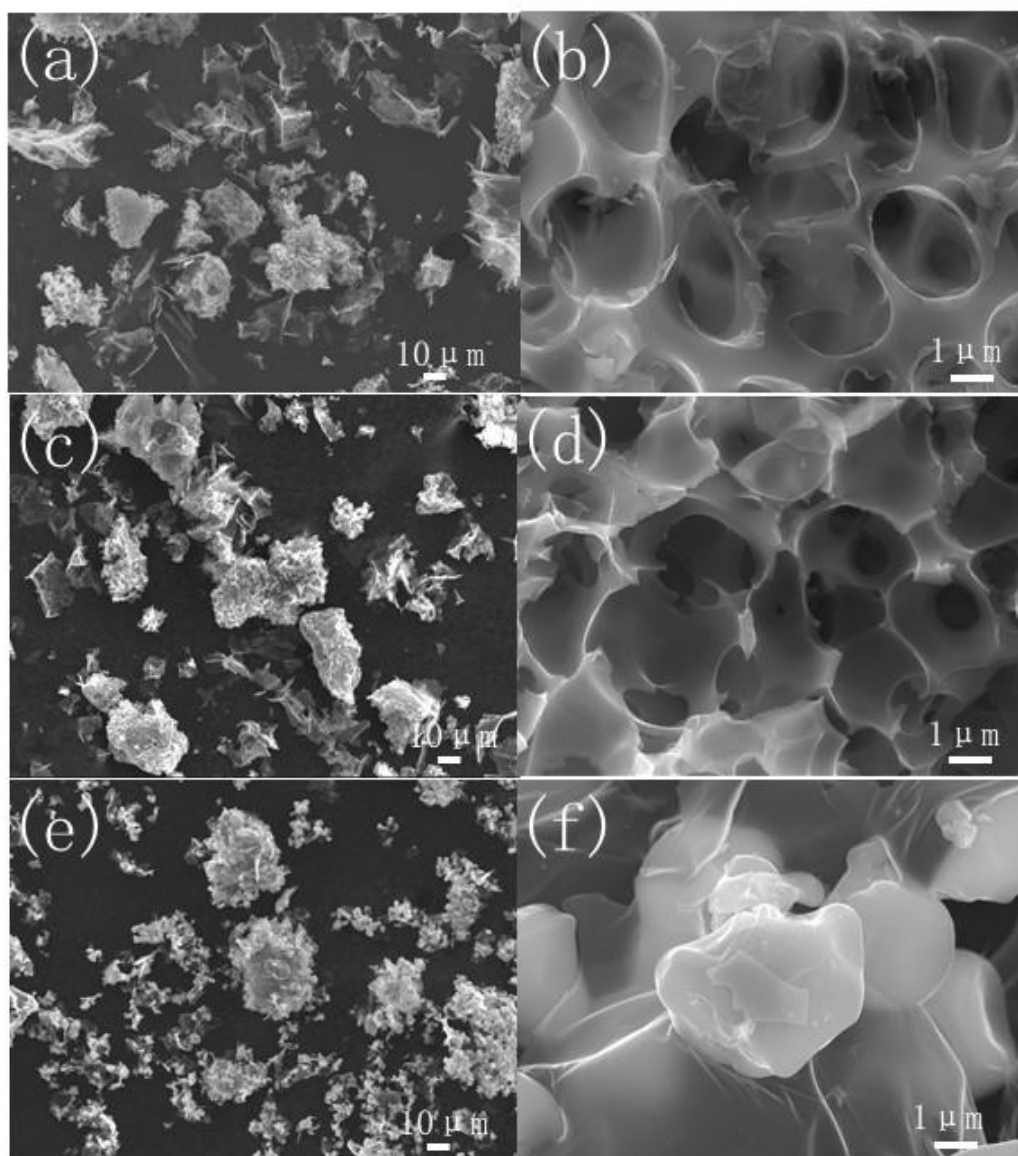


Figure 3.4: SEM images of: (a, b) $N-C-A(1:9)_{10,900}$; (c, d) $N-C-A(1:3)_{10,900}$; and (e, f) $N-C-A(1:1)_{10,900}$, at two different magnifications.

The materials synthesized using Method B, Figure 3.5 (a-d) have similar particle size distribution and porous structure as those using Method A. This confirms that as well as increasing the product mass and yield scale, and using a safer / less energy intensive process, the same general structure can be obtained. It also confirms the high reproducibility of materials produced using this technique, despite the completely different precursor ratios, pyrolysis conditions, and synthesis methods. The pore size in N-C-B(1:3)_{5,1000} (Fig. 3.5 (c, d)) appears to be much smaller (i.e. ~250-500 nm) than in N-C-B(1:3)_{2,1000} (Fig. 3.5 (a, b)). This is attributed to the increase in heating rate in the first “structure-forming” step, again changing the way in which the sodium alkoxides precursor melts, foams and decomposes. Having smaller pores is expected to improve the volumetric activity of any resulting catalyst, and therefore is more desirable.

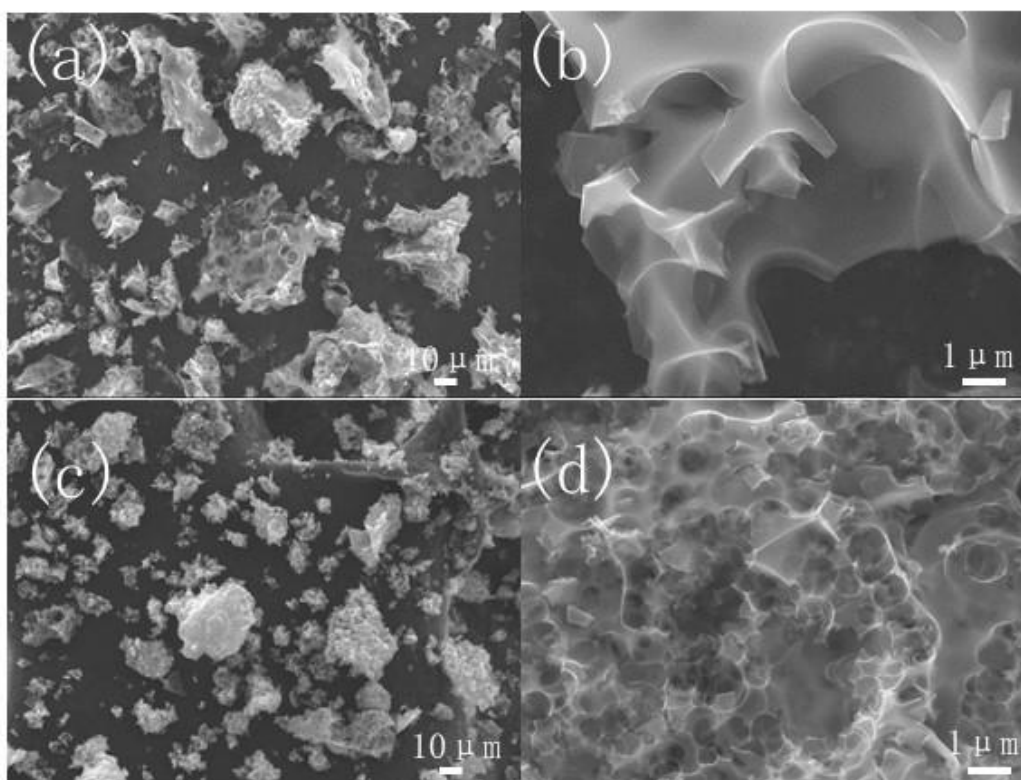


Figure 3.5: SEM images of: (a, b) $N-C-B(1:3)_{2,1000}$; and (c, d) $N-C-B(1:3)_{5,1000}$, at two different magnifications.

Figure 3.6 shows SEM images of samples synthesized using “metallic sodium free” Method C, after heat treatment at 1000 and 1400 °C. Again, these samples have similar microstructure to those made from Methods A and B, despite the use of completely different starting materials for making the nitrogen-rich sodium alkoxide. This again confirms the general applicability of this synthesis technique. The macropore size in both samples is $\sim 1\ \mu\text{m}$, also similar to that obtained in Methods A and B.

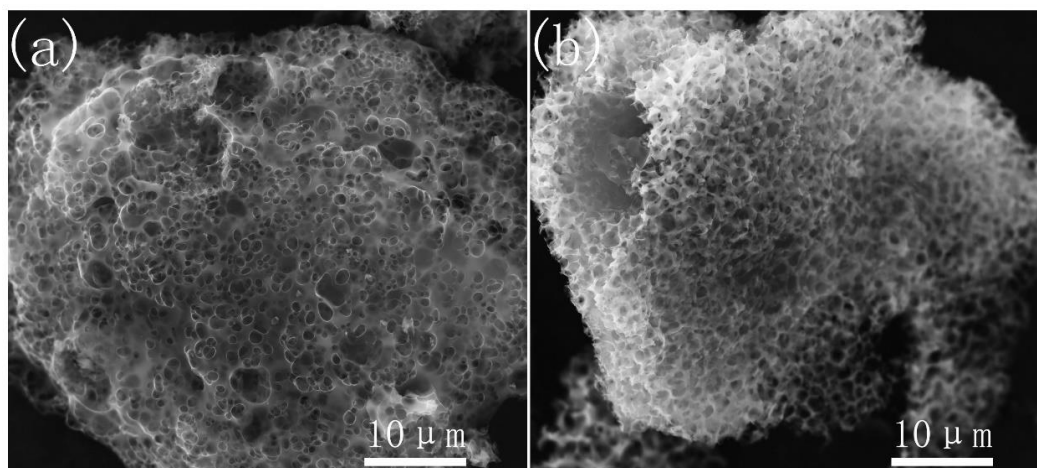


Figure 3.6: SEM image of nitrogen-doped carbon foams: (a) $N-C-C(1:3)_{5,1000}$ and (b) $N-C-C(1:3)_{5,1400}$.

Figure 3.7 shows a typical low-magnification SEM image of one of the catalysts. This highlights the highly uniform and reproducible nature of the carbon powders synthesized using this technique.

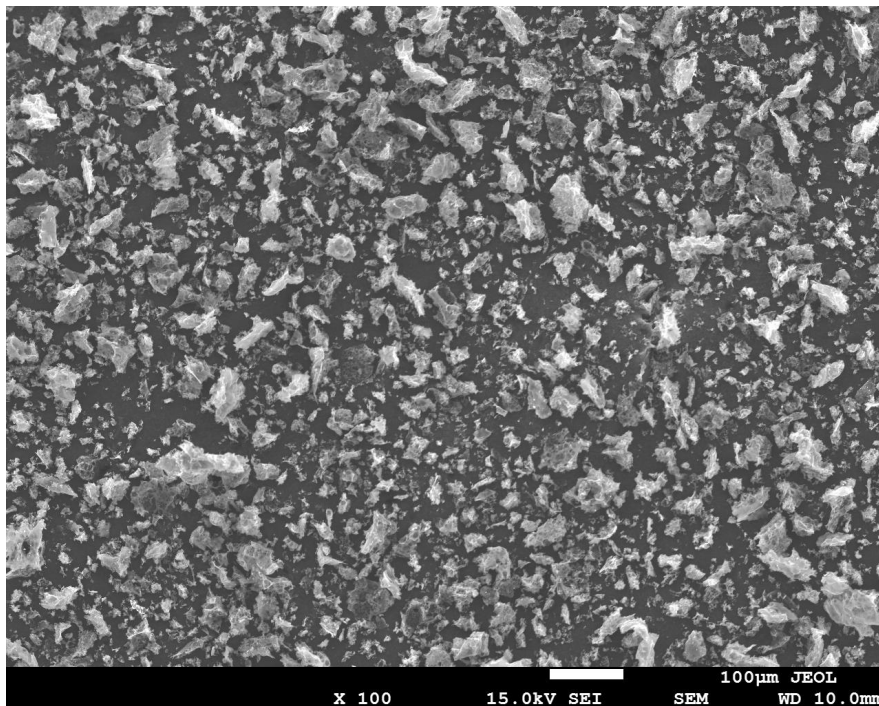


Figure 3.7: Low magnification SEM image of carbon foam catalyst sample N-C-B(1:3)_{5,1000}, which is representative of all the samples studied here.

3.3.3 Surface Area and Porosity

The porosity and surface area of the different nitrogen-doped carbon foams (Table 3.1) were determined from the N₂ adsorption/desorption isotherms in Figures 3.8, 3.9 and 3.10 of the samples obtained using the three different synthesis methods. For Method A, Figure 3.8 (a) the measured surface areas are 346, 400, 351 and 100 m²g⁻¹ for N-C-A(1:9)_{10,900}, N-C-A(1:3)_{10,900}, N-C-A(1:3)_{10,1000}, and N-C-A(1:1)_{10,900}, respectively (average: 299 m²g⁻¹). Despite the changing TEOA:EtOH ratio, the first three samples have similar surface

area. However, N-C-A (1:1)_{10,900} has significantly lower surface area, which is attributed to the spherical closed-cell structures observed by SEM, preventing infiltration of nitrogen gas to the interior, and thus lowering the accessible surface area. In the case of the more open porous structures, nitrogen can access every surface. This influenced the decision to use a ratio of 1:3 in Method B, to combine the relatively high nitrogen content with reasonable surface area.

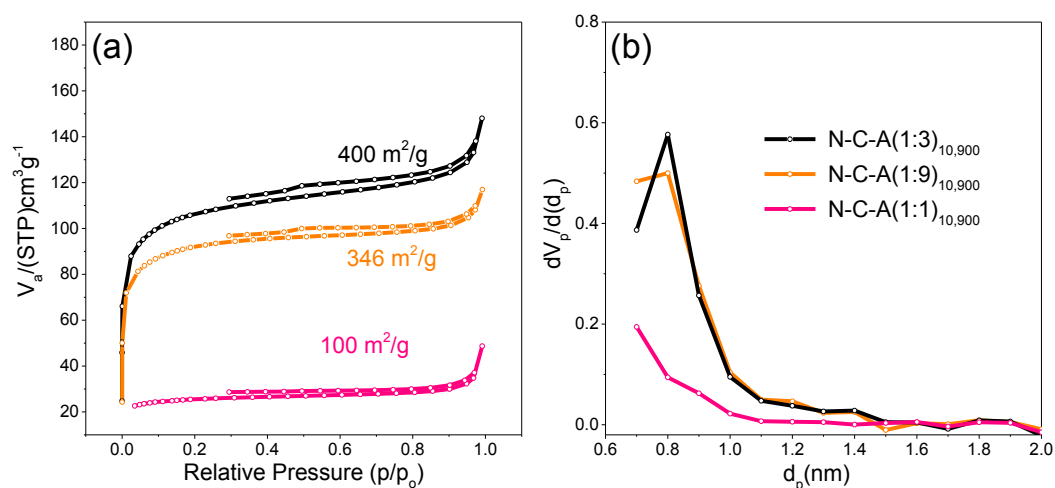


Figure 3.8: (a) BET surface area, and (b) MP-plots of Method A samples.

The samples synthesized using Method B, Figure 3.9 (b), have a much higher average surface area of 1360 m²g⁻¹. This clearly shows that Method B is an improved synthesis method. There is a trend of increasing surface area with decreasing ramp rate with average

surface areas of 944, 1393, and 1743 m^2g^{-1} for ramp rates of 10, 5, and 2 $^\circ\text{C}/\text{min}$, respectively. This may be connected to the amount of time available for micropore formation during the carbonization process when a lower ramp rate is used. There is also a decrease in surface area when a higher temperature is used in the second pyrolysis step, which is a commonly observed effect for carbon.

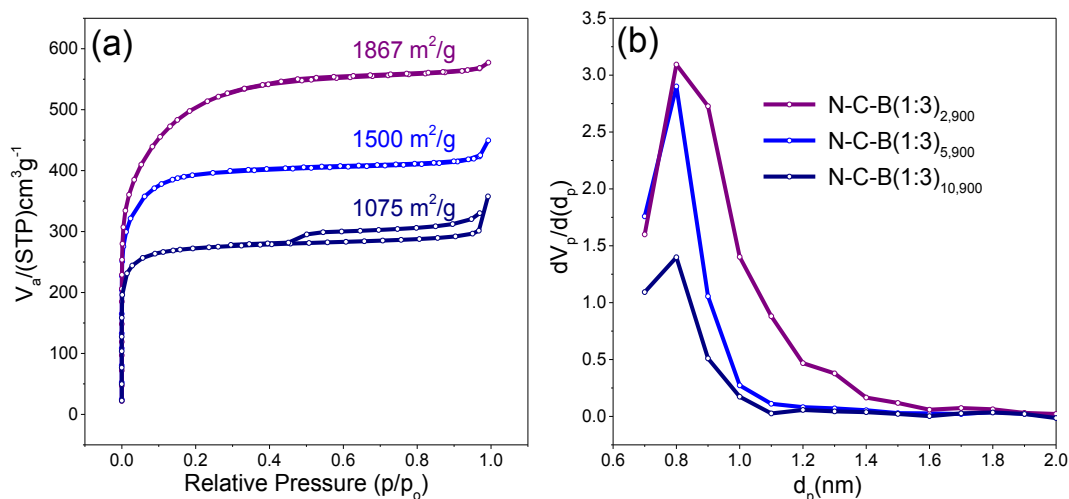


Figure 3.9: (a) BET surface area, and (b) MP-plots of Method B samples.

Figure 3.10 (a) shows the isotherms for Method C samples heat treated at 1000 and 1400 $^\circ\text{C}$. The respective surface areas of these samples are 710 and 615 m^2g^{-1} . These samples therefore show a significant decrease in BET surface area compared to Method B, despite having similar isotherms and morphology (as observed in the SEM images). In addition, the micropore size distribution is significantly narrower than in Method A or B.

This could be due to the absence of metallic sodium in this technique, which could have some templating or etching effect (forming e.g. sodium carbides) and widening the pore size distribution. As such, the deprotonation of TEOA using sodium ethoxide instead of metallic sodium seems to result in a more uniform product.

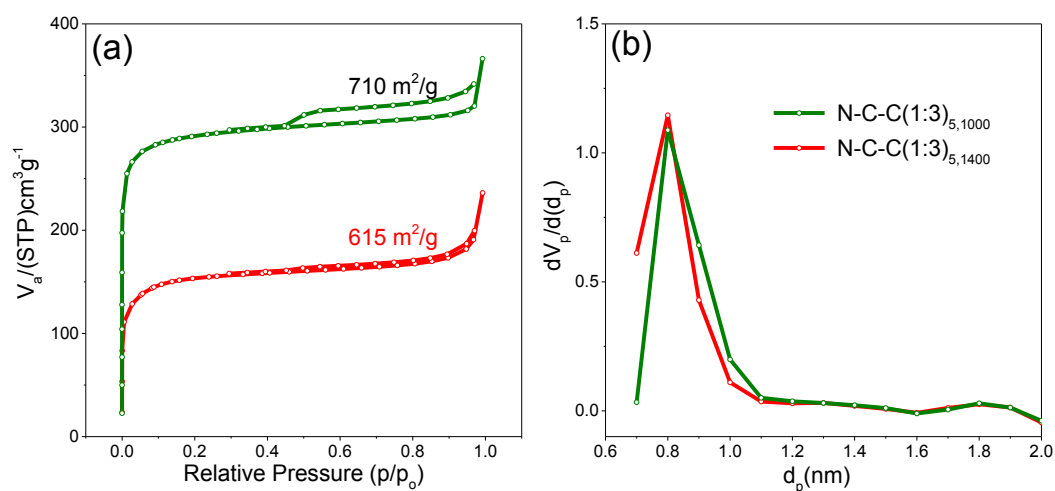


Figure 3.10: (a) BET surface area, and (b) MP-plots of Method C samples.

Most of the isotherms of the carbon foams have Type I(a) characteristics, indicating microporous materials with narrow micropores (of $<1 \text{ nm}$). The inflection at higher relative pressure ~ 1 indicates a contribution from Type II isotherms, indicating non-porous or macroporous regions of the sample, which may correspond to the surfaces of the large micron-scale macropores observed by SEM.^{33,34} In addition, Type H4 hysteresis loops are observed in the Method A, B and C samples, which indicate a micro-

mesoporous nature, normally associated with micropore filling in micro-mesoporous carbons, providing further evidence of their micro-mesoporous nature. The exception is N-C-A(1:1)_{10,900} which has a Type III isotherm associated with non-porous or microporous solids, reflecting the unusual closed-cell morphology as observed by SEM.^{34,35}

The presence of micropores is supported by the MP method analysis shown in Figures 3.8 (b), 3.9 (b) and 3.10 (b) where V_p is the pore volume, and r_p is the pore radius. The peak pore radius ranges from 0.65 to 0.80 nm in all cases. Method B has the highest micropore volume followed by Method C and then Method A samples, which correlates with the BET surface area. In the case of N-C-A(1:1)_{10,900} the micropore volume is very small, suggesting that nitrogen adsorption occurs mostly over the external surface area of the closed-cells,³⁵ in agreement with the Type III isotherm and the SEM images.

Meanwhile, Method C samples, shows a decrease in BET surface area as pyrolysis temperature is increased from 1000 to 1400 °C, coupled by increase in both the average pore diameter, and the $V_{\text{meso}}/V_{\text{micro}}$ ratio. This is as anticipated since higher temperature treatment graphitizes the sample by removing contaminants on the surfaces of the porous

structure. In theory, the 1400 sample should be more graphitized, hence should be more electrically conductive and this is expected to aid in electronic conduction during electrochemical processes.

The BJH pore size distributions for selected samples from Methods A, B and C are plotted in Figure 11 below, highlighting the meso- and macropore ranges. The maximum observable pore size using this technique is ~ 100 nm, so the micron-scale macropores seen in the SEM images are not manifested in this data. The mesopore distribution is remarkably similar Method A and B samples. There is a small peak at a pore radius of ~ 35 nm in all cases. Meanwhile, the majority of pores have a radius of less than 10 nm, in agreement with the MP-plots. In addition to Method C samples having the majority of pores with radius less than 10 nm, the pores with ~ 22 and ~ 35 nm radii are quite significant. This suggests a unique development of the mesopores for Method C samples.

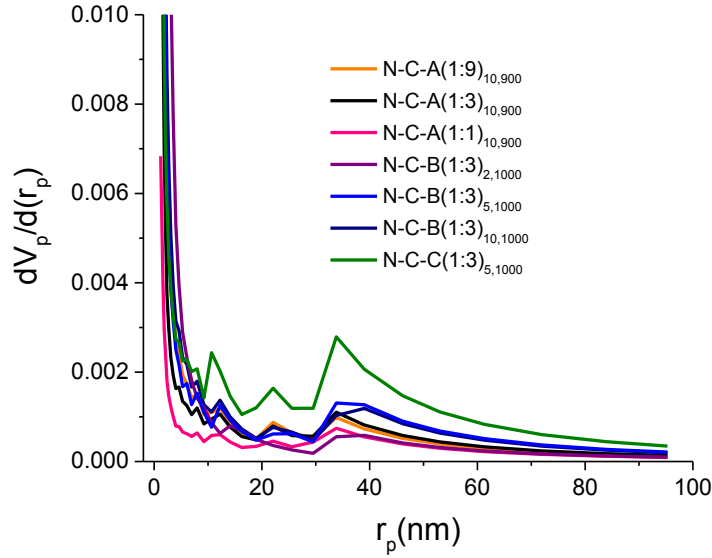


Figure 3.11: BJH-plots of Method A, B and C samples.

In summary of the surface area and porosity data, these materials have broad distributions of micropores (highlighted by the MP method), mesopores (shown in the BJH data), and the macropores observed by SEM. Method B results in larger micropore volume, Table 3.2. Since the surface area, porosity, and pore connectivity have a significant influence on the accessibility of catalytic active sites, it is expected from the above results that Method B would be most suited to electrochemical applications. Method C samples have a lower surface area than Method B samples, but with a well-developed porosity distribution (evidenced by higher $V_{\text{meso}}/V_{\text{micro}}$ ratio, Table 3.2) it is also expected that these samples will show good results in electrochemical tests.

Table 3.2: Summary of the N_2 adsorption/desorption-based surface area, microporous surface area, isotherm type, pore diameter (2t) and V_{meso}/V_{micro} ratio of Method B sample and Method C samples pyrolyzed at 1000 and 1400 °C.

Pyrolysis Temperature °C	BET (m ² /g)	Microporous area (m ² /g) MP (T-plot)	Isotherm type	Pore Diameter 2t (nm)	V_{meso}/V_{micro}
N-C-B(1:3) _{5,1000}	1280	(1342) (1350)	1a	0.76	0.30
N-C-C(1:3) _{5,1000}	710	700 (707)	1a	0.76	0.60
N-C-C(1:3) _{5,1400}	615	588 (582)	1a	0.80	0.80

3.3.4 X-ray Photoelectron Spectroscopy (XPS)

The XPS survey scans, and C1s and O1s narrow scans of samples prepared by Method A, B, and C are shown in Figures A3.1, A3.2 and A3.3 in the appendix, whilst the N 1s narrow scans are shown in Figure 3.12, and the elemental compositions are summarized in Table 3.3. The XPS surveys for all samples show a predominant C 1s peak at ~284.5 eV, an O 1s peak at ~532 eV, and an N 1s peak at ~398.2 eV.

In the catalysts synthesized using Method A, the final nitrogen content increases with increasing TEOA:EtOH ratio, from 2.0 to 2.9 to 4.3 wt% for 1:9, 1:3 and 1:1, respectively.

This is as expected, correlating with the amount of nitrogen in the precursor, and showing that this synthesis method is suitable for tailoring the nitrogen-content of the carbon foams.

For Method B, the nitrogen content increases as the ramp rate increases (saturating at

about 3.5 wt%), suggesting that more nitrogen is lost from the sample when the pyrolysis process is slower/longer, as expected. The oxygen content is significantly lower for Method B compared to Method A, suggesting that performing the reaction under nitrogen atmosphere helps to suppress the incorporation of oxygen-containing surface functional groups, and/or results in less adsorbed water on the surface (possibly due to enhanced hydrophobicity). There is a significant difference in residual sodium content depending on whether the second pyrolysis step is performed at 900 or 1000 °C, for both Method A and Method B. This could be attributed to heating the sample to well above the boiling point of sodium (882.8 °C); and/or the decomposition/reaction of residual NaOH and Na₂CO₃ to form Na and CO₂ at elevated temperature. For Method C samples, the elemental compositions are quite similar to Method B when comparing samples heat-treated to 1000 °C, respectively. In particular, the carbon, nitrogen and oxygen contents of N-C-B(1:3)_{5,1000} and N-C-C(1:3)_{5,1000} are: 92.0 and 92.5 at%; 3.4 and 3.3 at%; and 3.5 and 3.1 at%; respectively (shown in Table 3.3). This is reassuring evidence of the reproducibility of the chemical composition of the two methods, despite using completely different chemical synthesis protocols. Meanwhile, the carbon content increases between the 1000 and 1400 °C samples as expected during graphitization, resulting in reductions in the nitrogen and oxygen contents. These results are evidence of the removal of less

stable functional groups on the carbon surface, e.g. pyrrolic nitrogen or OH groups, resulting in the formation of more stable nitrogen and oxygen functional groups e.g. the formation of graphitic nitrogen bonds.

The pyrrolic, pyridinic, and graphitic C-N bonds observed in the deconvolution of the N 1s peak (Figure 3.12) confirm that nitrogen atoms were successfully doped into the carbon matrix. Most of the samples have remarkably similar profiles, further highlighting the reproducibility and consistency of these three different synthesis protocols. Peak fitting mainly reveals the presence of pyridinic (~398.2 eV); pyrrolic (~399.3 eV), and graphitic / tertiary (400.8 eV) nitrogen, as well as oxygen-coordination peaks (> 402 eV).³⁶ The ratio of graphitic nitrogen to pyridinic nitrogen intensities is 1.2 ± 0.2 in all cases. The two exceptions are N-C-B(1:3)_{2,1000} and N-C-C(1:3)_{5,1400}, which have much lower nitrogen contents (attributed to the slower heating rate and higher graphitization temperature, respectively), resulting in a low signal to noise ratio, and thus preventing realistic peak fitting. The high proportion of pyridinic species in these samples are expected to provide suitable sites for Fe coordination for catalyst synthesis, as discussed in the final section of this study. Meanwhile, for Method C the relative intensity of the pyridinic peak centered around 398.3 eV is dramatically decreased after pyrolysis at 1400

°C, leaving a high proportion of graphitic nitrogen. This is because graphitic nitrogen is more thermodynamically stable than pyridinic nitrogen.

Table 3.3: XPS analysis of the materials used in this study after the 1st (black text) and 2nd (red text) pyrolysis steps.

Sample Name	XPS (wt. %)							
	C		N		O		Na	
	1 st	2 nd	1 st	2 nd	1 st	2 nd	1 st	2 nd
N-C-A(1:9) _{10,900}	73.5	73.7	3.7	2.0	19.2	21.3	3.6	3.0
N-C-A(1:3) _{10,900}	76.4	79.5	4.9	2.9	16.0	15.9	2.7	1.7
N-C-A(1:3) _{10,1000}	76.4	90.0	4.9	3.5	16.0	5.5	2.7	0.8
N-C-A(1:1) _{10,900}	62.8	65.9	6.3	4.3	24.6	22.1	6.3	7.7
N-C-B(1:3) _{10,900}	-	90.4	-	3.8	-	4.0	-	1.7
N-C-B(1:3) _{5,900}	72.5	77.8	6.7	5.2	14.9	11.0	5.9	5.9
N-C-B(1:3) _{2,900}	76.3	82.5	1.7	1.8	15.4	10.0	6.6	5.7
N-C-B(1:3) _{10,1000}	-	92.0	-	3.4	-	3.5	-	1.0
N-C-B(1:3) _{5,1000}	72.5	92.6	6.7	3.4	14.9	3.7	5.9	0.4
N-C-B(1:3) _{2,1000}	76.3	88.6	1.7	1.0	15.4	10.3	6.6	0.1
N-C-C(1:3) _{5,1000}	77.8	92.5	10.8	3.3	8.9	3.1	2.6	1.1
N-C-C(1:3) _{5,1400}	77.8	96.8	10.8	1.1	8.9	1.9	2.6	0.3

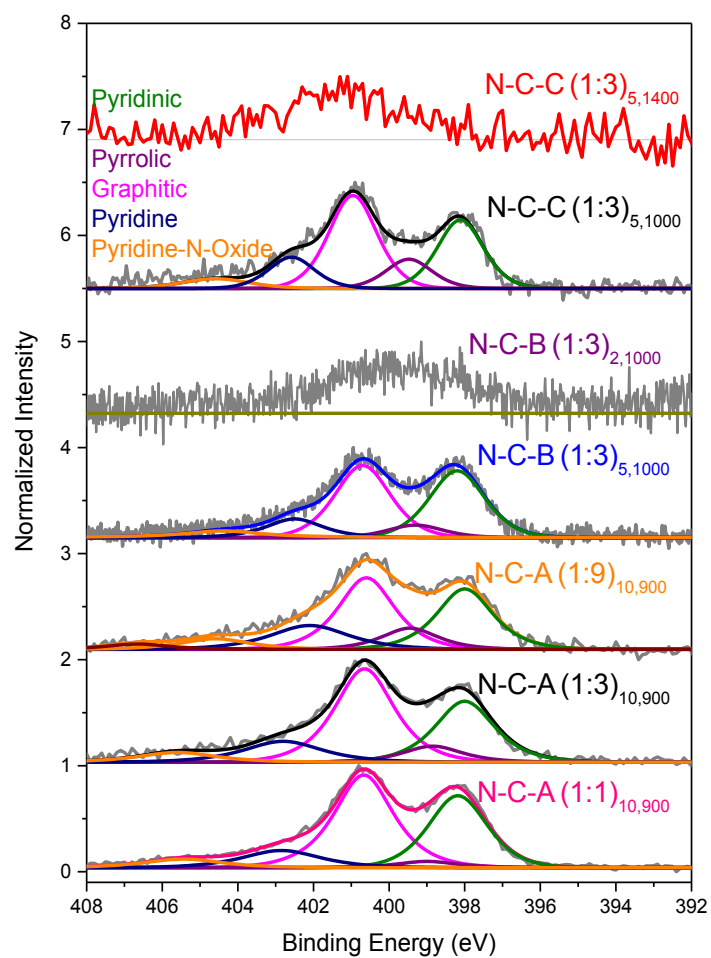


Figure 3.12: *N 1s* spectrum of selected samples: Method A samples heat-treated at 900 °C; Method B samples heat-treated at 1000 °C; and Method C samples heat-treated at 1000 and 1400 °C.

3.3.5 X-ray Diffraction (XRD)

Figure 3.13 shows XRD spectra for the samples synthesized using Method A, B and C.

These are all almost identical, with a broad diffraction peak at 22° , which corresponds to typical (002) interlayer spacing of 0.4 nm for amorphous or nitrogen-doped carbons^{37,38}.

A smaller peak centered at 44° is associated with the (100) in-plane hexagonal atomic arrangement of sp^2 carbon (i.e., 0.2 nm).

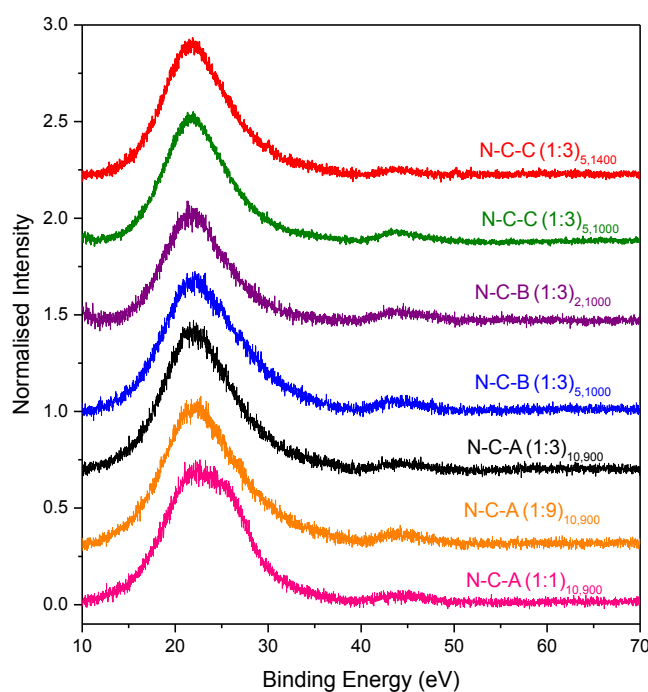


Figure 3.13: XRD spectra of: Method A samples heat-treated at 900 °C; Method B samples heat-treated at 1000 °C; & Method C samples heat-treated at 1000 and 1400 °C.

3.3.6 Raman Spectroscopy

Figure 3.14 shows Raman spectra of the samples synthesized using Method C. Both spectra have a first order D peak at 1353 cm^{-1} (induced by nitrogen doping effect on the breathing mode of aromatic rings of the graphene layer); a G peak at 1591 cm^{-1} (corresponding to the in-plane vibration of the C-C bonds); and a low intensity second order 2D peak at 2635 cm^{-1} (an overtone of D peak). As expected, the sample heat-treated at 1400°C shows slight improvement in crystallinity as observed in sharpness of the peaks and slight increase in intensity of the peaks, due to graphitization.

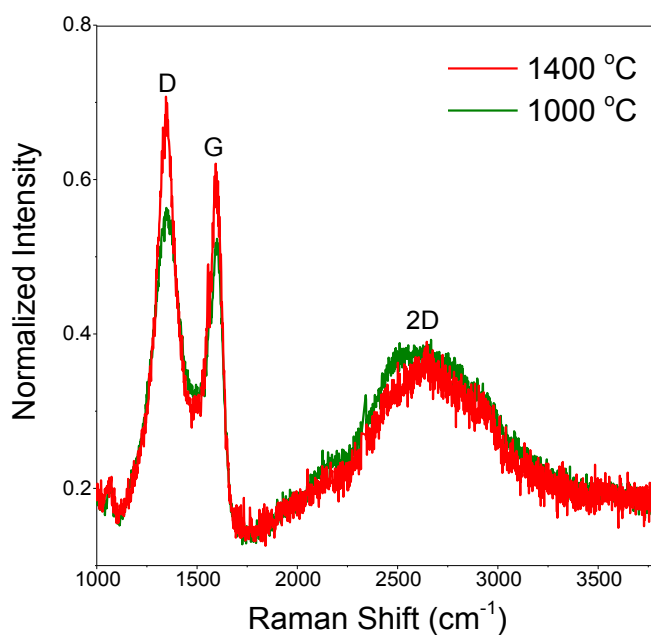


Figure 3.14: Raman spectrum of Method C samples pyrolyzed at 1000 and 1400 °C.

3.3.7 Electrochemical Characterization

In order to screen which of these nitrogen-doped carbon foams are suitable as supports for Fe-N-C catalysts, or even as “metal-free” (or “no metal added”) catalysts in their own right, electrochemical analysis was performed. Cyclic voltammograms (CVs) of all of the samples measured in N₂ are shown in Figure 3.15 (a). These quasi-rectangular traces are typical for carbon materials with large surface area. Most of the CV plots are remarkably similar despite the different synthesis methods, pyrolysis temperatures, nitrogen contents etc. The differences in their surface areas does not seem to significantly influence the double layer capacitance, suggesting that surface area alone is not the only contributing factor. In fact, the porosity, and specifically the $V_{\text{meso}}/V_{\text{micro}}$ ratios seem to be more influential.^{39,40}

However, two samples stand out as having significantly higher double layer capacitance, both synthesized using Method B, namely N-C-B(1:3)_{2,1000} and N-C-B(1:3)_{5,1000}. This simply reflects the relatively high surface area of these samples, as measured by BET. Similarly, one sample N-C-A(1:1)_{10,900} has noticeably lower double layer capacitance, corresponding with the lower surface area and the unusual microstructure observed by SEM. Meanwhile, at potentials of around 0.4 V_{RHE} and 0.65 V_{RHE}, small peaks are

observed in some of the plots, suggesting that oxygen-containing functional groups on the surface undergo redox transitions.⁴¹

Figure 3.15 (b) shows linear sweep voltammograms (LSVs) measured in O₂ (after subtraction of linear sweep data performed in N₂). Some activity for the oxygen reduction reaction is observed in all of the samples. Nitrogen-doped carbons are already well-known to be ORR active in acid media even in the absence of iron or other transition metals.⁴² However, this is usually attributed to production of hydrogen peroxide followed by reduction to water, in a 2+2 electron transfer step, rather than a direct 4 electron transfer which is preferred for use in practical applications.^{43,8} For samples synthesized using Method A, the electrochemical current densities are all relatively low, reflecting the lower surface area. The highest ORR activity for samples synthesized using Method A is recorded for N-C-A(1:3)_{10,1000}, and this therefore influenced the decision to choose the ratio of TEOA:EtOH = 1:3 for use in Method B.

For samples synthesized using Method B, the highest ORR current density is observed for N-C-B(1:3)_{5,1000}, with very low ORR activity for the other samples. The large difference in LSV performance based only on the change in the heating rate in Method B is striking. This may reflect the higher oxygen content in N-C-B(1:3)_{2,1000} as observed in XPS (also associated with the REDOX couple observed in the CV plots); the limited pore

connectivity in N-C-B(1:3)_{10,1000} (as inferred from the lower mass limited current density); the smaller pore size of N-C-B(1:3)_{5,1000} as observed in SEM; or the higher nitrogen content of N-C-B(1:3)_{5,1000} as measured using XPS, potentially providing a higher density of metal-free ORR active sites.

The sample synthesized using Method C, followed by heat treatment at 1000 °C (i.e. N-C-C(1:3)_{5,1000}) has similarly high activity to Method B sample N-C-B(1:3)_{5,1000}, with similar onset potential, slightly lower half wave potential, and significantly higher mass diffusion limited current density. Their similarity in terms of electrochemistry despite the completely different synthesis methods is particularly striking, since they have the same precursor ratios, 1st step heating rate, and 2nd step graphitization temperature. *This is a clear indication of the similarities in the available nitrogen-based ORR active sites in both samples.* Their excellent metal-free ORR activity is likely due to a combination of large surface area, the presence of pyridinic nitrogen, and high mesoporous to microporous ratio. Meanwhile, graphitization at 1400 °C (i.e. N-C-C(1:3)_{5,1400}) results in a significant decrease in ORR activity, which could be due to the lower nitrogen content, and specifically the very low proportion of pyridinic nitrogen in this sample, which is thought to be ORR active.^{44,45}

Despite these metal-free nitrogen-doped carbons not having sufficient activity to be useful catalysts in their own right (at least in acid medium), this electrochemical data suggests that N-C-B(1:3)_{5,1000}, N-C-C(1:3)_{5,1000} and N-C-C(1:3)_{5,1400} are promising as support materials for the synthesis of Fe-N-C catalysts. This will be explored further in the following section.

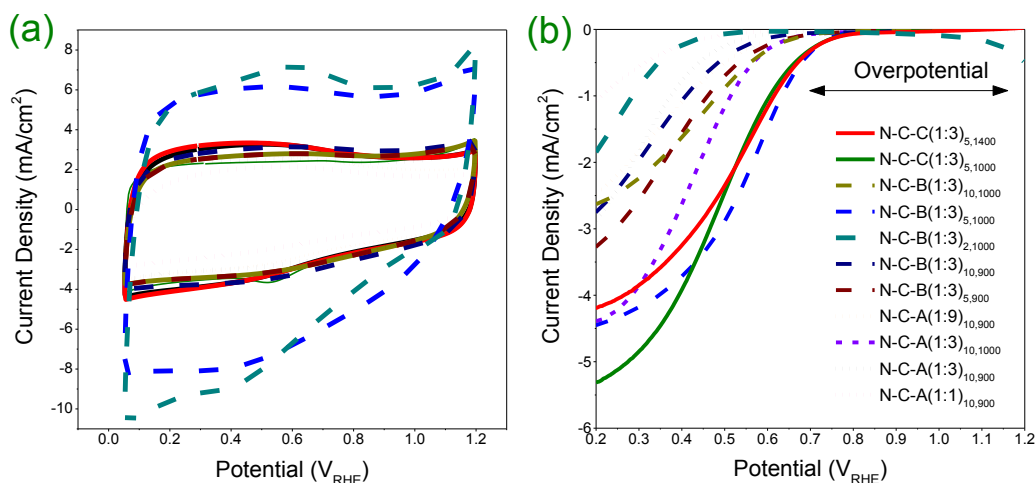


Figure 3.15: (a) Cyclic voltammograms (CVs), and (b) linear sweep voltammograms (LSVs) of the nitrogen-doped carbon foam materials from Method A (dotted lines), Method B (dashed lines) and Method C (solid lines).

3.3.8 Iron Decoration on Nitrogen-Doped Carbon Foams

The most suitable candidates for use as Fe-N-C supports for Pt-free ORR electrocatalysis were selected with regards to optimized yield, nitrogen content, surface area, and electrochemical response, i.e. N-C-B(1:3)_{5,1000}; N-C-C(1:3)_{5,1000}; and N-C-C(1:3)_{5,1400} (herein labelled Fe-N-C-B₁₀₀₀; Fe-N-C-C₁₀₀₀; and Fe-N-C-C₁₄₀₀, respectively, for

simplicity). As such, FeAc was infiltrated onto these nitrogen-doped carbon foam supports, and then pyrolysis was carried out in NH_3 atmosphere at 900 °C, according to established protocols previously developed by Dodelet et al.^{7,46} The samples were then washed using acid (1 M H_2SO_4) using the protocol explained in Chapter 2, in order to dissolve residual Fe nanoparticles, which are inactive for the ORR.⁴⁷ The resulting Fe-N-C catalysts are compared with a commercially-sourced non-PGM catalyst benchmark also based on a carbon, nitrogen and iron structure (NPC-2000, Pajarito Powder, transition metal content ~0.7%; nitrogen content 3.0%).⁴²

The microstructure of the Fe-N-C-B₁₀₀₀ catalyst is shown in the SEM images in Figure 3.16. The foam-type structure is retained after iron decoration, and the SEM images at low magnification are similar to the images of the undecorated support. However, at higher magnification, Figure 3.16 (b), nanoparticles can be seen decorating the surface. In some regions, agglomerations of nanostructures are observed (Figure 3.16 (c)), including carbon nanotubes grown via the catalytic action of Fe at elevated temperature.^{48,49} Figure 3.16 (d) shows a higher magnification image of some of the nanoparticles, revealing a bright iron core encapsulated by carbon. The TEM image in Figure 3.16 (e) shows a metallic Fe nanoparticle size of ~30 nm diameter. This is

encapsulated by a few layers of graphitized carbon with a lattice spacing of ~ 0.35 nm, which is slightly larger than that of graphite (i.e. 0.335 nm). Selected area electron diffraction (SAED, Figure (3.16 (f))) confirmed that the nanoparticle core is metallic Fe, and the shell is graphitized carbon. Characterisation of the Fe-N-C-C₁₀₀₀ and Fe-N-C-C₁₄₀₀ samples was not performed, and the decomposition of FeAc on their surface is presumed to be similar to the case of Fe-N-C-B₁₀₀₀.

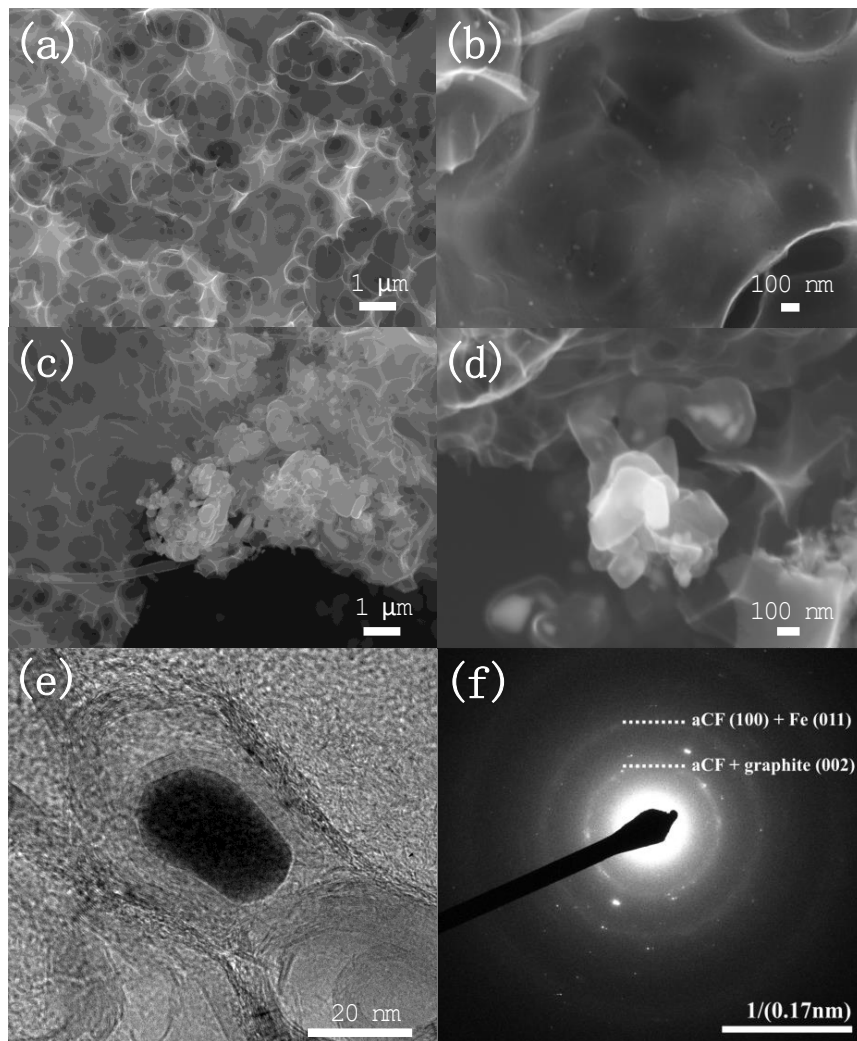


Figure 3.16: (a-d) SEM and (e, f) SAED and TEM images of the Fe-N-C-B(1:3)_{5,1000} catalyst.

All of the samples have reasonably large surface area, most of which is attributed to the large micropore area (Table 3.4) The BET surface area of Fe-N-C-B₁₀₀₀ increases from 1286 to 1600 m²/g after iron decoration and acid washing. The total pore volume increases from 0.64 to 0.77 cm³/g; the micropore volume does not significantly change; and the

mesopore volume increases from 0.12 to 0.26 cm³/g after Fe decoration (Table A3.2). This increase in surface area and porosity is attributed to the creation of additional carbon nanostructures as observed in Figure 3.16, and the action of NH₃ on the support, which is known to increase porosity. The micropore surface area generated during heat-treatment is believed to assist in hosting ORR accessible active sites.¹⁵ For Fe-N-C-C₁₀₀₀ the surface area increases from 710 to 900 m²/g. It has an average pore diameter of 1.1 nm and a mesopore to micropore ratio of 1.1. This sample is thus rich in mesopores, which is reported to be favourable for efficient mass transport.⁴⁰ For Fe-N-C-C₁₄₀₀ the surface area increases from 615 to 788 m²/g. It has similar pore diameter (0.8 nm) and mesopore to micropore ratio (0.5) to Fe-N-C-B₁₀₀₀. Meanwhile, the commercial NPC-2000 catalyst is largely mesoporous.³⁴

Table 3.4: Comparison of the BET surface area, micropore area, and pore diameter for selected Method B and Method C samples decorated with iron.

Sample Name	BET (m ² /g)	Micropore area (m ² /g)	Pore Diameter 2t (nm)	V _{meso} /V _{micro}
N-C-B(1:3) _{5,1000}	1286	1342	0.76	0.3
N-C-C(1:3) _{5,1000}	710	700	0.76	0.6
N-C-C(1:3) _{5,1400}	615	588	0.8	0.8
Fe-N-C-B(1:3) _{5,1000}	1600	(1213)	0.8	0.5
Fe-N-C-C(1:3) _{5,1000}	900	810	1.1	1.1
Fe-N-C-C(1:3) _{5,1400}	788	712	0.8	0.5

The electrochemical performance of the three electrocatalysts is shown in Figure 3.17 and Table 3.5. The initial activity of Fe-N-C-B₁₀₀₀ is slightly higher than that of NPC-2000, with similar onset potential, similar half-wave potential, higher mass diffusion limited current density; and slightly lower electron transfer number. These measured values are slightly lower than those reported in the literature for NPC-2000.³⁹ This may be due to deactivation of the catalyst through exposure to oxygen and/or high atmospheric humidity levels, or differences in measurement protocols. For Fe-N-C-C_{5,1000}, the onset potential, half-wave potential, and mass activity are higher than N-C-B(1:3)_{5,1000}. The enhanced activity may be due to the higher mesopore: micropore ratio. The slightly lower mass diffusion limited current density may be a reflection of the lower total micropore surface area. Finally, FeAc-N-C-C_{5,1400}(900-NH_{3-Aw}) has onset potential similar to Fe-N-C-B_{5,1000}, as well as the lowest half-wave potential, mass diffusion limited current density and mass activity. This slightly poorer performance is attributed to the lowest micropore surface area. In addition, the low nitrogen content may be significant, providing fewer sites for Fe to bind onto the surface and create Fe-N_{2/4} type active sites.⁵⁰

In general, the active sites are believed to largely reside in micropores, whilst mesopores contribute to enhanced mass transport.⁵¹ As such, the co-existence of meso- and micropores in a suitable ratio has been reported to enhance mass diffusion in activated

carbon-based electrocatalysts.^{52,53,54} Here, the mesopore to micropore volume ratios for Fe-N-C-B₁₀₀₀ and NPC-2000 are 0.5 and 2, respectively, contrary to expected values for enhanced mass transport. Therefore, the improved mass transport in Fe-N-C must be attributed to a different factor such as: the much larger total surface area (1600 vs 775 m²/g); the higher mesopore/external surface area (656 vs 256 m²/g); the higher microporous surface area (951 vs 519 m²/g); the higher total pore volume (0.77 vs 0.70 cm³/g).

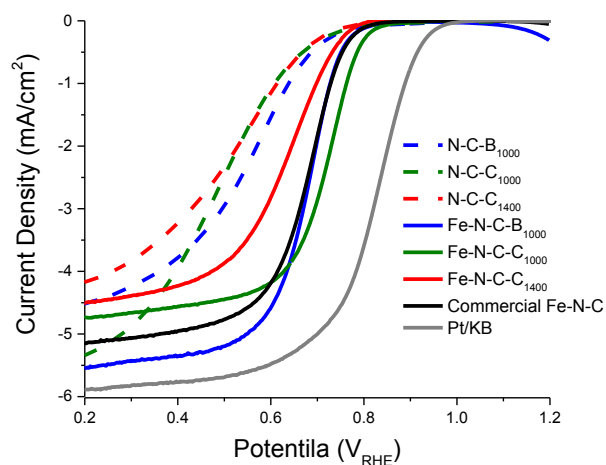


Figure 3.17: Linear sweep voltammograms (LSVs) of FeAc-N-C-B_{5,1000}(900-NH_{3-AW}), FeAc-N-C-C_{5,1000}(900-NH_{3-AW}); FeAc-N-C-C_{5,1400}(900-NH_{3-AW}); and a commercially available reference samples (Pajarito Powder, NPC-2000).

Table 3.5: Comparison of the electrochemical performance of the synthesized catalysts with conventional catalysts.

	Onset Potential (V_{RHE})	Half-Wave Potential (V_{RHE})	Mass Diffusion Limited Current Density (mA/cm^2)	Mass Activity (A/g @ $0.8 V_{\text{RHE}}$)
N-C	0.7	0.5	-4.2	0
Fe-N-C-B _{5,1000}	0.88	0.68	-5.56	0.03
Fe-N-C-C ₁₀₀₀	0.90	0.72	-4.80	0.10
Fe-N-C-C ₁₄₀₀	0.88	0.63	-4.50	0.02
NPC-2000	0.88	0.68	-5.11	0.03
Pt/C	1.03	0.8	-5.91	208

Additionally, the durability of these Fe-N-C-B₁₀₀₀ catalysts against carbon corrosion was investigated using start-stop potential cycling (Figure A3.9). Whilst the initial activity of these catalysts is promising, they quickly degrade under start-stop potential cycling. This may be due to the relatively amorphous nature of the carbon foam support (as observed by XRD), and/or the relatively high iron content, leading to carbon corrosion via the action of hydrogen peroxide. Improving the durability is a topic for further study.

The main conclusion of these electrochemical experiments is that careful optimization and selection of nitrogen-doped carbon foam supports can result in high-performance Fe-N-C electrocatalysts. This is attributed to high nitrogen content in the support, the large surface area, the large pore volume for effective mass diffusion, and screening of the

metal-free supports using cyclic voltammetry. Another important conclusion of this work is that it is possible to decouple the introduction of nitrogen atoms in the support material and the introduction of iron atoms without compromising ORR activity. This is an advantage in comparison with more generalized Fe-N-C catalyst synthesis protocols in which the nitrogen and iron atoms are introduced in the same step. As such, this new protocol for synthesis of nitrogen-doped carbon foam supported Fe-N-C electrocatalysts could have important implications in the design and optimisation of new electrocatalysts.

3.4 Summary and Conclusions

In summary, we investigated how optimization of nitrogen-doped carbon supports can be used to improve the design of Fe-N-C ORR electrocatalysts. Template-free nitrogen-doped carbon foams with large surface area were developed using three different synthesis protocols. Method A was a high pressure and high temperature solvothermal technique. Method B was an ambient temperature-and-pressure solution-based technique designed to make the process cheaper, more scalable, and safer. Method C removed the requirement of metal sodium lumps, and was also an ambient temperature-and-pressure technique. Method A has relatively low yield, surface area, and porosity. Method B successfully improved the yield, surface area, porosity, and nitrogen content compared to

Method A. Method C resulted in increased yield and similar nitrogen content, but lower surface area and different pore size distribution. The metal-free ORR activity of the samples was measured in order to screen the techniques for their suitability in electrochemical applications.

The results of this electrochemical screening suggested that samples N-C-B(1:3)_{5,1000}, N-C-C(1:3)_{5,1000} and N-C-C(1:3)_{5,1400} were suitable for further investigation. As such they were decorated with FeAc, pyrolyzed in NH₃, and acid washed. The resulting catalytic activity was comparable to that of a commercially available Fe-N-C electrocatalyst (NPC-2000). The highest ORR activity was obtained for Fe-N-C-C(1:3)_{5,1000}. This was attributed to: suitable nitrogen content, providing sufficient adsorption sites for Fe atoms; high micropore surface area, providing ample sites for Fe adsorption; the high mesopore to micropore ratio, facilitating mass diffusion.

These results confirm that careful optimization and selective design of the pore size, surface area, nitrogen content, and heating rate of carbon-based supports can result in highly active Fe-N-C catalysts. In the next Chapter, these supports are further developed and optimized to seek further improvements in activity, and the Fe decoration protocols

are optimised by using different iron precursors. Durability and full cell testing measurements are also performed.

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Chapter 4 The Effect of Varying the Fe Precursor on Fe-N-C Catalyst Performance

4.1 Introduction

A wide range of Fe-N-C electrocatalyst synthesis methods and precursors are used worldwide, all yielding materials with different morphology, porosity, surface area and chemical structure. However, these different methods have surprisingly comparable catalytic activities. Although the ORR mechanisms depend entirely on the aforementioned properties, lack of understanding of the active site chemistry and the mechanisms involved is hindering their further development.^{1,2} Therefore, a well-understood empirical approach is needed, rather than the more random synthesis approaches generally used to date. Systematic probing of factors that contribute to effective performance of non-PGM catalysts is of paramount importance. This will entail understanding: i) the carbon support properties; ii) how the catalytically active elements behave on the support; and iii) their combined effect on performance. A combination of the above-mentioned properties is desirable in the design of catalysts for oxygen reduction reactions. Various Fe-precursors have previously been used to make Fe-N-C electrocatalysts for the ORR, including: iron (II) acetate (FeAc); iron (III) chloride

(FeCl₃); and iron phthalocyanine (FePc). These are also used in this study (Figure 4.1), and their properties are outlined below.

FeAc is an orange-red solid coordination complex, that is soluble in water. The chemical formula is Fe(C₂H₃O₂)₂. Note there is carbon, but no nitrogen in the molecule. The molar mass is 173.933 g/mol, with a melting point of 180 to 182 °C, and a decomposition temperature of 190 to 200 °C. It is used industrially as a dye fixative, because of its ability to form coordination complexes with dyes.³ FeAc has been used in many cases as an iron source to make high performance Fe-N-C catalysts.⁴ For example, Lefèvre et. al reported Fe-N-C electrocatalyst based on a mixture of FeAc and carbon black, heat-treated first in Ar and then in NH₃, in one of the pioneering works reporting the presence of ORR active Fe-N sites.⁵

Meanwhile, FeCl₃ has also commonly been used as an iron source for Fe-N-C electrocatalysts. It is a red, solid hexahydrate salt with chemical formula FeCl₃·6H₂O. Note that there is no carbon or nitrogen in this hydrated molecule. The molar mass is 270.29 g/mol, and the decomposition temperature is 280 °C. It has solubilities of 912 g/L in water, and 830 g/L in ethanol, at 25 °C.⁶ Fe-N-C electrocatalysts based on FeCl₃ and

polyaniline have been synthesized using Ketjenblack as a carbon support, and Fe-N_x ORR active moieties were considered to be located in the micropores and at edges/defects in the highly microporous carbon.^{7,8} Alternatively, a one pot synthesis method based on combining FeCl₃, an aniline oligomer and Ketjenblack (EC-300J) was used to show that the iron loading affects the surface area, porosity, and morphology, with the formation of iron nanoparticles encapsulated in carbon agglomerates.⁹

FePc is dark purple solid metal complex that already has Fe-N₄ based chemical structure, making it a natural candidate for inclusion in non-PGM electrocatalysts. It has the chemical formula C₃₂H₁₆FeN₂ (note the inclusion of carbon *and* nitrogen), a molar mass of 568.4 g/mol, a decomposition temperature of ≥ 550 °C,¹⁰ and is insoluble in water.^{11,12} FePc supported on carbide-derived porous carbon followed by pyrolysis has been reported to result in the formation of ORR active electrocatalysts containing FeN_x phases and iron nanoparticles.¹³ Meanwhile, a hybrid catalyst comprising FePc mixed with a 2-dimensional Ti₃C₂T_x support (i.e. MXene) was also used to obtain ORR active FeN₄ moieties in Fe-N-C electrocatalysts.¹⁴

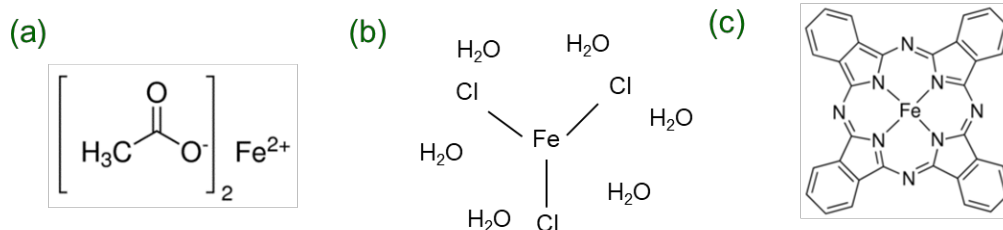


Figure 4.1: Chemical structures of the three iron precursors used in this study: (a) iron (II) acetate (FeAc); (b) iron (III) chloride (FeCl₃); and (c) iron phthalocyanine (FePc).

This chapter focuses on directly comparing FeAc, FeCl₃ and FePc as precursors for Fe-N-C electrocatalysts. These precursors are decorated on nitrogen-doped carbon foam, followed by pyrolysis and acid washing. Since the properties of the nitrogen-doped carbon foam are the supposedly the same in every case and do not change significantly with temperature, this unique catalyst synthesis technique makes it much easier to observe changes occurring due to the specific iron precursors. The resulting catalysts are characterized in detail, and their ORR activity and long-term stability are investigated, whilst differences resulting from the use of the different precursors are discussed.

4.2 Experimental

Figure 4.2 shows the protocols used for methodically synthesizing the different catalysts used in this study and comparing them at every step in the process. The nitrogen-doped foam which was optimized in Chapter 2 was used as a support for the different precursors.

Detailed procedures of the synthesis of the nitrogen-doped carbon foam and the Fe-adsorption protocols were given in Chapter 2.1 and 2.2. The sample nomenclature used in this chapter is: $P-N-C(T-G-Aw)$, where: P is the type of iron precursor (i.e. FeAc, FeCl₃ or FePc); N-C denotes the nitrogen-doped carbon support pyrolyzed at 1000 °C used in all cases; T is the heat-treatment temperature after iron-adsorption; G is the gas environment used during this heat treatment (i.e. N₂ or NH₃); and Aw denotes the acid washing step. For example, in this chapter the nitrogen-doped carbon foam starting material is N-C. After iron adsorption it is denoted as FeAc-N-C. After heat treatment in ammonia it is named FeAc-N-C-NH₃. Finally, after acid washing it is called FeAc-N-C-NH₃-Aw. Sample synthesis was also repeated in all cases on nitrogen-free, undoped carbon foam prepared in a similar manner.

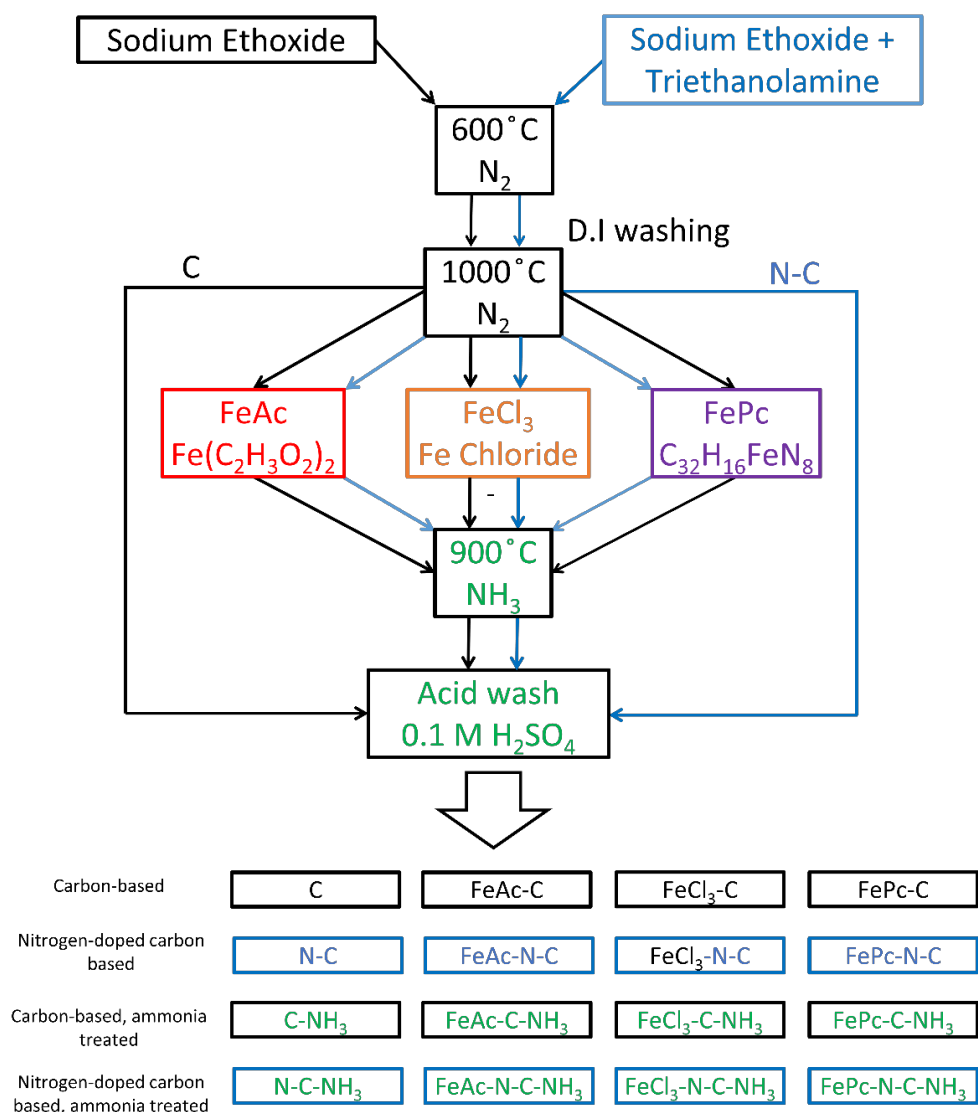


Figure 4.2: Schematic showing the Fe-salt precursors and routes used for decorating carbon foam and nitrogen-doped carbon foam with iron (top); and the different samples that are generated (bottom).

The chemical structures which are expected to be generated in the Fe-N-C electrocatalysts were hypothesized based on the chemical structure of the precursors (Figure 4.1). The precursor composition increases in complexity from FeCl₃ to FeAc to FePc. For the FeAc precursor, the carbon atoms were expected to form carbon nanoparticles (C-C coordination bonds), Fe-Fe, Fe-O, Fe-C bonds and Fe-N_x moieties, whilst the acid washing was expected to get rid of any metallic particles. On the other hand, for the FeCl₃ precursor, the chlorine atoms were expected to gasify, and any metallic phases were expected to be removed by acid washing. As such, Fe-C and Fe-N bonds were expected to be observed. Lastly, for the FePc precursor, Fe-N_x, Fe-Fe, C-N and C-C bonds were expected to be formed. In addition, since both FeCl₃ and FePc precursors do not have oxygen, Fe-O bonds were not expected to be formed. For reference purpose the Fe-precursors were also adsorbed onto carbon foams without nitrogen-doping, especially to check the effect of nitrogen on the electrochemical performance.

4.3 Results and Discussion

4.3.1 Surface Area and Porosity

The porosity and surface area of the samples were determined from the N₂ adsorption/desorption isotherms (Figure 4.3, Table 4.1). The BET surface area of the

initial N-C starting material is $768 \text{ m}^2\text{g}^{-1}$, with a Type I (a) isotherm indicating a microporous material with narrow micropores ($<1 \text{ nm}$), and a pore diameter of 0.70 nm . It has a Type H4 hysteresis loop which indicates a micro-mesoporous nature.

After iron precursor adsorption and then heat treatment in NH_3 , the surface area of FeAc-N-C₁₀₀₀(900-NH₃) increases to $980 \text{ m}^2\text{g}^{-1}$, whilst the pore diameter increases to 0.96 nm . A larger increase in surface area to $1268 \text{ m}^2\text{g}^{-1}$ is observed for FeCl₃-N-C₁₀₀₀(900-NH₃), with a slightly smaller increase in pore diameter to 0.85 nm . The isotherms are both Type I (b), which is characteristic of wider micropores as well as possibly narrow mesopores ($\leq \sim 2.5 \text{ nm}$). The H4-type hysteresis at $> 0.4 \text{ p/p}_0$ also reveals the presence of mesopores. These changes are possibly attributed to: i) reactive etching of the carbon by ammonia gas, resulting in large pores;¹⁵ and ii) etching of the carbon support by molten iron nanoparticles. This is also supported by the observed increase in the mesopore to micropore volume ratio ($V_{\text{meso}}/V_{\text{micro}}$). This development of micropores is critical for ORR activity as the micropores host most of the active sites. A nearly linear correlation between the micropore surface area of Fe-N-C catalysts and the ORR activity has been reported.¹⁶

Meanwhile, for FePc-N-C₁₀₀₀(900-NH₃) there is no significant change in surface area or pore size, and the only notable change in the isotherms is the appearance hysteresis, which is characteristic of mesopores. The lack of significant changes compared to FeAc- and FeCl₃ could be due to the large diameter of FePc molecules (i.e. ~ 1 nm) preventing them from entering the micropores in the support (with ~ 0.7 nm diameter). As such they would only adsorb on the outer surface of the carbon support, and not affect the micropore distribution, which is the biggest contributor to the surface area of these materials.

After acid washing, there are further changes in the surface area and pore size distribution. For FeAc-N-C₁₀₀₀(900-NH₃-Aw) the surface area significantly increases to $1746 \text{ m}^2\text{g}^{-1}$ and the pore diameter increases to 1.1 nm. For FeCl₃-N-C₁₀₀₀(900-NH₃-Aw), the surface area increases to $1812 \text{ m}^2\text{g}^{-1}$ and the pore diameter increases to 1.0 nm. In both cases, the isotherm shifts to Type II, whilst the mesoporous to microporous volumes ratio also increases. This increase in surface area and average pore diameter is likely to be due to the action of the acid as it dissolves e.g. metallic iron (Fe-Fe), iron oxide (Fe-O), or iron carbide (Fe-C) phases, especially from inside the micropores.

Meanwhile, for FePc-N-C₁₀₀₀(900-NH₃-Aw) there is a slight increase in surface area to 993 m²g⁻¹, but no significant change in the pore diameter, or the isotherm type. The fact that the pore diameter does not change during acid washing further supports the idea that FePc molecules do not enter the micropores during the adsorption step. The increase in surface area is therefore attributed to removal of material (i.e. mass) only from outside the micropores, i.e. on the outside surface of the nitrogen-doped carbon foam support.

In summary, both FeAc-N-C₁₀₀₀(900-NH₃-Aw) and FeCl₃-N-C₁₀₀₀(900-NH₃-Aw) have large microporous surface area and well-developed pore size distributions. This is attributed to the easy access of FeAc and FeCl₃ molecules into the micropores of the nitrogen-doped carbon support upon adsorption, leading to etching of the micropores from within during heat treatment. This may lead to enhanced ORR activity due to e.g. hosting of Fe-N₄ active sites within the micropores, and increased accessibility to these micropores.¹⁷ In contrast, FePc-N-C₁₀₀₀(900-NH₃-Aw) has relatively low microporous area and narrow micropore diameter. This is attributed to the fact that the relatively large FePc molecules cannot enter the narrow micropores, adsorbing only on the outside surface. This may lead to poor ORR activity, due to a lack of Fe-N₄ sites residing in micropores, decreasing the active site density. As such, it is concluded that the choice of

the Fe precursor used in Fe-N-C electrocatalysts can have a significant effect on the microstructure of the support.

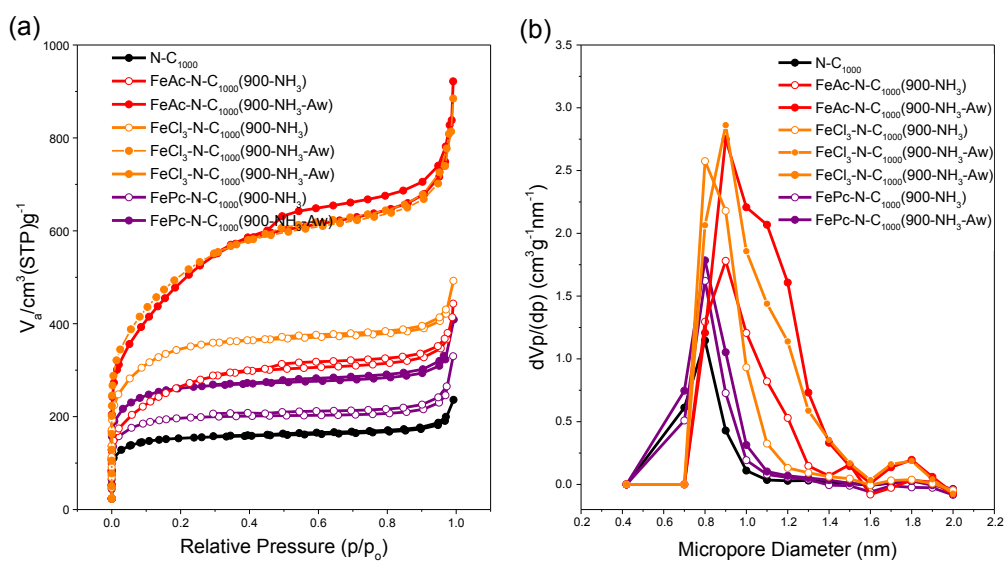


Figure 4.3: N_2 adsorption-based (a) isotherm plot and (b) micropore distribution.

Table 4.1: N_2 adsorption-based surface area, isotherm type, pore size and the ratio of V_{meso}/V_{micro} .

Sample Name	BET (m ² /g)	Microporous area (m ² /g) MP (T-plot)	Isotherm type	Pore Diameter 2t (nm)	V_{meso}/V_{micro}
N-C	768	818 (860)	Ia / H4	0.7	0.4
FeAc-N-C ₁₀₀₀ (900-NH ₃)	980	840 (894)	Ib / H4	0.96	0.8
FeAc-N-C ₁₀₀₀ (900-NH ₃ -Aw)	1746	1447 (1608)	II / H4	1.05	1.1
FeCl ₃ -N-C ₁₀₀₀ (900-NH ₃)	1268	1229 (1224)	Ib / H4	0.85	0.6
FeCl ₃ -N-C(900-NH ₃ -Aw)	1812	1586 (1660)	II / H4	1.02	1.0
FePc-N-C ₁₀₀₀ (900-NH ₃)	751	756 (775)	Ia / H4	0.76	0.73
FePc-N-C ₁₀₀₀ (900-NH ₃ -Aw)	993	1000 (1011)	Ia / H4	0.77	0.6

4.3.2 Raman Spectroscopy

Figure 4.4 shows the Raman spectra for N-C, and the three iron-adsorbed samples after heat treatment in ammonia and acid washing. All spectra are typical of amorphous

carbons, with: a first order D peak at $\sim 1353\text{ cm}^{-1}$ (induced by nitrogen doping effect on the breathing mode of aromatic rings),¹⁸ a G peak at $\sim 1591\text{ cm}^{-1}$ (corresponding to the in-plane vibration of C-C bonds),^{19,20} and a low intensity second order 2D peak at 2635 cm^{-1} (an overtone of the D peak). The sharp peak at 2330 cm^{-1} is a measurement artefact due to the light source changing within the machine.

All of the samples have similar I_D/I_G ratio of 1.04 ± 0.02 , as summarized in Table 4.2. This confirms that the crystallinity of the underlying carbon support does not significantly change during the different processing steps. The most striking difference in the spectra is in the second order peak in the 2D region for samples derived from FeAc and FeCl₃, in which enhanced fine structure is observed (i.e. doublet peaks at 2680 and 2929 cm^{-1}). This doublet is indicative of crystalline graphitic materials such as carbon nanotubes or graphene.²¹ As such, this 2D peak indicates the presence of graphitic carbon nanostructures in these samples, as commonly formed through the catalytic action of iron nanoparticles at elevated temperature, in the presence of a carbon source. The intensity of these peaks is higher for FeAc, suggesting the highest degree of nanostructure formation. This may be due to the presence of carbon atoms in the FeAc molecule which can be used as a carbon source for generating graphitic carbon. Meanwhile fewer

graphitic nanostructures may be generated through the pyrolysis of FeCl_3 , and very few or no graphitic phases are detected through the action of FePc.

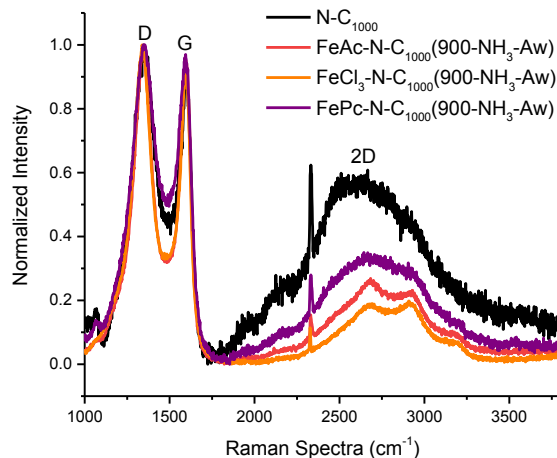


Figure 4.4: Raman spectra of N-C_{1000} , $\text{FeAc-NC}_{1000}(900\text{-NH}_3\text{-Aw})$, $\text{FeCl}_3\text{-NC}_{1000}(900\text{-NH}_3\text{-Aw})$, and $\text{FePc-NC}_{1000}(900\text{-NH}_3\text{-Aw})$. *All data was normalized to D intensity.

Table 4.2: The calculated D/G ratios of the Raman spectra for the nitrogen-doped sample and the iron-adsorbed samples.

Sample	D/G ratio
N-C	1.04
FeAc-N-C RT	1.02
FeAc-N-C-NH ₃	1.04
FeAc-N-C-NH ₃ -Aw	1.05
FeCl ₃ -N-C RT	1.05
FeCl ₃ -N-C-NH ₃	1.03
FeCl ₃ -N-C-NH ₃ -Aw	1.07
FePc-N-C RT	1.01
FePc-N-C-NH ₃	1.03
FePc-N-C-NH ₃ -Aw	1.04

4.3.3 X-ray Diffraction (XRD)

Figure 4.5 shows XRD spectra of N-C and the three Fe-N-C electrocatalysts using different Fe precursors. In all cases, there is no significant change. There is a broad diffraction peak at 22° , which corresponds to typical (002) interlayer spacing of 0.4 nm for amorphous or nitrogen-doped carbons. A smaller peak centered at 44° is associated with the (100) in-plane hexagonal atomic arrangement of sp^2 carbon (i.e., 0.2 nm). This mainly reflects the nitrogen-doped carbon support, and the generation of graphitic phases as observed in the Raman spectra are too small to observe by XRD. No peaks are observed corresponding to e.g. metallic iron, iron oxide, or iron carbides,^{22,23} even before acid washing of the samples. These phases are expected to be present, but due to the low Fe content of the samples the signals are probably below the detection limit of this characterization technique.

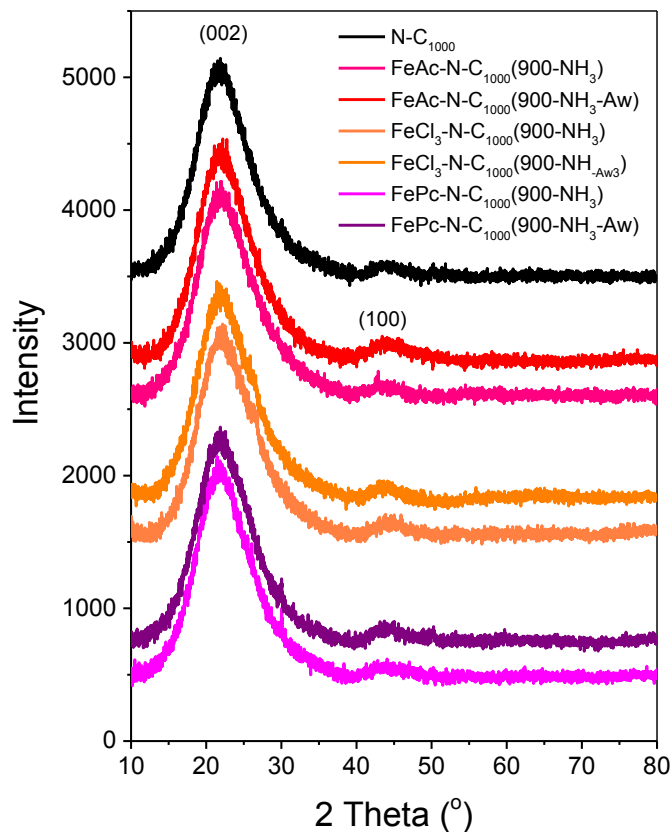


Figure 4.5: XRD spectra of comparing Fe-N-C electrocatalysts prepared using different Fe precursors.

4.3.4 X-ray Photoelectron Spectroscopy (XPS)

Survey Scans and Elemental Analysis: XPS was performed to determine the elemental composition of the catalysts. The survey scans (Figure 4.6a) reveal the presence of carbon (~285 eV), nitrogen (~399 eV), and oxygen (~531.5 eV). Features at ~500 eV and ~980 eV correspond to the Auger peaks of sodium and oxygen, respectively. The iron and

sodium contents of the samples are very low, so they are not visible in the survey scans.

The elemental compositions of the samples are summarized in Figure 4.7 and Table 4.3.

After Fe precursor adsorption, the carbon content decreased in all cases compared to the pristine N-C support, due to the introduction of oxygen and iron atoms for FeAc; chlorine, oxygen and iron for FeCl₃; and iron and nitrogen atoms for FePc. This decrease is slightly less in the case of FeAc, because the precursor also contains carbon. After the Fe precursor adsorption step there is also a small increase in nitrogen content in all cases, despite the fact that FeAc and FeCl₃ do not contain nitrogen atoms. This unexpected increase could be partly due to the removal of impurities in the nitrogen-doped carbon foam, such as sodium oxides and sodium carbonates during this step (as supported by the decrease in the sodium and carbon contents). However, it is unclear if this can fully account for the observed change, so the reason is thus currently under further investigation. However, after FePc adsorption, the nitrogen content increases by a significantly larger amount, as expected due to the nitrogen atoms present in the FePc molecule.

Similarly, the amount of oxygen increased in all cases after adsorption of the precursors.

This is as expected due to oxygen atoms in the precursors (in the cases of FeAc and FeCl₃),

as well as from oxygen atoms present in the solvents (for all three samples). The increase was highest in the case of FeCl_3 , attributed to its associated water molecules in the hexahydrate form.

In addition, the Fe content increases after Fe precursor adsorption in all cases, as expected. The nominal Fe loading values calculated from the ratio of precursors used during the adsorption step (0.5 wt%) do not match the values obtained by XPS. However, it should be noted that because of the very low signal, there is a high degree of error in the Fe at% values, which could account for this difference.

As a reference sample, the nitrogen-doped carbon foam (N-C) was heat treated in ammonia to assess the effect of ammonia in the absence of the adsorbed precursors. The nitrogen content increased from 3.26 to 3.78 at%, confirming that heat treatment in ammonia incorporates nitrogen into the carbon support. This is reportedly important for the initial ORR activity, due to an increase in the basicity of the surface, affecting the adsorption of reactive species. Meanwhile, a decrease in the oxygen and sodium contents is observed, showing that heat treatment in ammonia improves the sample purity.

After heat treatment, the nitrogen slightly increases in the case of FeAc. This may indicate an enhancement of nitrogen doping through chemical reaction with ammonia (forming e.g. ammonium acetate and metallic iron), or the incorporation of nitrogen atoms into the graphitic carbon nanostructures formed during heat treatment. In the cases of both FeCl₃ and FePc, the nitrogen content decreases after heat treatment. In the case of FeCl₃ this is attributed to a different chemistry compared to FeAc. For example, FeCl₃.6H₂O is expected to decompose at high temperature to form Fe₂O₃, which in turn reacts with NH₃ to form Fe, N₂ (g), and H₂ (g). As such the nitrogen may preferentially react with the formed iron oxide over the carbon support surface. Meanwhile in the case of FePc, the lower nitrogen content is attributed to blocking of micropores by the adsorbed FePc molecules, preventing ammonia from reacting with the inner surface, as well as sublimation of the FePc molecule itself during high temperature treatment. However, the FePc molecule does contain nitrogen, so the final nitrogen content is higher than that of FeCl₃.

For FeAc, the iron content does not change after heat treatment in NH₃, suggesting that most of the iron is retained in the sample, for example forming Fe-N_{2/4} sites, or being reduced to metallic iron. FeCl₃ and FePc appear to lose some iron during this step,

possibly due to sublimation or gasification of these small molecules. However, again it should be noted that the error is significant for such low iron abundance in the samples, so it is difficult to draw concrete conclusions between samples.

After the acid washing step, the carbon content increases in all cases, reflecting the removal of carbon-free iron phases such as metallic iron, iron oxide, and/or iron carbides. The nitrogen content slightly decreases in all cases, suggesting that e.g. iron nitride formed during heat treatment is dissolved during acid washing. The oxygen content significantly decreases in all cases, suggesting that acid washing removes oxygen-containing phases such as iron oxide. The iron content slightly decreases in the case of FeAc and FeCl₃, due to the dissolution of e.g. metallic iron, iron oxide, and/or iron nitride phases. Meanwhile, the iron content does not change for FePc, suggesting that metallic iron, iron oxide, and iron nitride are present in much smaller quantities. The sodium content also decreases after acid washing at this stage, removing e.g. sodium oxides and sodium carbides remaining after the carbon foam synthesis step.

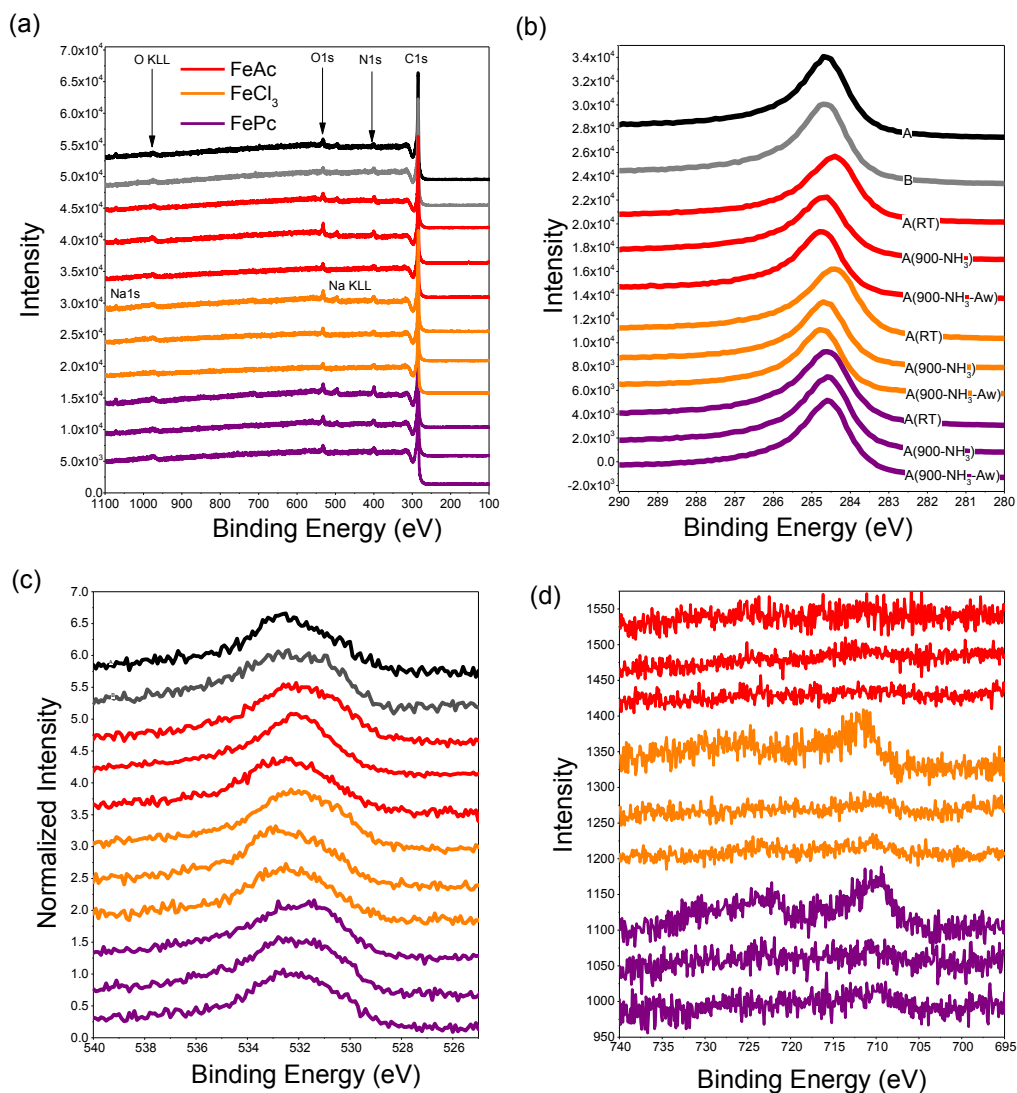


Figure 4.6: XPS Results: (a) survey scans; (b) C 1s narrow scans; (c) O 1s narrow scans; and (d) Fe 2p narrow scans of the FeAc-, FeCl₃-, and FePc-derived samples after adsorption; heat treatment in ammonia, and acid washing steps. For clarity, A = N-C₁₀₀₀; and B = N-C₁₀₀₀(900-NH₃).

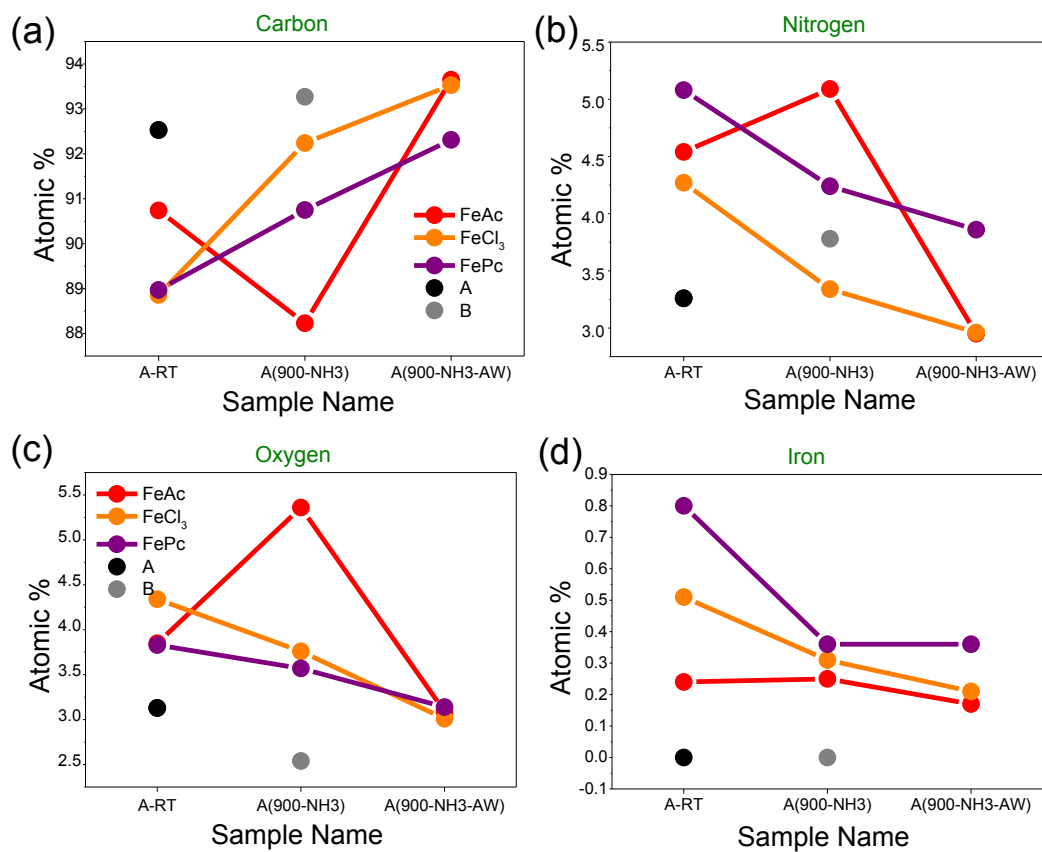


Figure 4.7: Changes in at % of: (a) carbon, (b) nitrogen, (c) oxygen, and (d) iron, for the FeAc-, FeCl₃, and FePc-derived samples with each processing step. For clarity, A = N-C₁₀₀₀; and B = N-C₁₀₀₀(900-NH₃).

Table 4.3: XPS elemental analysis (at%) for selected catalysts.

	C 1s	N 1s	O 1s	Na 1s	[Fe 2p]
N-C (N ₂)	92.53	3.26	3.13	1.08	-
N-C (NH ₃)	93.27	3.78	2.54	0.41	-
FeAc-N-C-RT	90.74	4.54	3.85	0.64	0.24
FeAc-N-C-900 (NH ₃)	88.23	5.09	5.36	1.07	0.25
FeAc-N-C-900 (NH ₃ -AW)	93.65	2.95	3.09	0.14	0.17
FeCl ₃ -N-C-RT	89.86	4.27	4.34	0.8	0.51
FeCl ₃ -N-C-900 (NH ₃)	92.24	3.34	3.76	0.34	0.31
FeCl ₃ -N-C-900 (NH ₃ -AW)	93.52	2.96	3.01	0.3	0.21
FePc-N-C-RT	88.97	5.08	3.83	1.31	0.8
FePc-N-C-900 (NH ₃)	90.75	4.24	3.57	1.09	0.36
FePc-N-C-900 (NH ₃ -AW)	92.31	3.86	3.14	0.33	0.36

N 1s Narrow Scans: Narrow scans were conducted to determine the chemical environment of iron in the different precursors at different stages of synthesis. This is especially important for Fe-N-C electrocatalysts, because nitrogen atoms reportedly provide nucleation sites for iron atoms.²⁴ Figure 4.8 shows the N 1s high resolution scan for N-C-, FeAc-, FeCl₃-, and FePc-based samples.

N-C heat treated in nitrogen has two main peaks at ~398 eV and ~401 eV which are associated with pyridinic-N and graphitic-N bonds, respectively. Other smaller peaks include pyrrolic-N (~399 eV), hydrogenated-pyridinic-N (~403 eV) and pyridine-N-

oxide (~ 404 eV). As stated above, heat treatment in ammonia increases the nitrogen content. Here, this is confirmed by corresponding increases in the relative intensities of pyridinic-N, pyrrolic-N, and pyridine-N-oxide spectral lines after heating in ammonia.

After adsorption of both FeAc and FeCl₃ precursors, an increase at ~ 399 eV is observed, corresponding to the formation of Fe-N bonds. Since neither FeAc nor FeCl₃ molecules contain nitrogen, this is attributed to the formation of bonds between the adsorbed iron in the precursor molecule, and the nitrogen atoms in the nitrogen-doped carbon support. For FePc, the increase at ~ 399 eV is less significant, and is likely to be due to Fe-N₄ center of the FePc molecule, rather than the formation of Fe-N bonds with the substrate.

After heat-treatment in ammonia, the abundance of Fe-N bonds decreases for both FeCl₃ and FePc-based catalysts, suggests that not all of the Fe-N bonds formed during the adsorption step are retained during heat treatment. This may be due to reduction of the Fe to metallic or oxide phases. Interestingly, the relative intensity of Fe-N bonds for FeAc slightly increases after heat treatment, reinforcing the idea that FeAc enhances nitrogen doping via NH₃ treatment, via formation of an ammonia-acetate chemical complex.

After the acid washing step, abundance of Fe-N bonds significantly decreased, suggesting that the Fe-N bonds formed during heat treatment are dissolved during acid washing. This supports the hypothesis that ammonia reacts with the acetate to form a complex, which is subsequently dissolved, rather than being incorporated into the catalyst structure. Alternatively, there may be a high proportion of iron nitrides formed, which are subsequently dissolved in the acid. Interestingly, there are no significant changes in the intensities of Fe-N bonds for both FeCl₃ and FePc, showing that the Fe-N bond formed in these materials are likely to be part larger insoluble organic motifs, i.e. similar to the ORR active sites proposed by most groups.

In summary, XPS results suggest that FeAc and FeCl₃ form Fe-N bonds with nitrogen atoms in the support immediately upon adsorption, whereas in FePc the Fe atom is already fully coordinated and therefore does not form bonds with the surface. After heat treatment and acid washing, stable ORR active Fe-N bonds are retained in the three catalysts.

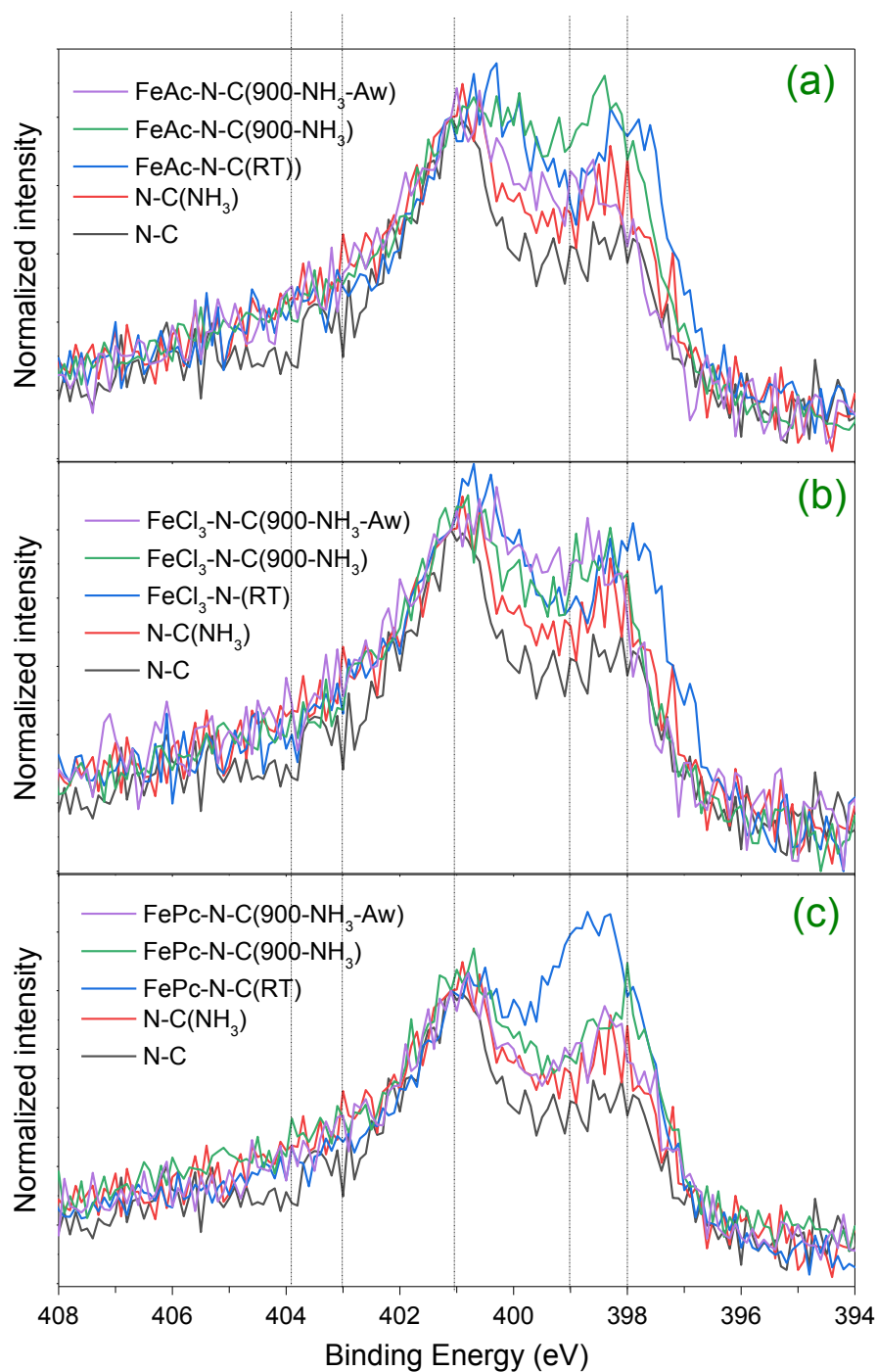


Figure 4.8: N 1s of: (a) FeAc-; (b) FeCl₃-; and (c) FePc-based electrocatalysts after precursor adsorption; heat treatment in ammonia; and acid washing. All data was normalized to the 401 eV peak.

4.3.5 X-ray Absorption Spectroscopy (XAS)

Since the Fe concentration in these samples is very low (< 1 at%), it is not possible to obtain sufficient resolution to identify different bonding configurations using conventional XPS. As such, high energy X-rays generated by a synchrotron were used to perform X-ray absorption spectroscopy (XAS). This is a powerful technique for detecting lower concentrations of Fe, and it can provide useful information on the oxidation state, the atomic bond coordination and the bond lengths. Details of the experimental technique is outlined in Chapter 2.3.7.

XAFS of reference samples including FeAc, FeCl₃, FePc, Fe₂O₃, Fe₃O₄ and Fe foil were also measured for comparison, and their X-ray absorption near edge structure (XANES) and Fourier transform of the extended X-ray absorption fine structure (FT-EXAFS) data is shown in Figure 4.9 below. The pre-edge and edge structures of XANES spectra correspond to electronic transitions and can thus provide information on the Fe oxidation state and the geometrical coordination of Fe-related moieties. Whereas, the EXAFS region provides information on the type of nearest neighboring atoms and bond distances. At the pre-edge, features at 7112 eV correspond to Fe²⁺ 1s to 3d transitions, and features at 7115 eV correspond to Fe³⁺ 1s to 3d transitions.^{25,26} At the edge, features at 7117 eV

correspond to dipole-allowed 1s to 4p transitions e.g. in square planar structure in Fe^{2+} phthalocyanine.²⁷ This is important in terms of the ORR, because iron with an oxidation state of 2^+ (e.g. square planar $\text{Fe}^{2+}\text{-N}_4$ structure) is reported to be preferable over a 3^+ oxidation state.²⁸

Figure 4.10 shows the Fe K-edge XAFS data, including the XANES (left hand column); the 1st derivative of the XANES spectra (middle column); and the (FT-EXAFS, right hand column), for (a-c) $\text{FeAc-N-C}_{1000}(900\text{-NH}_3\text{-Aw})$, (d-f) $\text{FeCl}_3\text{-N-C}_{1000}(900\text{-NH}_3\text{-Aw})$ and (g-i) $\text{FePc-N-C}_{1000}(900\text{-NH}_3\text{-Aw})$ catalysts. No Fe K-edge was detected for the pristine nitrogen-doped carbon support (N-C_{1000}), confirming that no iron is present in the sample before absorbing the iron precursors, to within the detection limit of the technique.

Before heat treatment, FeAc- and $\text{FeCl}_3\text{-adsorbed-N-C}$ samples all display a pre-edge peak in their XANES spectra at ~ 7114 eV (more clearly visible in the 1st derivative data), which is characteristic of Fe^{3+} species. This is as expected for iron (III) chloride, since the oxidation number of Fe in this case is 3^+ . However, the oxidation state of iron in FeAc molecules is 2^+ . The change in oxidation state may be due to the formation of an Fe-N bond between the FeAc molecule and the nitrogen-doped carbon surface, as also

suggested by the XPS data. FePc has an oxidation state of Fe^{2+} , and the pre-edge feature is correspondingly centered at 7112 eV, as expected.

After heat-treatment in ammonia, there is a general shift of the K-edge towards the lower energy region (~ 7112 eV), for all samples. This indicates a decrease in the oxidation state of iron. Fe^{2+} species may be generated during heat treatment, possibly corresponding to $\text{Fe-N}_4\text{C}_{10}$, $\text{Fe-N}_{2+2}\text{C}_{4+4}$ and/or $\text{Fe-N}_4\text{C}_{12}$ type moieties.²⁹ However, there are also changes observed in the shape of the spectra for FeAc and FeCl_3 , after the rising edge, where spectra tend to flatten out (reduction in the magnitude of the oscillations) resembling the spectra of the Fe foil or iron carbide (Fe_3C) reference samples.³⁰ This suggests the generation of metallic iron with an oxidation state of 0. This is more noticeable in the FeAc sample, in agreement with e.g. the Raman data in which the formation of graphitic carbon was implied, requiring the action of metallic iron or iron carbide particles.

The FT-EXAFS data gives more specific information related to the bond lengths present in the samples, from which we can infer the types of different bonds between iron and carbon or nitrogen, or oxygen. A radial distance of ~ 1.5 Å is assigned to Fe-N and/or Fe-O bonds. These can sometimes be distinguished by a small peak shift, with ~ 1.5 Å

assigned to both the Fe-N bonds in FePc and Fe-O bonds in Fe₂O₃; and ~1.6 Å assigned to Fe-O in FeAc. Peaks at ~2.2 and ~4.4 Å correspond to Fe-Fe bonds, as observed in Fe foil; and ~3.3 Å is ascribed to Fe-C in e.g. iron carbide.^{29,31}

After adsorption of FeAc on the nitrogen-doped carbon support, i.e. FeAc-N-C there is a high signal intensity at ~1.4 Å, assigned to Fe-N/O bonds, and a peak at 2.8 Å assigned to Fe-C bonds. This is very similar to that of the unsupported FeAc reference sample, as expected (Figure 4.9). However, a small peak shift to 1.4 Å suggests that some Fe-N coordination may have formed between the iron atoms in FeAc and the nitrogen atoms in the N-C support, as also suggested by the XPS data. After heat-treatment in ammonia, there is a decrease in the intensity of the Fe-N/O peak, accompanied a significant increase in the intensity of the Fe-Fe peak at 2.1 Å, and the appearance of an Fe-C peak at ~3.3 Å. This suggests that metallic iron is formed during heat treatment in ammonia, at the expense of Fe-N coordination. This is in agreement with the graphitic carbon signals observed using Raman, which require metallic iron (and/or iron carbide) to catalyse their formation. After acid washing, there is a decrease in the Fe-N/O peak intensity, suggesting that some acid-soluble iron oxide and iron nitride species are dissolved, leaving only the more acid resistant Fe-N_x species.³² Meanwhile, there is still a large Fe-Fe peak at 2.1 Å,

despite the fact that metallic iron dissolves in acid. This suggests that the remaining metallic iron is encapsulated by graphitic carbon during the growth of nanostructure. Finally, the peak assigned to Fe-C does not significantly change after acid washing, suggesting that Fe₃C species are also encapsulated in graphitic carbon. It is also reported that Fe₃C species are resistant to acid washing.^{30,33} Overall, these results suggest that i) Fe-N bonds form between FeAc and the nitrogen-doped carbon support upon adsorption; ii) that metallic iron is formed from FeAc during heat treatment; iii) carbon dissolves in the metallic iron to form iron carbide, which then precipitates as graphitic carbon; iv) the graphitic carbon encapsulates the iron / iron carbide particles, protecting them during the acid washing step.³³ Meanwhile, there is still a significant proportion of Fe-N bonds remaining after the acid washing step in agreement with the XPS results in Section 4.3.1, and these are proposed to be ORR active.

The unsupported FeCl₃ reference sample has a single large peak at 1.7 Å, assigned to Fe-Cl bonds (Figure 4.9). After adsorption of FeCl₃ on the nitrogen-doped carbon support, the FT-EXAFS spectra look surprisingly different, with a major peak at 1.5 Å (Fe-N/O) and a smaller peak at 2.7 Å (Fe-C). This suggests that a high proportion of Fe atoms in the precursor coordinated directly with nitrogen and carbon atoms support, forming Fe-

N_{2/4} and Fe-C species.³¹ After heat treatment in ammonia the intensity of the Fe-N/O peak slightly decreases, and there a peak at 2.0 Å appears. This is attributed to the formation of metallic iron particles during heat treatment, at the expense of Fe-N and Fe-C bonds on the surface. The Fe-C signal completely disappears after heat treatment, suggesting that graphitic carbon are not formed (to the same extent as in FeAc). This is in agreement with the results in previous sections – FeCl₃.6H₂O decomposes to Fe₂O₃ at high temperature, but this would be further reduced to metallic iron, nitrogen gas and hydrogen gas in ammonia atmosphere. After acid washing, there is a slight decrease in the Fe-N/O peak at 1.5 Å, and a slight increase in the Fe-Fe peak at 2.0 Å. This suggests that the Fe-N_x species formed during heat treatment are acid-stable, and that some of the phases formed during heat treatment were indeed metal oxides, which are subsequently dissolved during acid washing. The proportion of remaining Fe-N bonds is much higher in the case of FeCl₃ than the case of FeAc.

Overall, these results suggest that: i) FeCl₃ readily dissolves in water, and the resulting Fe³⁺ ions readily form direct Fe-N and Fe-C bonds with the nitrogen-doped carbon substrate; ii), iron oxide is probably formed by decomposition of FeCl₃.H₂O during heat treatment, but is reduced to metallic iron by reaction with ammonia; iii) graphitic

nanostructures are probably not formed, as indicated by the absence of iron carbide after heat treatment; iv) a relatively high proportion of Fe-N bonds remain after acid washing, which may be ORR active. These conclusions are consistent with the results from previous sections.

The unsupported FePc reference sample (Figure 4.9) has major FT-EXAFS peaks at 1.6 Å (assigned to Fe-N bonds in the central Fe-N₄ motif), and 2.6 Å (due to the scattering from second carbon shell), in agreement with the literature.^{30,34} The peak at 1.6 Å may also be partly attributed to Fe-O bonds in accordance with the fact that pristine FePc is oxidized once exposed to oxygen. After adsorption of FePc onto the nitrogen-doped carbon support the spectrum does not significantly change, with prominent peaks at 1.6 and 2.6 Å. After heat-treatment in ammonia, there is a more significant change in the FT-EXAFS spectrum. There is a small decrease in intensity of the Fe-N/O peak, and a shift to ~1.7 Å suggesting a reorganization of carbon and/or nitrogen related ligands. A small shoulder appears at ~2.0 Å which can be attributed to a small amount of metallic iron formed due to decomposition of FePc. However, this signal is much lower than in the cases of FeAc or FeCl₃. Meanwhile, the peak at 2.6 Å, due to scattering from the second carbon shell in the FePc molecule, completely disappears after heat treatment, suggesting

that the FePc molecule has decomposed. After acid washing, the spectrum does not change significantly. There is a slight increase in the intensity of the Fe-N/O peak at 1.6 Å. The shoulder at 2.0 Å does not change, suggesting that the small amount of metallic iron produced by decomposition of FePc is encapsulated within graphitic carbon structures. Overall, these results suggest that: i) FePc is weakly adsorbed onto the nitrogen-doped carbon support without forming new bonds; ii) the FePc molecule decomposes, but the Fe-N₄ structure is retained after heat treatment in ammonia (FeN₄ is a surprisingly stable organometallic moiety);³⁵ iii) a small amount of carbon-encapsulated metallic iron is generated during decomposition.

In summary of the XAFS results, FeAc likely decomposes on nitrogen-doped carbon decomposes to form a high proportion of carbon encapsulated iron nanoparticles which are co-existing with a small proportion of Fe-N species. FeCl₃ probably decomposes to form some carbon-encapsulated metallic iron, but with a relatively high proportion of Fe-N₄ species. FePc retains a high proportion of Fe-N₄ moieties when it decomposes, and a relatively small amount of carbon-encapsulated metallic iron is generated. Assuming that the ORR reportedly occurs at atomically dispersed FeN₄ sites,^{36,37} the electrochemical activity of these electrocatalysts may be expected to increase in proportion to the amount

of Fe-N present in the material, i.e. $\text{FeAc-N-C}_{1000}(900\text{-NH}_3\text{-Aw}) < \text{FeCl}_3\text{-N-C}_{1000}(900\text{-NH}_3\text{-Aw}) < \text{FePc-N-C}_{1000}(900\text{-NH}_3\text{-Aw})$.

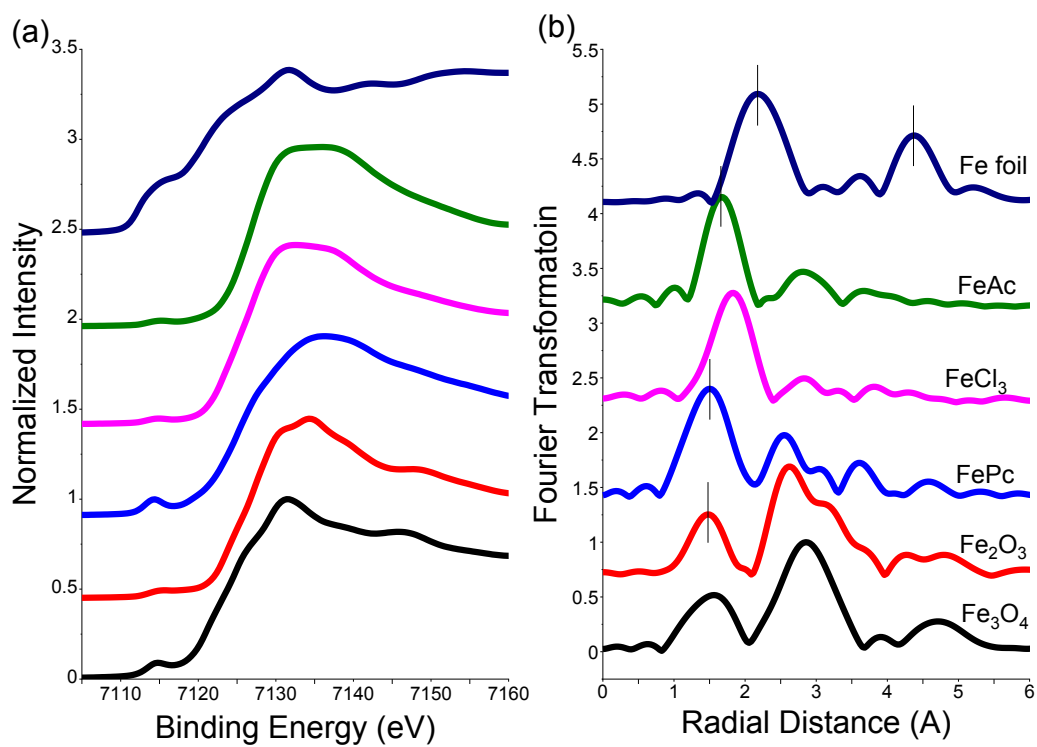


Figure 4.9: (a) XANES and (b) FT-EXAFS spectra of various reference samples.

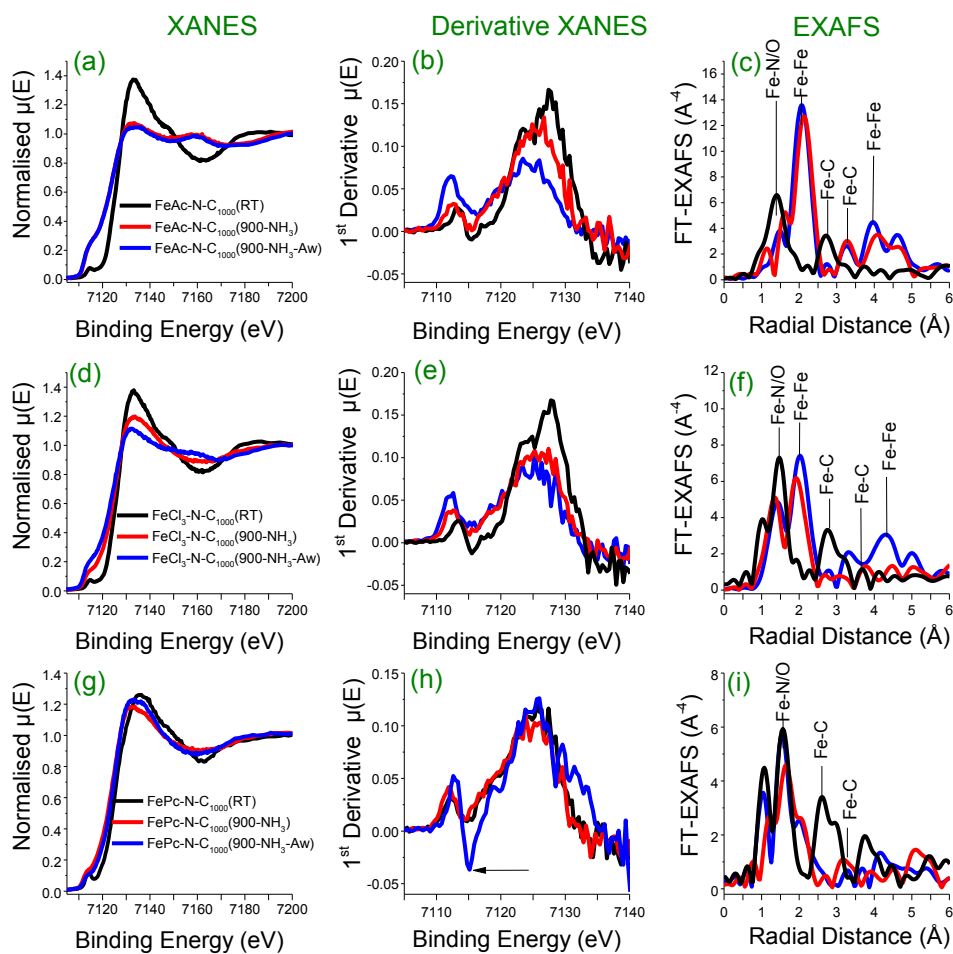


Figure 4.10: X-ray absorption spectra (XAS): XANES (left hand column); 1st derivative XANES (middle column) and FT-EXAFS (right hand column) for: (a-c) FeAc-; (d-f) FeCl₃-; and (g-i) FePc-derived electrocatalysts at different stages of the synthesis process.

4.3.6 Scanning Electron Microscopy (SEM)

In order to provide further insight into the differences between electrocatalysts made with different Fe precursors, scanning electron microscopy (SEM) was performed. Figure 4.11 shows SEM images of the pristine nitrogen-doped carbon, and the three electrocatalysts derived from FeAc, FeCl₃, and FePc, after heat treatment in ammonia and acid washing. The 3-dimensional porous open-cell structure of the nitrogen-doped carbon foam is preserved in all cases, even after all of the processing steps. This demonstrates the high mechanical stability of the support material. There are no visible traces of surface features such as e.g. iron nanoparticles at this magnification.

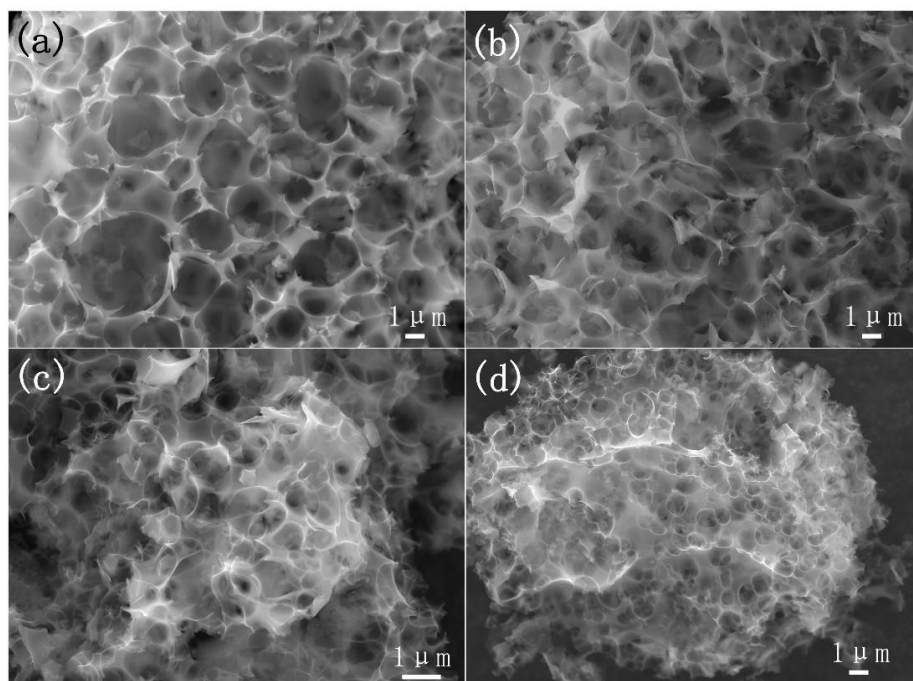


Figure 4.11: SEM images of: (a) N-C₁₀₀₀; (b) FeAc-NC₁₀₀₀(900-NH₃-Aw); (c) FeCl₃-NC₁₀₀₀(900-NH₃-Aw); and (d) FePc-NC₁₀₀₀(900-NH₃-Aw).

4.3.7 Transmission Electron Microscopy (TEM) & Selected Area Electron Diffraction (SAED)

TEM was performed in order to observe the microstructure of the different electrocatalysts in finer detail. Figure 4.12 shows TEM and SAED images of FeAc-N-C before and after acid washing. Before acid washing, metallic iron nanoparticles encapsulated by graphitic carbon can be clearly observed.

The lattice spacing in the graphitized shells is measured to be 0.35 nm, slightly larger than the 0.335 nm expected for graphite, and as expected for slightly less crystalline, or nitrogen-doped carbons. The SAED rings, Figure 4.12 (c) correspond to the presence of graphitic carbon and metallic Fe.

After acid washing, a high proportion of graphitic carbon nanostructures and carbon-encapsulated iron nanoparticles are still observed in the sample. The SAED rings correspond to the presence of graphitic carbon and metallic Fe. As such, it is confirmed that when FeAc decomposes, metallic iron nanoparticles are formed, which catalyse the growth of graphitic carbon nanostructures (such as carbon nanotubes, carbon nanofibers, and nano-onions). This is in agreement with the presence of iron nanoparticles as

suggested by XPS, presence of graphitic nanostructure as suggest by Raman analysis and proposed mechanisms based on the N₂ uptake discussion.

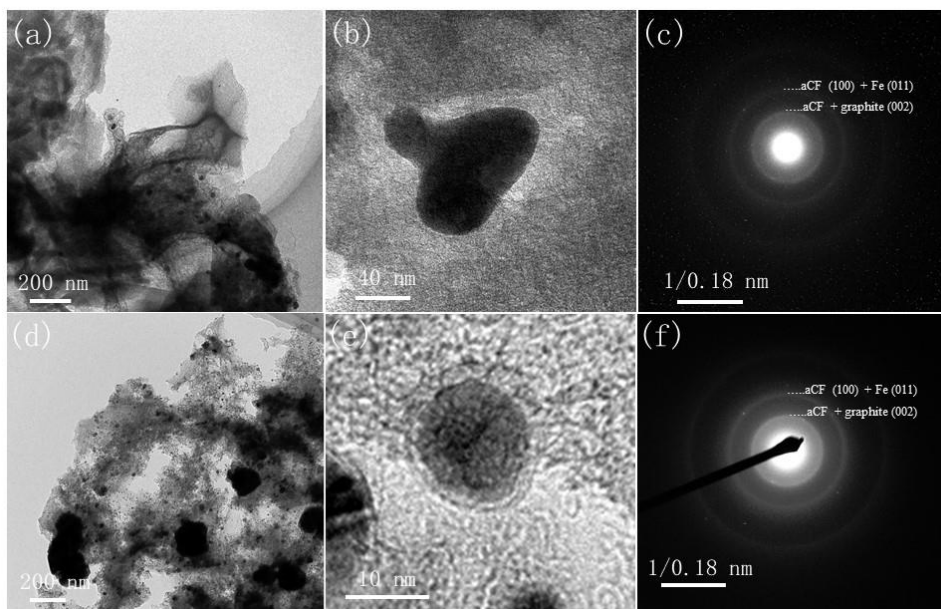


Figure 4.12: TEM images for FeAc-N-C: (a, b) before acid washing; (d, e) after acid washing; and their respective SAED images (c) and (f).

The TEM images of FeCl₃-N-C before acid washing (Figure 4.13) also confirms the presence of iron nanoparticles. However, in this case the nanoparticles don't all appear to be encapsulated, and there appears to be a lower proportion of graphitic carbon nanostructures compared to the case of FeAc. The SAED correspond to amorphous carbon (100), graphitic carbon (002), and metallic iron (011). After acid washing, there appears to be a lower proportion of nanoparticles, and the remaining iron nanoparticles appear to be encapsulated in layers of graphitic carbon. As such, in the case of FeCl₃ it appears that a higher proportion of Fe₂O₃ nanoparticles are generated during

decomposition, and that these are dissolved during the acid washing step. This is in agreement with reduction in Fe content after acid washing as discussed in the XPS section above.

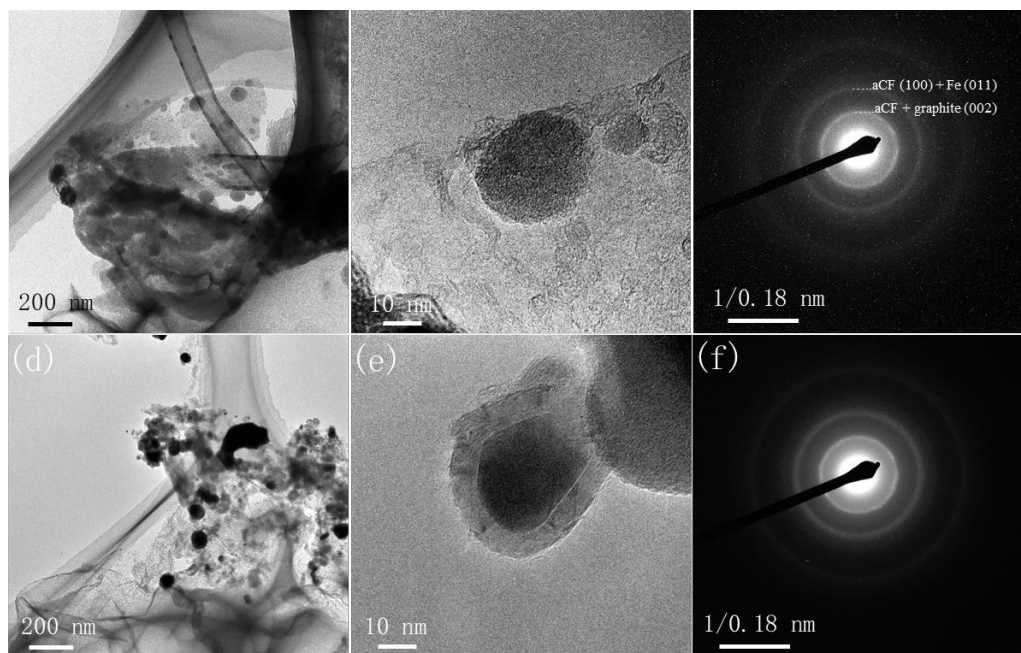


Figure 4.13: TEM images for FeCl₃-N-C: (a, b) before acid washing; (d, e) after acid washing; and their respective SAED images (c) and (f).

Lastly, the TEM images of FePc-N-C before acid washing reveal the lowest abundance of Fe nanoparticles and graphitic carbon nanostructures. Several carbon nanofibers are observed, terminated with the Fe nanoparticle that formed them.³⁸ After acid washing, the proportion of nanoparticles appears to decrease, suggesting that they were partially exposed in this case, and not entirely protected from the acid washing step by graphitic carbon layers. The SAED image (representative of both before and after acid washing) in

Figure 4.14 (d) shows a bright graphitic ring revealing the presence of graphitised carbon nanofibers. However, there are no prominent metallic iron-related diffraction points. As such, in the case of FePc it appears that only a small amount of iron is generated during heat treatment, resulting in a relatively low amount of graphitic carbon nanostructures on the surface. The remaining iron may be still in the form of Fe-N₄ sites, as suggested by the presence of Fe-N bonds in the N1s after acid washing and lack of increase in porosity analysis.

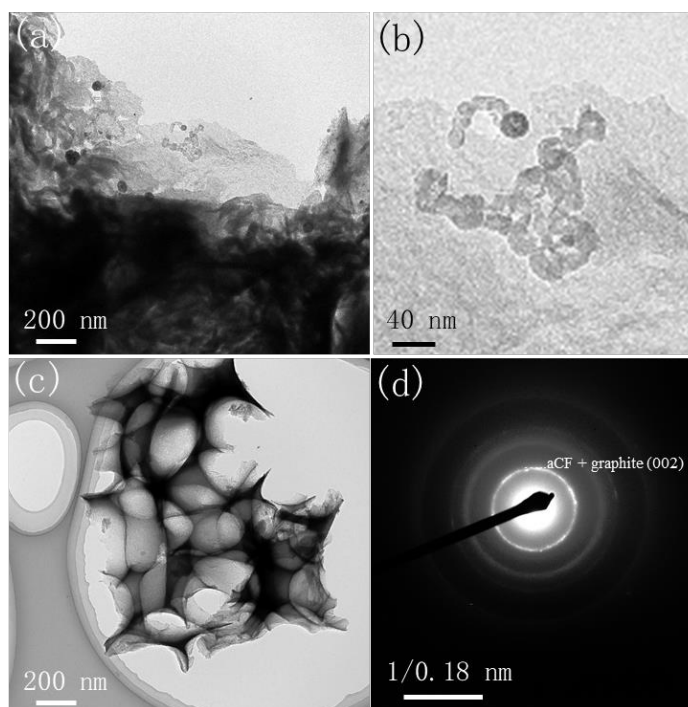


Figure 4.14: High and low resolution TEM images for FePc-N-C: (a, b) before acid washing; (d, e) after acid washing; and their respective SAED images (c) and (f).

4.3.8 Electrochemical Characterization

The three Fe-N-C electrocatalysts derived from FeAc, FeCl₃, and FePc after heat treatment in ammonia and acid washing were then subjected to electrochemical characterization. The nitrogen-doped support was also investigated before and after ammonia heat-treatment. For simplicity, in this section the samples are identified simply as N-C, N-C(NH₃), FeAc-N-C, FeCl₃-N-C and FePc-N-C. Figure 4.15 shows the LSVs recorded from RRDE experiments carried out in oxygen-saturated 0.1 M HClO₄ solution at a rotation speed of 1600 rpm. The effects of heat treatment and acid washing on the activity of Fe-N-C electrocatalysts were discussed in a previous chapter, and therefore only the final stage catalysts are presented here. The electrochemical performance indicators are summarized and compared in Table 4.4.

As a metal-free electrocatalyst, N-C actually performs surprisingly well in acid electrolyte, with an onset potential of 0.78 V_{RHE}. However, as expected, the electron transfer number is relatively low (3.2). After heat treatment in ammonia, N-C(NH₃) demonstrated improvement in all performance indicators compared to N-C. Indeed, this activity is amongst the highest reported for a metal-free ORR catalyst in acid medium.³⁹ This is attributed to both an increased porosity due to ammonia etching of the carbon, as well as

increased basicity of the surface due to the introduction of nitrogen functional groups (as observed in XPS, Table 4.4).⁴⁰

All three Fe-N-C catalysts show excellent initial activity, comparable with state-of-the-art Fe-N-C catalysts published in the literature, with onset potential $\sim 0.85 V_{\text{RHE}}$.^{8,41} They all have similar onset potentials of $0.85 V_{\text{RHE}}$, and half wave potentials of $\sim 0.71 V_{\text{RHE}}$. The main difference in the LSVs (Figure 4.15) is the mass diffusion limited current density, which increases in the order: FePc < FeAc < FeCl₃. Meanwhile, the electron transfer numbers are also relatively high for non-PGM electrocatalysts, and also increase in the order FePc-N-C ($n = 3.87$) < FeAc-N-C ($n = 3.92$) < FeCl₃-N-C ($n = 3.94$). Accordingly, the mass activities at $0.7 V_{\text{RHE}}$ increase in the same order: 0.88 A/g (FePc), 1.01 A/g (FeAc) and 1.14 A/g (FeCl₃). These values are relatively high compared to values reported in the literature.⁴²

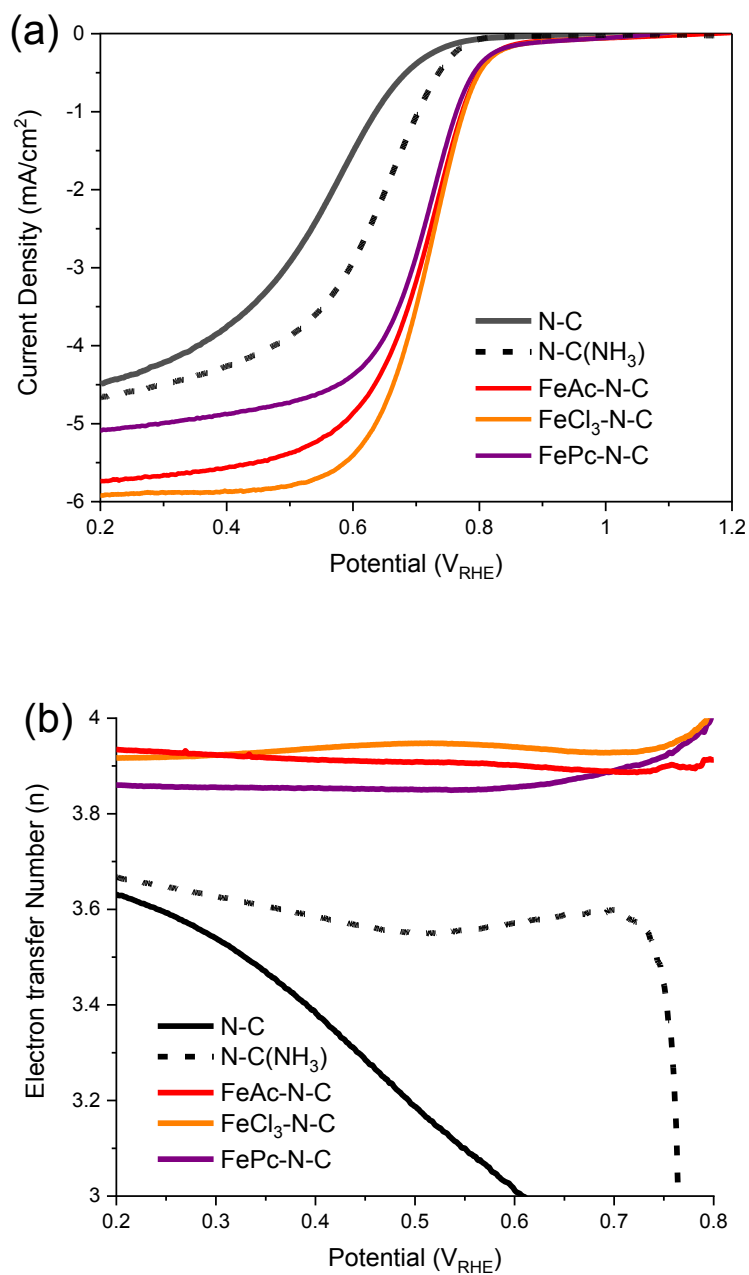


Figure 4.15: (a) Linear sweep voltammograms and (b) electron transfer number (n) of: $N-C_{1000}$, $N-C_{1000}(900-NH_3)$, $FeAc-NC_{1000}(900-NH_3-Aw)$, $FeCl_3-NC_{1000}(900-NH_3-Aw)$, and $FePc-NC_{1000}(900-NH_3-Aw)$ obtained in 0.1 M $HClO_4$ at 1600 pm.

Table 4.4: Table showing the activity markers used for comparing the activity of the samples.

	$E_{1/2}$ (V _{RHE})	E_o (V _{RHE})	I_d (mA/cm ²)	Avg. No. of Electrons (n)	Mass Activity @0.7 V _{RHE} (A/g)	Mass Activity @0.85 V _{RHE} (A/g)
N-C	0.55	0.78	-4.50	3.2	0.11	0
N-C(NH ₃)	0.64	0.80	-4.66	3.60	0.38	0
FeAc-N-C	0.71	0.90	-5.70	3.92	1.01	0.10
FeCl ₃ -N-C	0.71	0.90	-5.90	3.94	1.14	0.10
FePc-N-C	0.71	0.90	-5.10	3.87	0.88	0.10

The nitrogen-doped carbon support is effectively identical in all three Fe-N-C electrocatalysts, and therefore the differences in electrochemical activity must mainly result from changes in the adsorbed iron precursor, and its interaction with the support. Incorporating the information obtained by the various characterization techniques used in this chapter, we can draw some important conclusions about why the electrochemical activity of Fe-N-C materials synthesized using different precursors is different.

The FeAc-derived catalyst has high micropore surface area (1447 m² g⁻¹), wide pore diameter of 1.05 nm (due to etching by iron from within), and a high $V_{\text{meso}}/V_{\text{micro}}$ ratio of 1.1 (N₂-adsorption measurements). In addition, there is a high proportion of graphitic carbon and metallic iron (Raman / XAS / TEM), corresponding to a lower proportion of Fe-N bonds (XPS / XAS). Similarly, the FeCl₃-derived catalyst has higher micropore surface area (1586 m² g⁻¹), large pore diameter (1.02 nm), and a high $V_{\text{meso}}/V_{\text{micro}}$ ratio

(1.0). Compared to FeAc, there is a lower proportion of graphitic carbon and metallic iron, corresponding to a higher proportion of Fe-N bonds. Finally, the FePc-derived catalyst has low microporous surface area ($1000 \text{ m}^2 \text{ g}^{-1}$), narrow micropores (0.77 nm), and a lower $V_{\text{meso}}/V_{\text{micro}}$ ratio (0.6). It also has the lowest proportion of graphitic carbon and metallic iron, and the highest proportion of Fe-N bonds.

The onset potential is the same for all three electrocatalysts. This suggests that the nature of the active site is the same (likely Fe-N₄ sites), and that other factors probably contribute to the overall activity. High micropore surface area contributes to increased active site density, by providing more sites for Fe adsorption to create Fe-N₄ motifs. Meanwhile, wide pore diameter and high $V_{\text{meso}}/V_{\text{micro}}$ ratio contribute to enhanced mass diffusion of reactants / products to / from the ORR active.^{43–45} The proportion of Fe-N is assumed to directly corresponds to the number of potentially ORR active Fe-N₄ sites in the material. As such, the “medium” ORR activity of FeAc-N-C catalysts can be attributed to the high surface area (increased availability of Fe adsorption sites) and porosity (enhanced mass diffusion) combined with the low proportion of Fe-N sites (lower active site density). The “high” ORR activity of FeCl₃-N-C can be attributed to the large surface area (increased availability of Fe adsorption sites) and high porosity (enhanced mass diffusion) in

combination with the higher proportion of Fe-N sites (higher active site density). The “low” ORR activity of FePc-N-C is slightly more complicated. Despite having the highest proportion of Fe-N bonds due to the surprising stability of the central Fe-N₄ motif, these Fe-N sites are not thought to reside within the micropores because the FePc is too large, instead being situated on the outer surface. This severely limits the available surface area for adsorption on the surface, resulting in agglomeration of FePc. Agglomeration can lead to buried and therefore inaccessible active sites, decreasing the active site density. This may also explain the lower electron transfer number, and alternative 2-electron processes have more opportunity to occur at iron-free sites. Overall, FeCl₃-N-C provides an effective compromise, resulting in the highest ORR activity.

The micropore surface area, pore diameter, mesopore/micropore volume ratio, and Fe-N content of the different catalysts are plotted against the mass activity in Figure 4.16. The strongest correlation is between the micropore surface area, suggesting that this is the main driver of changes in ORR activity for these samples.

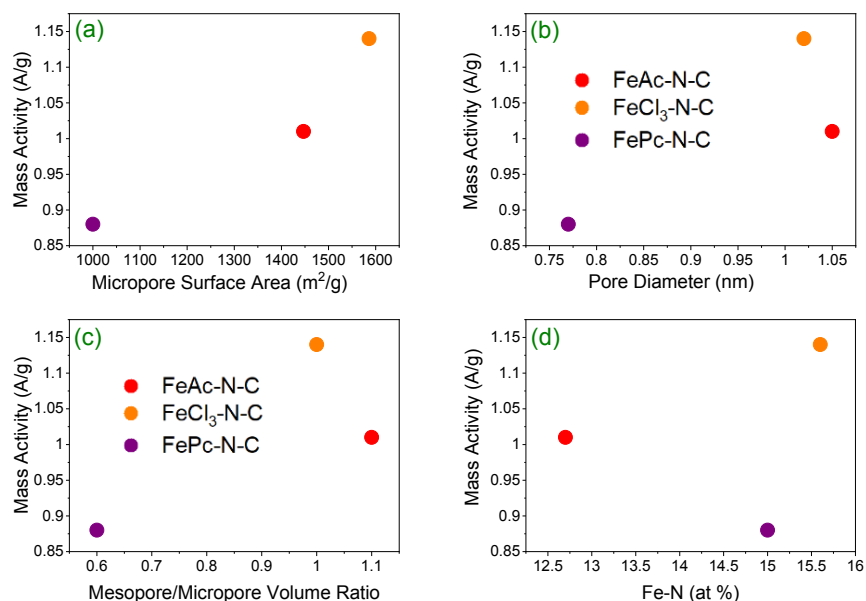


Figure 4.16: Dependence of the mass activity on the (a) micropore surface area, (b) pore diameter, (c) mesopore/micropore volume ratio, and (d) the abundance of Fe-N bonds. for FeAc-N-C, FeCl₃-N-C and FePc-N-C catalysts.

Figure 4.17 is a schematic summarizing these findings. For FeAc there is a large proportion of carbon-encapsulated Fe-nanoparticles, with fewer Fe-N motifs embedded in the micropores. For FeCl₃, there is a lower proportion of carbon-encapsulated iron nanoparticles, with a higher proportion of Fe-N sites in the micropores. Finally, there are very few carbon-encapsulated iron nanoparticles, and a thicker layer of Fe-N containing material residing outside the micropores, resulting in inaccessible active sites.

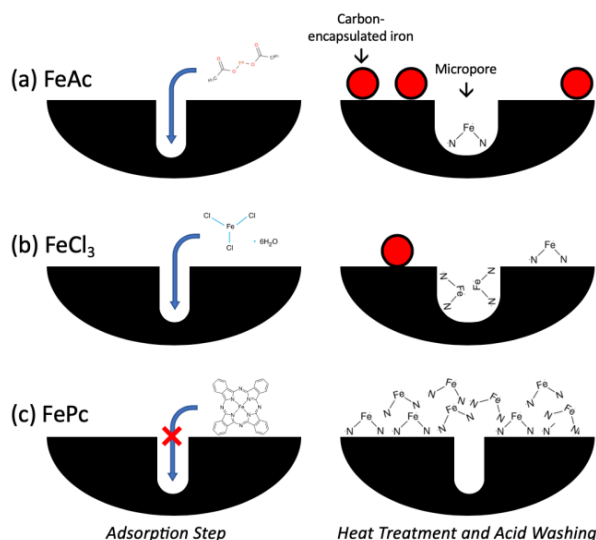


Figure 4.17: A schematic summarizing the proposed differences between the Fe-N-C electrocatalysts with different iron precursors.

Another set of samples was also fabricated by adsorbing the iron precursors onto a nitrogen-free carbon foam, rather than a nitrogen-doped carbon foam (i.e. FeAc-C and FeCl₃-C). These were used to investigate the effect of nitrogen in the support on the final electrochemical activity. These samples all displayed very poor electrochemical activity (Figure A4.11), with onset potentials of only 0.6 and 0.66 V_{RHE}, very low current density. In fact, the performance of these samples was even worse than N-C and N-C(NH₃). This confirms the importance of a nitrogen source in the adsorption of iron, and the formation of catalytic active sites. This was supported by XAS experimental data (Figure A4.12), where the nitrogen-free carbon supports resulted in a much higher proportion of Fe-Fe

coordination peaks, meaning that almost all the iron formed during heat treatment was metallic.

4.3.9 Electrochemical Durability: Load-cycling

Load-cycling durability measurements were carried out between 0.6 and 1.0 V_{RHE}, in 0.1 M HClO₄ in order to simulate potential fluctuations during the operation of fuel cell systems. Cycling was paused, and conventional LSVs were carried out at 0, 5,000 and 10,000 potential cycles (Figure 4.18). Figure 4.19 shows the resulting half-wave potential of the different catalysts, plotted against the number of cycles. In all cases, the half-wave potential decreases over the course of the durability measurements, as expected. The total decrease in half-wave potential after 10,000 potential cycles was 40 mV for the FeAc-derived electrocatalyst, 20 mV for the FeCl₃-derived electrocatalyst, and 28 mV for the FePc-derived electrocatalyst. These values are comparable to potential drops reported observed in the literature.⁴⁶ There was no significant change in the area within the cyclic voltammograms (corresponding to the double layer capacitance), suggesting that the support itself does not degrade. The main mechanism for the loss of activity is therefore likely to be due to Fe leaching from the active sites, as reported in previous studies.⁴⁷ The

rate of change of the half wave potential is similar in all three cases, with the most active sample, the FeCl_3 -derived electrocatalyst, having slightly higher stability.

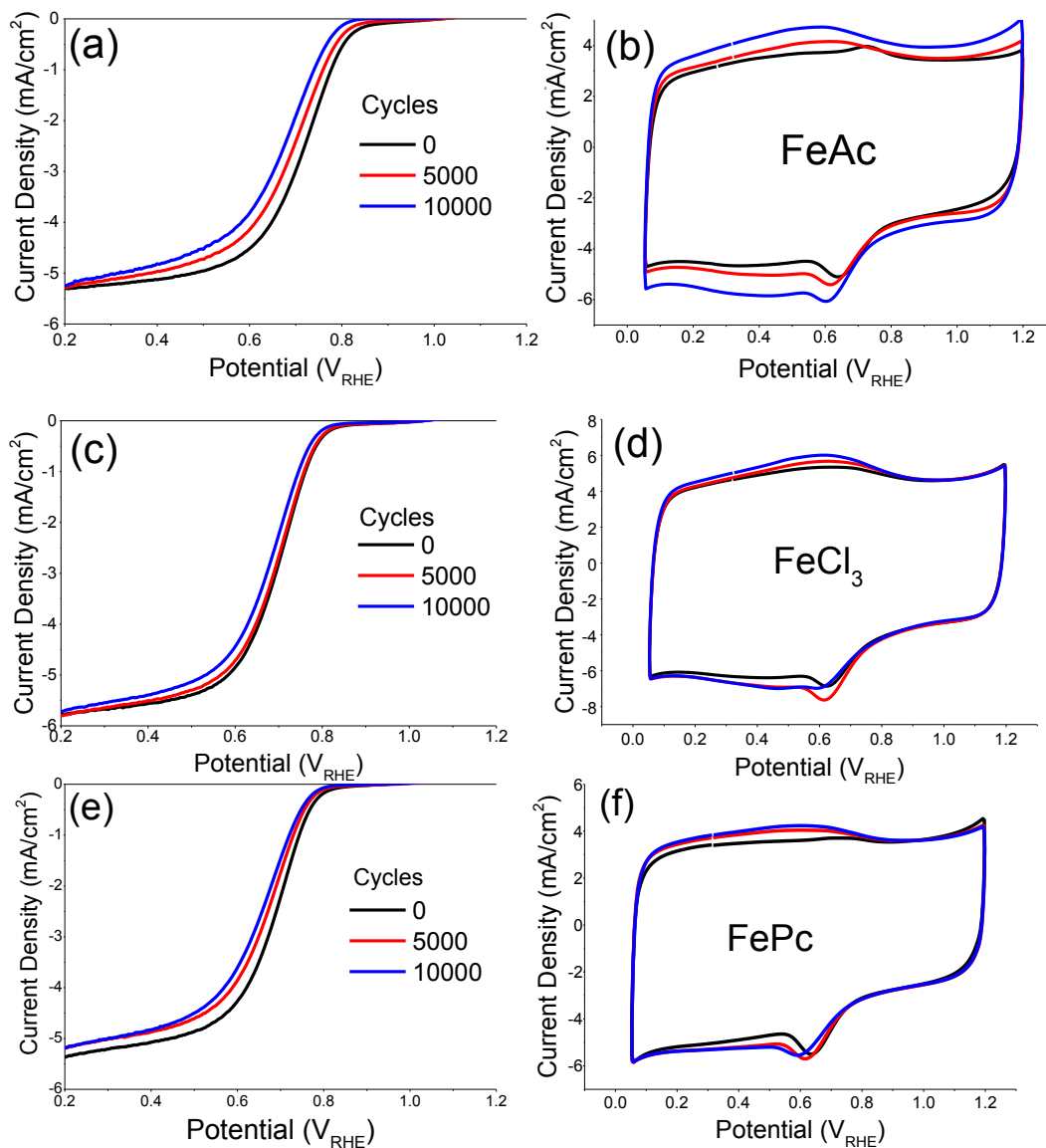


Figure 4.18: Linear sweep voltammograms and cyclic voltammograms recorded at 0, 5,000, and 10,000 cycles of load-cycle durability test performed in 0.1 M HClO_4 at 1600 rpm, for: (a, b) FeAc-, (c, d) FeCl₃-, and (e, f) FePc-derived electrocatalysts, after heat treatment in ammonia and acid washing.

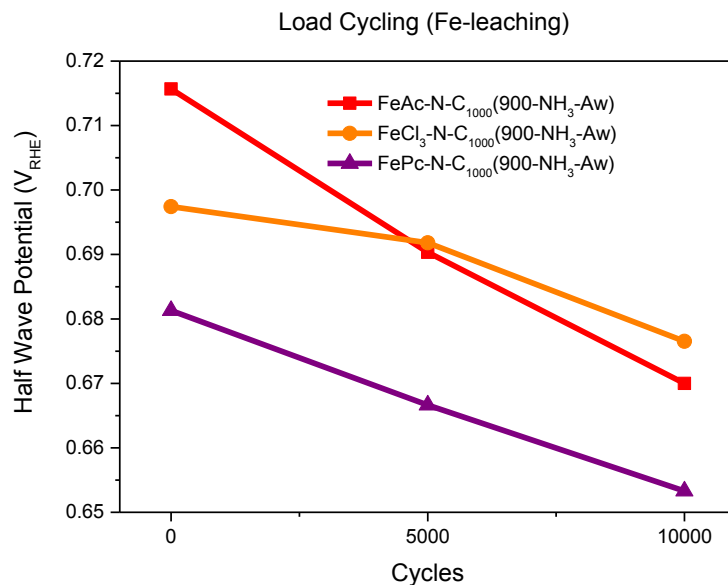


Figure 4.19: (a) Half-wave potentials of linear sweep voltammograms recorded at 0, 5,000 and 10,000 cycles of load-cycling for: $\text{FeAc-C}_{1000}(\text{900-NH}_3\text{-Aw})$, $\text{FeCl}_3\text{-C}_{1000}(\text{900-NH}_3\text{-Aw})$, and $\text{FePc-C}_{1000}(\text{900-NH}_3\text{-Aw})$ obtained in 0.1 M HClO_4 at 1600 rpm.

4.3.10 Electrochemical Durability: Start-Stop Cycling

Start-stop potential cycling durability measurements were carried out between 1.0 and 1.5 V_{RHE} , in 0.1 M HClO_4 in order to simulate turning fuel cell systems on and off. Cycling was paused, and conventional LSVs were carried out at 0, 5,000, 10,000 and 30,000 cycles (Figure 4.20). Figure 4.21 shows the resulting half-wave potential of the different catalysts, plotted against the number of cycles. Start-stop potential cycling is considered to be far more harsh testing condition compared to load cycling, as it induces carbon corrosion (i.e. gasification of the carbon support to CO_2). As such, the effect on the cyclic

voltammograms and LSVs is much more noticeable. Changes in the shapes of cyclic voltammograms after 30,000 cycles are clearly observed in all the three catalysts. The half wave potential decreases significantly over the duration of the test, for all samples, by a similar amount. Meanwhile, the onset potentials are remarkable stable throughout.

This indicates that the degradation in this protocol is due to changes in the nitrogen-doped carbon foam support, rather than the active sites themselves. Indeed, black flakes were observed in the electrolyte solution after the durability tests, indicating that some of the electrocatalyst layer was delaminated from the working electrode. This is a reflection of oxidation and changes in volume of the carbon support under this cycling protocol. Therefore, in order to improve the start-stop cycling durability in the future, improving the resistance to oxidation of the support is a priority. This may be achieved through e.g. graphitization, or inclusion of more graphitized carbons such as graphene / carbon nanotubes.

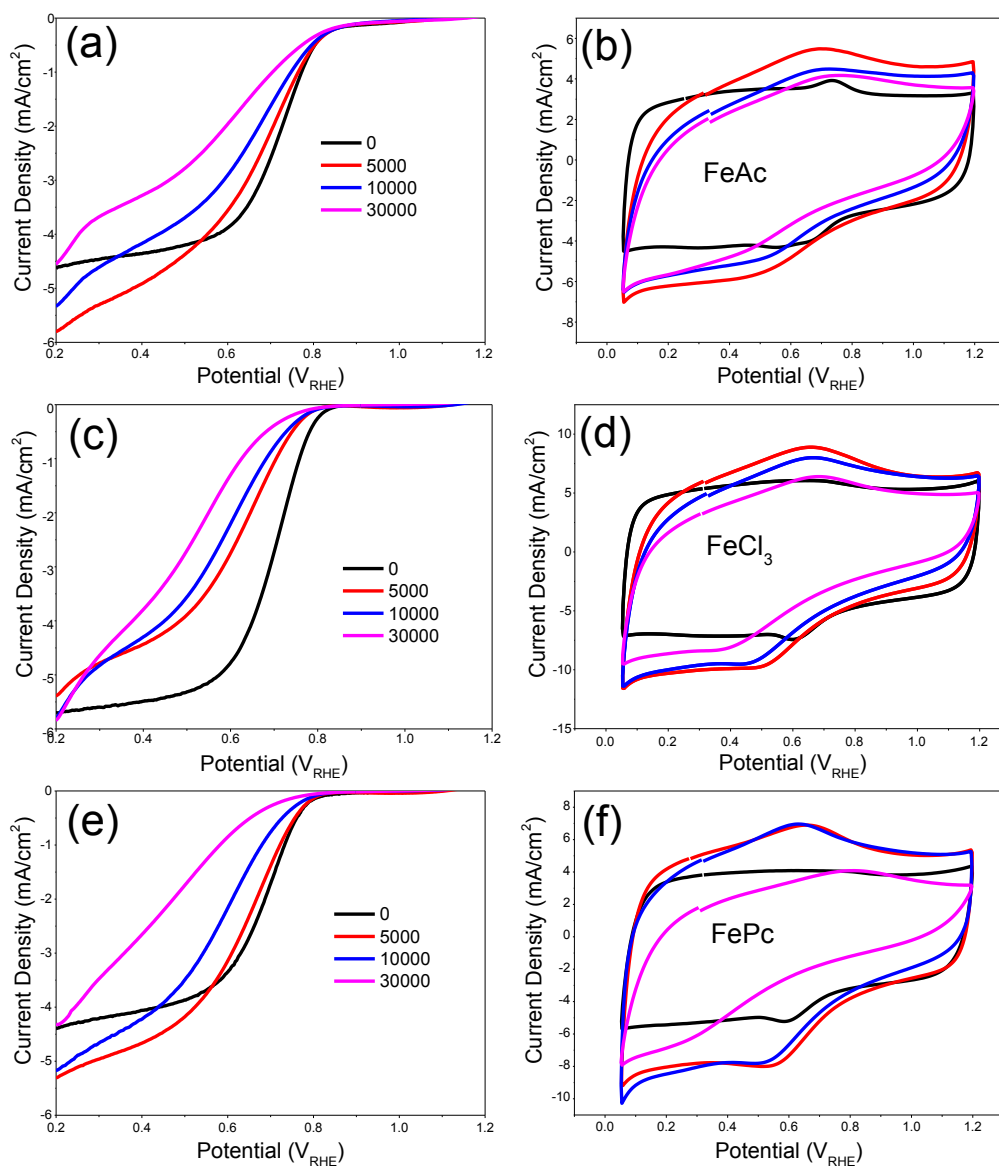


Figure 4.20: Linear sweep voltammograms and cyclic voltammograms recorded at 0, 5,000, 10,000 and 30000 cycles of start-stop durability test performed in 0.1 M HClO₄ at 1600 rpm, for: (a, b) FeAc-, (c, d) FeCl₃-, and (e, f) FePc-derived electrocatalysts, after heat treatment in ammonia and acid washing.

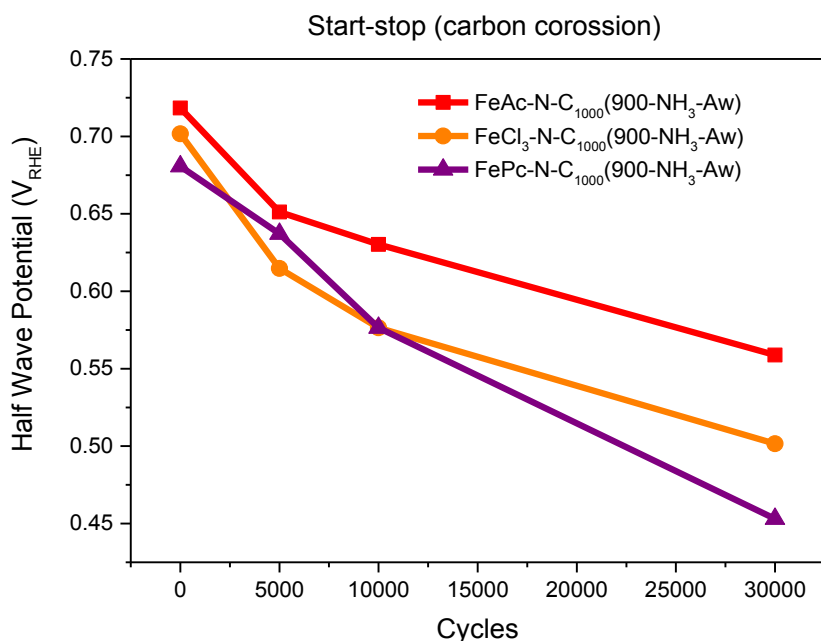


Figure 4.21: Half-wave potentials of linear sweep voltammograms recorded at 0, 5,000, 10,000 and 30,000 cycles of start-stop durability test performed in 0.1 M HClO₄ at 1600 rpm, for the FeAc-, FeCl₃-, and FePc-derived electrocatalysts, after heat treatment in ammonia and acid washing.

4.3.11 Single Cell Testing in a Membrane Electrode Assembly (MEA)

FeCl₃-N-C was selected as the cathode catalyst for MEA testing because of its superior performance in half-cell RRDE experiments. The only commercially available Fe-N-C catalyst, NPC-2000 (Pajarito Powder), was also tested as a reference. In both cases the anode was platinum decorated Ketjen black (Pt/KB Tanaka 45.6%, TKK Corp.). Inks were prepared according to the following protocols: (i) 100 mg Pt/KB 45.6% catalyst was dispersed in a solution of 5% Nafion ionomer, ethanol and H₂O, with a Nafion to Pt/C

ratio of 0.28 to 0.72; (ii) Fe-N-C catalyst was dispersed in 5 wt% Nafion and 2 ml of ethanol solution, and the Nafion to catalyst ratio was 1 to 2. The ink was sonicated for 30 minutes using an ultrasonic homogenizer (SMT Company, UH-600). The prepared inks were then sprayed onto both sides of Nafion[®] NRE-212 membrane (Dupont), within a circular area of 0.5 cm² using a spray printing machine (Nordson, C-3J) to get achieve loadings of 0.3 mg/cm² (Pt/KB on anode side) and 1 mg/cm² (non-PGM on cathode side) respectively. The resulting catalyst-coated membrane (CCM) was hot-pressed at 0.3 KN for 180 seconds.

The fabricated MEAs were then sandwiched between two sheets of hydrophobic carbon paper (Toray, EC-TPI-060T) with same area as the flow field of cell holder and assembled in a 1 cm² flow field NEDO cell holder. The holder was then placed in an oven, heated to 80 °C, and the anode and cathode were purged with N₂ gas (100 sccm) prior to the introduction of reactants. Then, 100 %-humidified H₂ gas and air were supplied to the anode and the cathode, respectively, at atmospheric pressure, with a flow rate of 100 sccm, and current-voltage (I-V) measurements were recorded. After the measurement, the gas lines were again purged with N₂ to remove residual hydrogen from the chamber.

The MEA using NPC-2000 achieved a maximum current density of 640 mA/cm², compared to 540 mA/cm² for FeCl₃-N-C (Figure 4.22). The two catalysts have similar open circuit voltages (OCV). The MEA power densities are 170 mW/cm² for NPC-2000 and 150 mW/cm² for FeCl₃-N-C.

From the I-V curves it is observed that there is a larger voltage drop in activation region for FeCl₃-N-C, as well as a steeper slope in the ohmic region. As such, the difference in performance is likely due to the ink preparation protocol. Optimization of Nafion is critical in the preparation of MEAs, having a strong effect on the triple phase boundary by delivering hydrogen ions to the ORR active sites. The FeCl₃-N-C catalyst has almost double the surface area (1812 m² g⁻¹) compared with NPC-2000 (970 m² g⁻¹), and therefore a higher Nafion content in the electrocatalyst layer may be required to improve Nafion coverage in the electrocatalyst layer, resulting in improved triple phase boundary, and increasing the charge transport in the cathode catalyst layer. In addition, the increased ohmic losses may be due to lower electronic conductivity in FeCl₃-N-C. This will be confirmed and resolved in future work. Whilst the activity of our electrocatalyst is slightly lower than the reference sample, there is still a lot of potential for optimization. As such

this electrocatalyst holds a lot of promise to compete with commercially available non-PGM electrocatalysts.

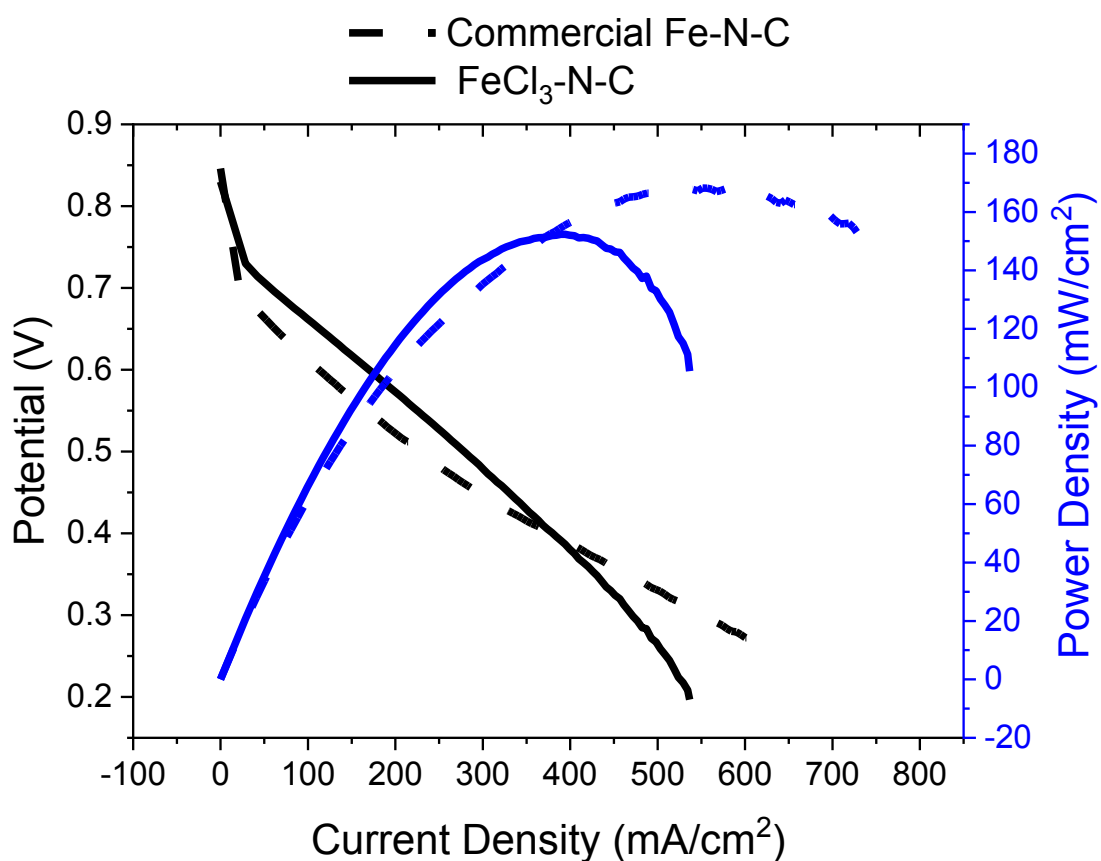


Figure 4.22: I-V and power density curves of MEAs using: (dotted line) commercial Fe-N-C, (NPC-2000) cathode; and (solid line) $\text{FeCl}_3\text{-N-C}$ cathode. Pt/KB was use as anode catalyst in both cells.

4.4 Summary and Conclusions

In this work, FeAc, FeCl₃, and FePc were adsorbed on carbon foam and nitrogen-doped carbon foam followed by heat-treatment at 900 °C in ammonia, and acid washing in 1 M H₂SO₄. The resulting catalysts were extensively characterized. For FeAc-N-C catalysts, there was a large microporous surface area, wide micropore diameter, and a high proportion of graphitic carbon-encapsulated iron nanoparticles coexisting with Fe-N₄ sites, leading to reasonable ORR activity. For FeCl₃-N-C there was also a large microporous surface area and wide micropore diameter, but in this case there was a lower proportion of carbon-encapsulated metallic iron, and a correspondingly higher proportion of Fe-N₄ sites, leading to high ORR activity. Meanwhile, FePc-N-C has very low microporous surface area and narrow micropore diameter, because the FePc molecules are too large to enter the micropores of the nitrogen-doped carbon support. This leads to the lowest ORR activity, despite possessing the highest proportion of Fe-N bonds. Load-cycling electrochemical durability revealed minor degradation in all three samples, probably due to iron leaching. On the other hand, start-stop durability resulted in severe carbon corrosion, suggesting the need for a more graphitized carbon support.

As such, new insights into the formation mechanisms of Fe-N-C electrocatalysts with different types of precursors were discovered. In particular, it is concluded that a combination of large microporous surface area, suitable porosity, and a high proportion of accessible Fe-N sites residing in the micropores is beneficial in creating highly active Fe-N-C electrocatalysts.

4.5 References

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Chapter 5 In situ High Temperature and Near Ambient Pressure Characterization of Fe-N-C Electrocatalysts

5.1 Introduction

In the previous chapter, three different iron precursors were used to synthesize new Fe-N-C catalysts on nitrogen doped carbon foam supports, resulting in promising activity and stability. Deeper understanding of how the metal precursors decompose and interact with atoms in the support during pyrolysis to form catalytically active materials will help to optimize the design of more efficient catalysts. In addition, characterizing the interaction between oxygen adsorbates and the catalyst surface under realistic PEFC operating conditions is of great interest.

In this chapter, an investigation of the behaviour of FeAc, FeCl₃ and FePc precursors adsorbed onto nitrogen-doped carbon foam both during pyrolysis to form electrocatalysts, and during exposure to humidified oxygen after electrocatalyst formation is performed. First the gaseous products evolved during heat treatment are analysed in-situ, using quadrupole mass spectrometry (QMS). Then, changes in the chemical structure are probed in-situ using high-temperature X-ray photoelectron spectroscopy (HT-XPS). Finally, the interaction between humidified oxygen and the synthesized electrocatalysts is investigated using near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS).

In situ studies on electrocatalysts are vital because they give insights on the structural and chemical properties in realistic physical conditions, and this may lead to a better understanding of the factors that control the catalytic properties. Therefore, offering a well-informed strategy for improving synthesis methods, which may improve performance of the catalysts.

Mass spectrometry is an analytical method used to accurately determine the mass of atoms and molecules. The technique involves measurements of the mass-to-charge ratios of the ions formed when a sample is ionized.¹ Mass spectrometers include an ion source, a mass analyser, and a detector. Recently, the quadrupole has become the most widely used mass analyser for this technique, because it is highly sensitive to the order of hundreds of ppm.² It comprises two radio frequency rods, and two direct current (DC) voltage rods. Quadrupole mass spectrometry (QMS) is used here to detect the pyrolysis products of the iron-adsorbed nitrogen-doped carbon supports in situ, as they decompose during heat treatment. To the best of our knowledge, this technique has not previously been used to investigate the formation of Fe-N-C electrocatalysts.

HT-XPS is an in situ technique where a sample is heat-treated in a specialized cell, and XPS spectra are recorded during the heating process. In-situ HT-XPS studies have been conducted on several model catalysts,^{3,4} but to the best of our knowledge, no work has been published using these techniques on Fe-N-C electrocatalysts for the ORR. As such this is a novel and worthy study. Here we use HT-XPS to probe the changes in the chemical structure of different iron precursors adsorbed on nitrogen-doped carbon foams as the samples are heated from room temperature up to 650 °C.

NAP-XPS is capable of measuring XPS spectra at pressures well above UHV, i.e. up to 13 kPa under different gas environments.⁵ This makes it possible to observe the interactions between adsorbents and surfaces. At these relatively high pressures, photoelectrons are strongly scattered by gas molecules. However, the use of several differential-pumping systems immediately adjacent to the in-situ sample cell for NAP-XPS (connected by a very small aperture) overcomes the problem of attenuation of the photoelectrons as they approach the electron analyser and detector.^{6,7} Since the initial step for ORR begins with O₂ adsorption, it is important to investigate the behaviour

of oxygen adsorbates on the surface of catalysts. This gives helpful information on surface coverage with oxygen-related adsorbates on the catalysts. Only a handful of studies have been conducted using NAP-XPS on Fe-N-C electrocatalysts.⁸

Previously, few QMS, HT-XPS and NAP-XPS studies have been conducted, especially on catalytic systems, partly because these are relatively new techniques requiring highly specialised equipment. Gunther *et. al.* studied the catalytic oxidation of ammonium on a Pt (533) surface between 26 and 526 °C at a pressure of 100 Pa, detecting chemisorbed oxygen and nitrogen-containing species.⁹ Meanwhile, Arrigo *et.al* used QMS to continuously monitor the product composition of water electrolysis over on Pt, in situ.¹⁰ Asset *et al.* employed NAP-XPS to investigate the nature of the electrochemical active sites for the CO₂ reduction reaction on nitrogen-doped carbon-based electrocatalysts, finding that pyridinic and pyrrolic nitrogen-moieties preferentially adsorbed CO₂.¹¹ Fantauzzi *et.al.* used NAP-XPS to show that the formation of stable surface oxides on Pt(111) requires a timescale of more than 4 hours at between 210 and 390 °C and at an O₂ partial pressure of 100 Pa.¹² In similar work, Naitabdi *et. al.* monitored the evolution of the oxidation states and surface elemental composition of pure Pt and PtZn nanoparticles under exposure to O₂ partial pressures.¹³ Bozzini *et. al* employed HT-XPS to investigate electrochemical processes in solid oxide fuel cells, in situ.¹⁴ Hong *et. al* used NAP-XPS to study the chemical species on Sr₂Co₂O₅ epitaxial thin films at high temperature, which desorbed oxygen as a function of temperature.¹⁵ To the best of our knowledge, ***these techniques have rarely, or never been used to investigate Fe-N-C electrocatalysts for the ORR.*** As such, these pioneering experiments give us new insights into the formation and mechanisms of Fe-N-C electrocatalysts. All the work in this chapter was performed with the assistance of Dr Břetislav Šmíd, using the NAP-XPS system

at Charles University in Czech Republic. The experiments were funded by the Central European Research Infrastructure Consortium (CERIC).

5.2 Experimental

Iron-adsorbed samples were prepared by mixing the iron precursor (i.e. FeAc, FeCl₃, or FePc) dissolved in a suitable solvent (i.e. water or ethanol) with the nitrogen-doped carbon support (N-C) dispersed in ethanol. The mixture was left to stir at 80 °C until all the solvent had evaporated, after which the iron-precursor-adsorbed-N-C catalyst powders were obtained.

A drop of isopropanol was added to a small amount of catalyst powder and this was mixed to a paste using a spatula. The paste was pressed onto a stainless-steel mesh, and the solvent was allowed to evaporate. The mesh was checked carefully to ensure sufficient adhesion, and then spot-welded onto a bespoke sample holder. This was then loaded into the specialised vacuum system (SPECs Surface Nano Analysis, GmbH Germany) at high vacuum, via an airlock. QMS, HT-XPS and NAP-XPS were all carried out in the same system.

Subsequently the sample was heated, and the gaseous pyrolysis products were analysed using a PHOIBOS 150 Hemispherical Energy Analyzer, coupled with a differentially-pumped electrostatic pre-lens system and a quadrupole mass spectrometer. The N-C sample was heated under vacuum to 330 °C, at 20 ° min⁻¹, and the Fe-adsorbed samples were heated under vacuum to 650 °C at 20 ° min⁻¹. Measuring to higher temperatures was not possible due to equipment and time constraints.

XPS spectra were first measured under vacuum before heating the samples. Then the samples were heated up to 650 °C, using a thermocouple to monitor the temperature, and HT-XPS spectra were

recorded at this temperature. For the N-C reference sample, the XPS data was recorded after degassing at 330 °C to remove surface adsorbates.

After recording the HT-XPS spectra, the sample was cooled, and then the cell was flooded with humidified oxygen. This was supplied using an O₂:H₂O ratio of 4:1. This humidified oxygen was injected into the NAP cell until a total pressure of 100 Pa was reached. Then after waiting 2 minutes for the pressure to stabilize, the NAP-XPS spectra were recorded.

C 1s spectra were deconvoluted into peaks assigned as sp² hybridized C=C (~284.5 eV); sp³ C-C (~285.5); C-O/C-N (~286.6 eV); O=C-N (~288.2 eV); and $\pi-\pi^*$ in the aromatic ring (~290.7 eV).^{16,17} The N 1s spectra were deconvoluted into peaks corresponding to: pyridinic-N (~398.2 eV); pyrrolic-N and/or Fe-N (~399.5 eV); graphitic-N (~401 eV); hydrogenated-pyridinic-N (~402.6 eV); and pyridine-N-oxide (~404.4 eV). The O 1s spectra were deconvoluted into peaks corresponding to: Fe-O (529-530 eV) and C=O (~531 eV); C-OH/C-O-C (~533 eV); chemisorbed oxygen (~534.7 eV); and the Na KLL (~537 eV).¹⁷ A summary of the relative abundance of the deconvoluted peaks for C 1s, N 1s and O 1s peaks are shown in Tables A5.4, A5.5 and A5.6.

N1s spectra were normalized to the peak at 401 eV, C1s spectra were normalized to the peak at 284.5 eV, and O1s spectra were normalized to the peak at 532.5 eV. After normalization, a difference-spectrum was obtained by subtracting the normalized HT-XPS spectrum from the normalized NAP-XPS spectrum.

All data was processed using KolXPD 1.8.0 (build 65) analysis software and then plotted using Origin software.

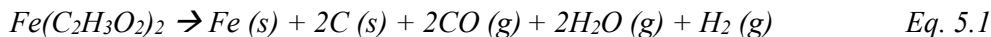
5.3 Results and Discussion

5.3.1 Quadrupole Mass Spectrometry (QMS)

Figure 5.1 shows the in-situ QMS data for N-C, FeAc-N-C, FeCl₃-N-C and FePc-N-C samples. In all cases, the detected pyrolysis products were H₂ (mass: 2 AMU), H₂O (mass: 18 AMU), CO/N₂ (mass: 28 AMU), O₂ (mass: 32 AMU) and CO₂ (mass: 44 AMU). For N-C, the sample was heated to 330 °C. At the start of the experiment (<30 °C) a signal spike containing H₂O, O₂, CO/N₂) and CO₂ species is detected, attributed to residual air in the QMS system, and is commonly detected when starting the measurements. As the temperature increases, there is an onset of detected H₂O, H₂, CO (and/or N₂) and CO gases at ~150 °C, peaking at around 300 °C. Water is likely physisorbed on the surface of the N-C foam, especially during sample preparation. The H₂ evolution peak may correspond to the removal of weakly bound terminal hydrogen from carbon atoms in the support. Hydrogen atoms are very reactive and have a lifetime of ~0.3 sec at 67 Pa, combining quickly to form hydrogen molecules,^{18,19} which are then detected at the quadrupole. Similarly, CO and CO₂ may be evolved from the decomposition of weakly bound species, e.g. COOH or C=O functional groups.

In the case of FeAc-adsorbed onto N-C, there are several major peaks in the QMS data, suggesting a multi-stage decomposition process. For reference, the decomposition temperature of FeAc is nominally 190 to 200 °C. The onset of the product gas detection is at ~150 °C, and the products detected are similar to the N-C support, suggesting that the same desorption processes occur. There is a second peak in the H₂O trace at around 400 to 480 °C accompanied by a significant increase in the amount of CO (and/or N₂), H₂, and CO₂. This peak is attributed to the thermal decomposition of FeAc. The temperature of this is higher than the nominal decomposition temperature, which

may be shifted due to adsorption on the support. The decomposition of FeAc simultaneously produces the detected gases, as well as generating graphitic carbon and metallic iron:



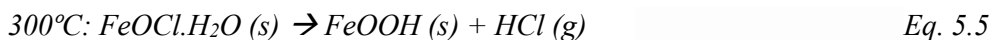
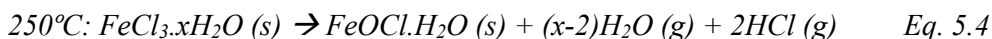
The generated CO and H₂O can further react to form H₂ and CO₂:

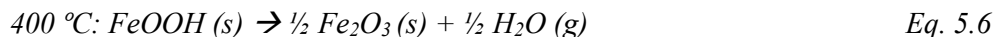


A third feature at a higher temperature of ~600 to 650 °C results in a significant increase in CO (and/or N₂) and H₂, as well as some CO₂. This corresponds well with the iron-catalyzed steam gasification of carbon to produce hydrogen and carbon monoxide,²⁰ (Eq. 5.3). The source of the H₂O may be from the decomposition of FeAc (Eq 5.1). Etching of the nitrogen-doped carbon support via gassification is expected to lead to increased porosity, as observed in the nitrogen uptake data (Chapter 4.3.1). In addition, the signal at 28 amu could be attributed to N₂, due to gasification of the nitrogen atoms in the support.



The QMS data for FeCl₃ adsorbed on the nitrogen-doped carbon foam is significantly different from that of FeAc precursor. At low temperature, the features are similar to that of N-C, and attributed to the same desorption processes. Above this temperature, there is a striking increase in the amount of H₂ gas detected. The thermal decomposition of FeCl₃, is reported to occur in three stages, according to the following scheme:²¹





At ~250 °C, the increase in H₂O corresponds well to the 1st stage of FeCl₃ decomposition. Meanwhile, it is unclear what happens to the HCl (g), which is not detected by QMS, but it may react with iron or residual sodium in the sample as follows, generating hydrogen gas:



The sharp peak detected at 420 °C contains mainly H₂, CO/N₂, H₂O and CO₂ in decreasing order of abundance. This temperature corresponds to third step decomposition of FeCl₃ to produce H₂O (Eq. 5.6). The spike in H₂ seems to be too high to attribute only to the decomposition of HCl. It should be noted that vacuum conditions are reducing (as in the case of ammonia in the ex situ pyrolysis measurement), and therefore Fe₂O₃ can be further reduced to Fe at this temperature:



The resulting O₂ would then quickly react with the carbon substrate to form the detected CO₂, then reacting with water to generate H₂ and CO (Eq. 5.3). The presence of some iron nanoparticles in the FeCl₃-N-C electrocatalysts was confirmed by TEM characterisation (Chapter 4).

A third large peak at ~620 °C, is almost entirely due to H₂ and CO. This is clearly attributed to iron-catalyzed steam gasification, consuming water from the decomposition of the hexahydrate. Just as in FeAc-N-C, this gasification is responsible for increasing the pore diameter and pore distribution of the support, in agreement with N₂ gas adsorption results (Chapter 4.3.1).

Finally, for FePc-N-C the QMS data is again completely different (Figure 5.1 d). There are three main QMS peaks as the temperature increases. The sublimation temperature of FePc is reported to be in the range 400-450 °C, and decomposition is reported to proceed at >550 °C.²²

The first decomposition peak at ~290 °C is mainly hydrogen. This is attributed to deprotonation of the iron phthalocyanine molecule. A second peak at ~450 °C contains mainly H₂O, followed by H₂, CO₂ and CO. This temperature corresponds to the sublimation point of FePc. In previous chapters it was determined that FePc does not enter the micropores of the support because the molecule is too large. Adsorbed molecules in these blocked micropores therefore can't escape until the FePc molecules stop blocking the pores. As such, the desorption peak observed for the N-C support is shifted to this higher temperature, the fingerprint being a large abundance of H₂O.

A third peak at ~570 °C generates a large abundance of hydrogen, corresponding well with the decomposition temperature of FePc.²² Decomposition of FePc reportedly forms carbon nanotubes with metallic iron at their tip or base, as confirmed in TEM images of our samples prepared ex situ (Figure 4.15).²² The byproduct of the growth of carbon nanostructures is hydrogen.²³ Meanwhile, the smaller signal at 28 AMU is attributed to gassification of nitrogen atoms in the FePc molecules during decomposition. Milev et. al. reported that higher temperatures (>800 °C) are required for complete decomposition of FePc, and it is reported that Fe-N moieties can still remain beyond this temperature.²²

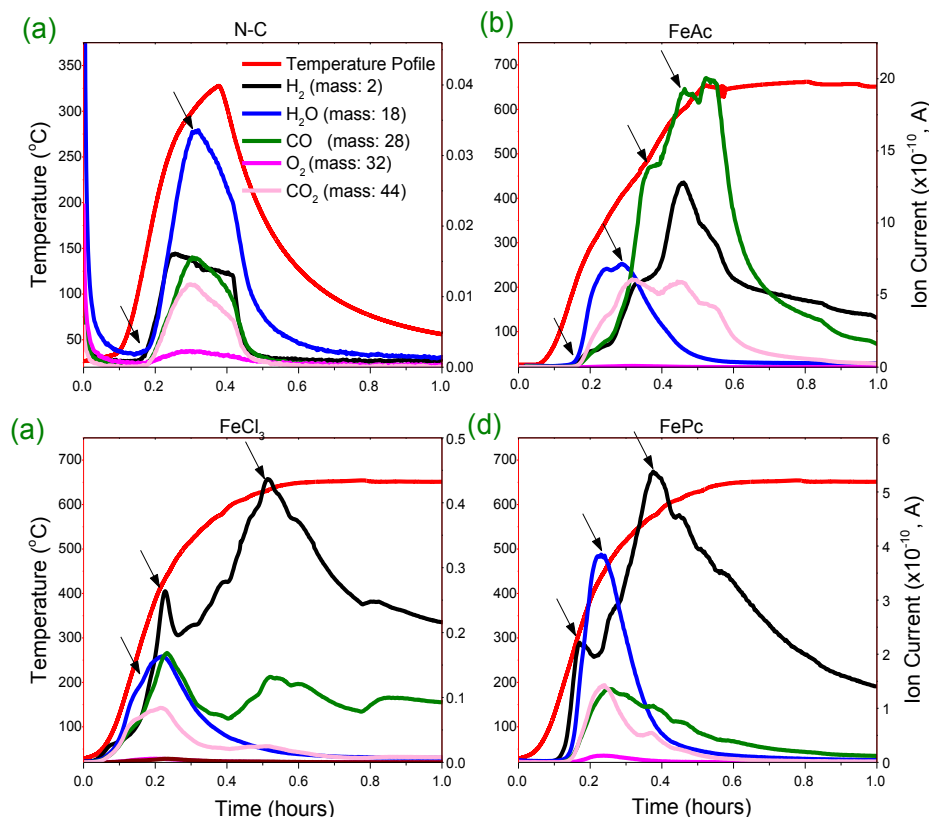


Figure 5.1: Quadrupole mass spectrometry (QMS) for: (a) N-C; and (b) FeAc-N-C; (c) FeCl₃-N-C; and (d) FePc-N-C samples.

As such, the mechanisms of the decomposition of iron precursors deposited on nitrogen-doped carbon foams were successfully elucidated using in-situ QMS. FeAc was found to decompose to metallic iron and solid carbon at above ~ 400 °C, in agreement with the high abundance of carbon-encapsulated iron nanoparticles observed in equivalent ex-situ samples (Figure 4.13). At above ~ 600 °C, iron-catalysed steam gasification of the carbon support was observed, providing an explanation for the wider of micropores and increased pore volume observed after heat treatment (Chapter 4.3.1). FeCl₃ was observed to decompose to Fe₂O₃ at above ~ 420 °C, being further reduced to metallic iron by the reducing vacuum environment, in agreement with TEM data (Figure 4.13). Iron catalysed steam gasification at higher temperature, was again linked to the

improved porosity observed in ex-situ samples. Sublimation of FePc at ~450 °C was found to release gases trapped in the micropores, confirming that the size of the FePc molecule results in blocking of the micropores rather than entering them, in agreement with nitrogen adsorption data on the ex-situ samples. At above ~650 °C, carbon nanotubes and iron were formed by the decomposition of FePc molecules, in agreement with TEM images. Steam gasification did not occur in this case, due to a lack of available water molecules, in agreement with the smaller pore volume observed in the ex situ samples. These results are in agreement with the characterisation used in previous chapters, and help to further explain the ORR activity of the Fe-N-C electrocatalysts derived from different iron-containing precursors.

5.3.2 In-situ High Temperature X-ray Photoelectron Spectroscopy (HT-XPS)

Figure 5.2 shows high-resolution C 1s, N 1s and O 1s spectra for the nitrogen-doped carbon support (N-C) at room temperature; FeAc adsorbed onto the nitrogen-doped carbon support (FeAc-N-C) at room temperature; and the same sample after heating to 650 °C in the XPS chamber (FeAc-N-C (650 °C)). For the N-C support, the N1s spectrum is deconvoluted into pyridinic (32.3 at%); pyrrolic and/or Fe-N (10.4 at%); graphitic (39.6 at%); hydrogenated-pyridinic-N (9.9 at%); and pyridine-N-oxide (7.7 %) contributions. These values provide a baseline for the changes observed after iron precursor adsorption and heating. In the N-C sample there is negligible iron content, and therefore the pyrrolic / Fe-N deconvolution is primarily assigned to pyrrolic bonding in the N-C support.

After FeAc adsorption, there is *little observable change in the C1s spectra*. This is because there is a high abundance of carbon in the N-C support, which masks the changes due to the carbon

atoms in the adsorbed FeAc. More significant changes are observed in the N 1s spectra. In particular, after FeAc adsorption there is a notable increase in the relative abundance of pyrrolic-N/Fe-N, from 10.4 to 24.1 %. Importantly, this suggests that the simple *adsorption of iron acetate onto the support can spontaneously result in the formation Fe-N_x bonds* with nitrogen-atoms at the carbon surface (see the schematic diagram, Figure 5.3).²⁴ Minimal changes are observed in the O1s peak after FeAc adsorption.

At 650°C, there is still little change in the C1s spectrum, for the reasons outlined above. Meanwhile, *the relative abundance of Fe-N_x decreases at high temperature*, from 24.1 to 12.7 %. This may be due to the breaking of Fe-N_x bonds as the FeAc decomposes to form iron nanoparticles and carbon, in agreement with the QMS results, and summarised schematically in Figure 5.3. *However, it is important to note that some Fe-N_x bonds remain, as possible ORR active site candidates.* At 650 °C there is also a significant change in the O 1s spectrum, with a significant decrease in the relative abundance of C-OH/C-O-C species, corresponding with the decomposition of the FeAc molecule to form carbon (C-C bonds) accompanied by the loss of oxygen via the production of H₂O, CO₂ and CO. Meanwhile, the complete removal of the Na KLL peak at high temperature confirms that this heat-treatment step helps to remove residual the sodium impurities.

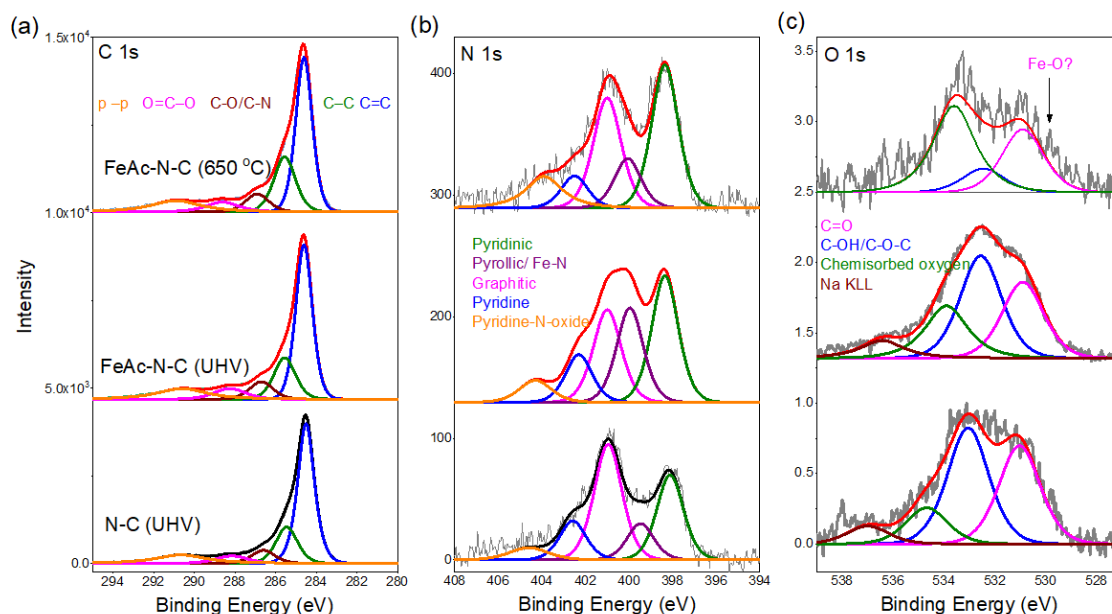


Figure 5.2: XPS spectra of the N-C support (ambient temperature); FeAc-N-C adsorbed onto N-C (room temperature); and HT-XPS spectra of FeAc-N-C recorded at 650 °C: (a) C 1s; (b) N 1s; and (c) O 1s.

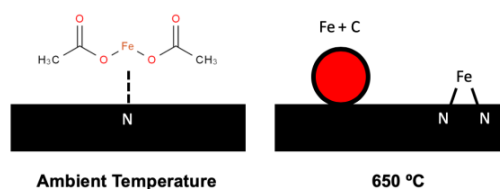


Figure 5.3: Schematic showing how the FeAc precursor interacts with the carbon surface at ambient temperature and at 650 °C during active site formation.

Results for the FeCl₃-adsorbed sample are shown in Figure 5.4. Again, there is little change in the C1s spectra after FeCl₃ adsorption for the reasons outlined above. For the N1s, similar behaviour to FeAc was observed, with a substantial increase in the abundance of pyrrolic/Fe-N bond from 10.4 to 29.8 %. This corresponds to the formation of Fe-N bonds between the precursor and the

support, as shown schematically in Figure 5.5. For the O 1s spectra, the only significant change is the new peak at ~538 eV, assigned to adsorbed water molecules,²⁵ probably arising due to the hexahydrate nature of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.

At 650 °C, the C1s again does not significantly change. The abundance of Fe-N_x bonds in the N1s spectrum decreases from 29.8 to 15.6 %, similar to the case of FeAc. This is attributed to decomposition of FeCl_3 to form Fe_2O_3 (followed by reduction to metallic iron in the reducing vacuum environment), breaking the Fe-N coordination. **However, it is important to note that some Fe-N_x bonds remain, as possible ORR active site candidates.** There is no notable change in the O 1s spectrum.

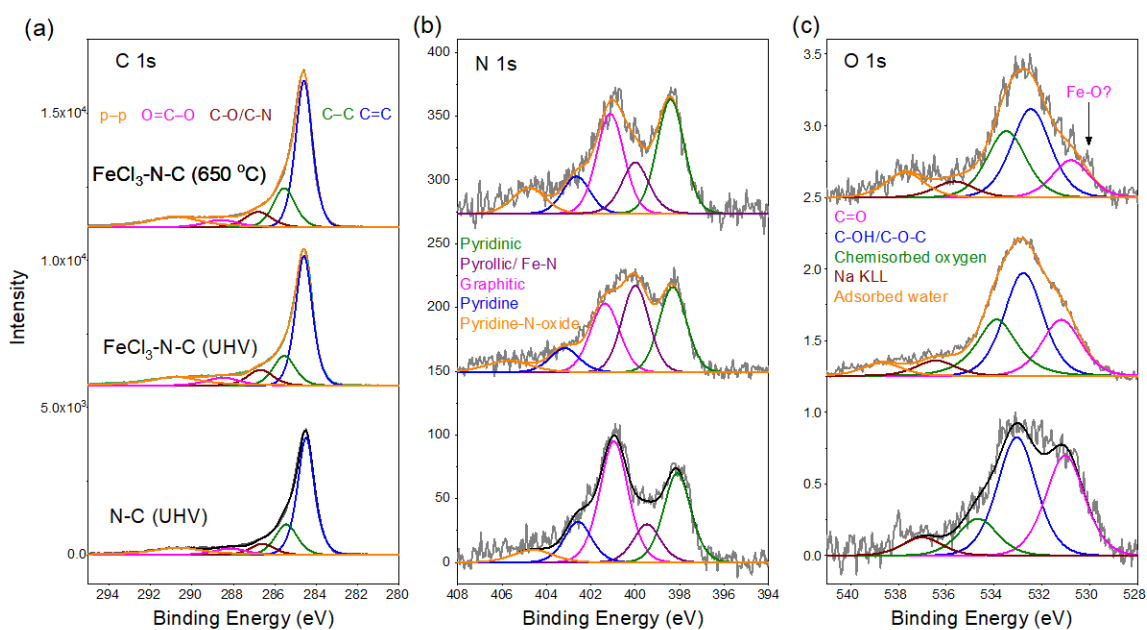


Figure 5.4: XPS spectra of the N-C support (ambient temperature); FeCl_3 -N-C after adsorbing onto N-C (room temperature); and HT-XPS spectra of FeCl_3 -N-C recorded at 650 °C. (a) C 1s; (b) N 1s; and (c) O 1s.

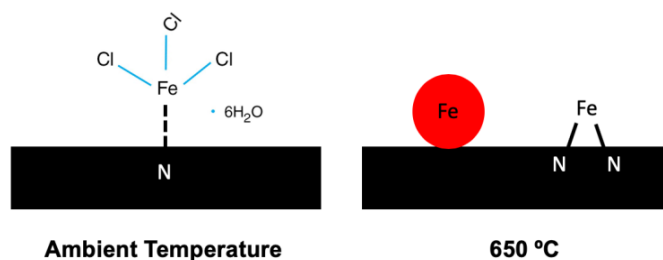


Figure 5.5: Schematic showing how the FeCl₃ precursor interacts with the carbon surface at ambient temperature and at 650 °C during active site formation.

For FePc adsorbed onto N-C (Figure 5.6), the results are rather different. Again, there is very little change in the C1s peak after adsorption for the reasons outlined above. In this case, there is also minimal change in the N1s or O1s spectra after adsorption. This suggests that in contrast to the cases of FeAc and FeCl₃, **FePc molecules do not form bonds with the nitrogen atoms in the carbon support**. This is in agreement with the fact that FePc molecules are too large to enter the micropores of the support. There is a slight increase in the proportion of Fe-N bonds, attributed to the FePc molecule itself, rather than interaction between the FePc and nitrogen in the support. **At high temperature, there are still no significant changes in either the C1s, N1s or O1s spectra.** This suggests that the decomposition products of FePc do not significantly change in terms of their chemical structure (i.e. retaining the central Fe-N₄ moiety) and they have little interaction with the nitrogen in the surface. This is summarised schematically in Figure 5.7.

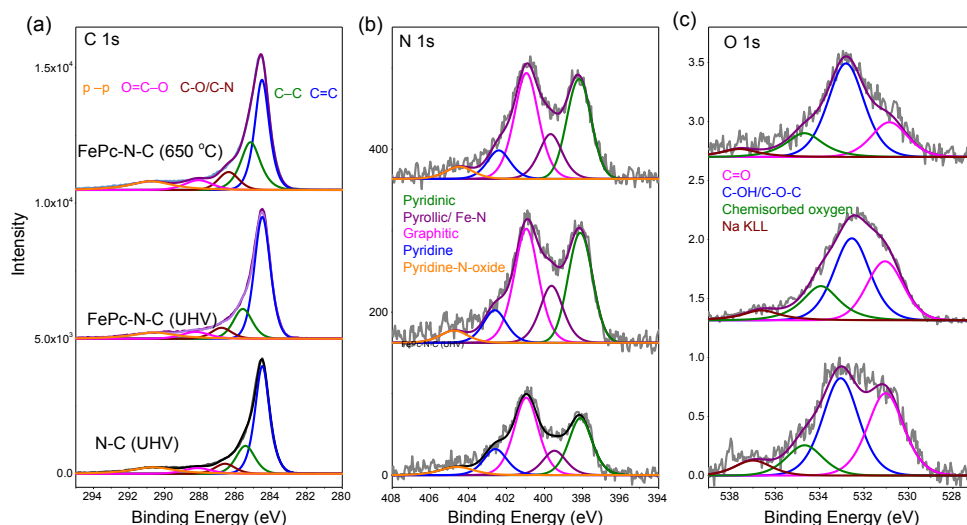


Figure 5.6: XPS spectra of the N-C support (ambient temperature); FePc-N-C after adsorbing onto N-C (room temperature); and HT-XPS spectra of FePc-N-C recorded at 650 °C. (a) C 1s; (b) N 1s; and (c) O 1s.

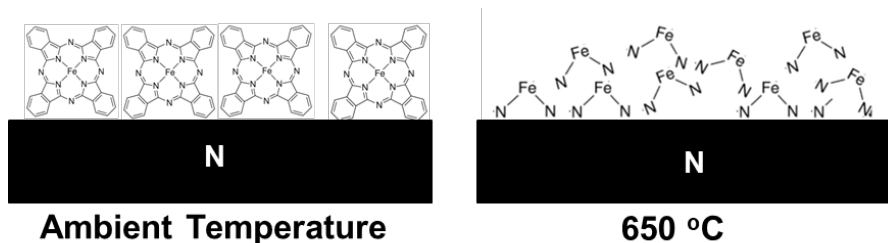


Figure 5.7: Schematic showing how the FePc precursor interacts with the carbon surface at ambient temperature and at 650 °C during active site formation.

Overall, these HT-XPS results provided new fundamental insights into changes that occur in Fe-N-C catalyst precursor materials during pyrolysis. The direct formation of bonds between the precursor molecule and nitrogen in the support was observed for both FeAc and FeCl₃, and this may help in the formation of ORR active Fe-N₄ sites since these are the most ORR active samples.

Meanwhile, no interaction with the support was observed for FePc, reflecting its poor ORR activity. After heat-treatment, the quantity of the Fe-N_x decreased due to the formation iron nanoparticles, but clearly these Fe-N₄ sites remain in sufficient quantities to promote efficient ORR activity. These results will help pave way for new strategies to improve the synthesis procedure in such a way that optimizes porosity of the support, whilst maintaining a large proportion of Fe-N sites, in order to synthesise high performance ORR catalysts.

5.3.3 Near Ambient Pressure X-ray Photoelectron Spectroscopy (NAP-XPS)

Figure 5.8 shows C1s spectra (a) at UHV, and then (b) at NAP in humidified oxygen gas. It is difficult to observe subtle differences from these plots, and therefore the NAP data was normalised to the UHV data (c). According to the relative abundance of species calculated by deconvolution of the C1s spectra (Table A5.4), there is no clear change (e.g. an increase in oxygen-containing species such as C-OH or C=O) after exposure to humidified oxygen, for any of the measured samples. The NAP normalized spectra confirm this, as no features are observed at e.g. ~286.6 or ~288.2 eV, corresponding to C-OH or C=O. This suggests that there is *minimal interaction between oxygen or water and the carbon atoms in the catalyst materials under these conditions*, or alternatively that the resolution of this technique is not high enough to observe the changes that are taking place. The features observed at ~284.5 eV in all samples seems to be artefact of the normalization procedure.

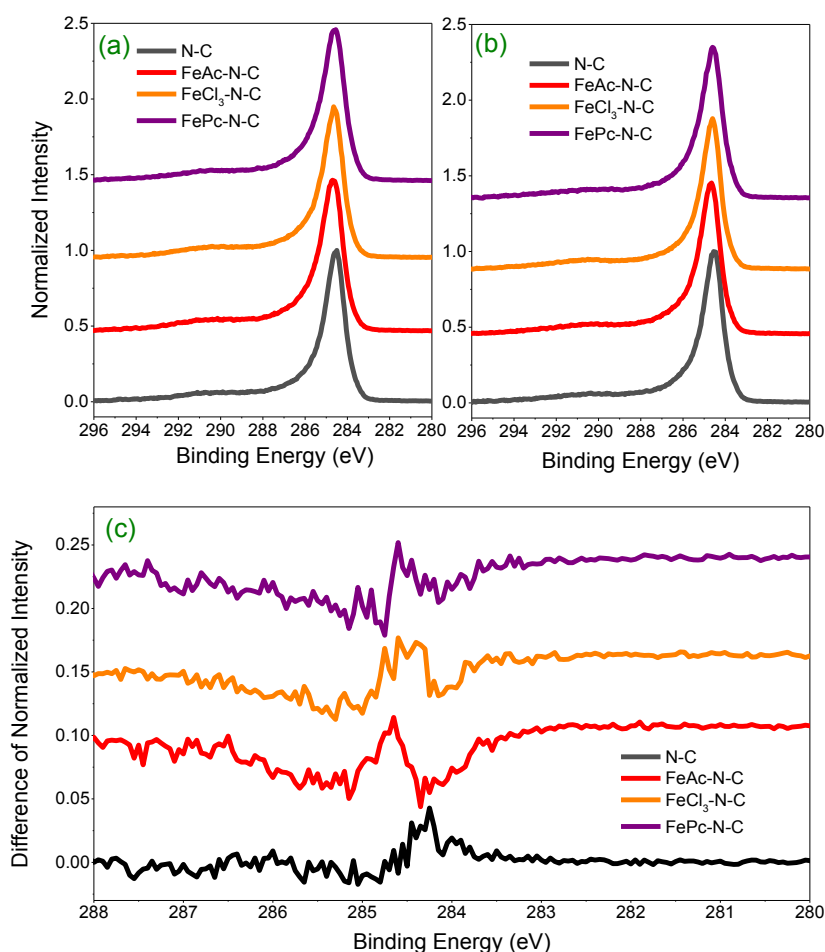


Figure 5.8: C1s spectra: (a) under UHV conditions; (b) after exposure to humidified O₂; and (c) the NAP data normalized to the UHV data.

Figure 5.9 shows the corresponding N1s spectra taken at UHV and at NAP in humidified oxygen gas. Again, according to the relative abundance of species calculated by deconvolution of the N1s spectra (Table A5.5), there is no clear change (e.g. an increase in oxygen-containing species such as N=O) after exposure to humidified oxygen, for any of the measured samples. This is also

supported by the normalised NAP data, where no clear features are observed indicating oxygen binding to the surface. This suggests that there is *minimal interaction between oxygen or water and the nitrogen atoms in the catalyst materials under these conditions*, or alternatively that the resolution of this technique is not high enough to observe the changes that are taking place.

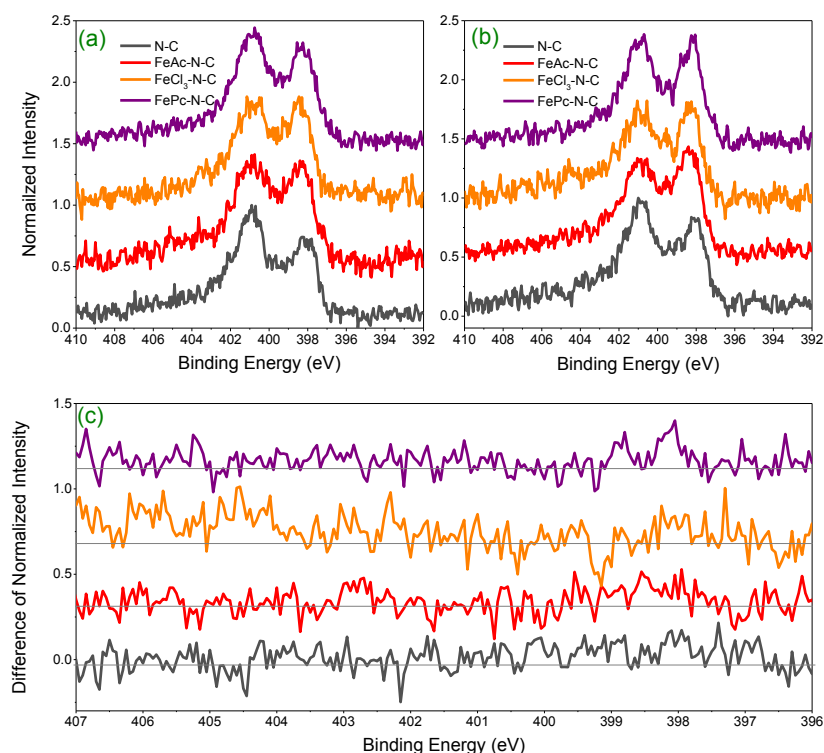


Figure 5.9: N1s spectra: (a) under UHV conditions; (b) after exposure to humidified O₂; and (c) the NAP data normalized to the UHV data.

Figure 5.10 and 5.11 show the corresponding O1s spectra taken in UHV and NAP conditions. As expected, in this case there is a significant difference, since water and oxygen are both physically present in the NAP chamber during the measurement, contributing to the O1s signal. After flooding the chamber with humidified oxygen, a large doublet peak appears at 539 and 540 eV in all cases (Figure 5.10), which is assigned to gaseous O₂ present in the NAP chamber.^{10,26,27,28} In

addition, a new peak emerges at 535.5 eV for all samples, attributed to a multilayer film of physisorbed water on the surface of the electrocatalysts.^{10,29} To confirm these assignments, the partial pressures of oxygen and water were varied (for the case of FeAc only). As expected, increasing the partial pressure of H₂O resulted in an increase in the peak intensity at 535.5 eV. Meanwhile, decreasing the partial pressure of oxygen gas decreased the peak intensity at 539 and 540 eV.

The changes in relative abundance of surface species after humidified oxygen exposure (i.e. not including gaseous oxygen or adsorbed water) are much clearer in the case of the O1s peak compared to the C1s or N1s peaks (Table 4). In all samples there is a significant increase in the relative abundance of the binding energy associated with adsorbed water, as expected due to the exposure to humidified atmosphere.

In the normalised NAP plot (Figure 10c) the only clear feature that appears is a small peak at ~532 eV, and this is only observed for the case of FeCl₃-N-C. This is assigned to C-O, and may indicate a slight increase in adsorption of oxygen species in this, the most active ORR electrocatalyst studies in this work. However, the signal is not strong enough to draw concrete conclusions.

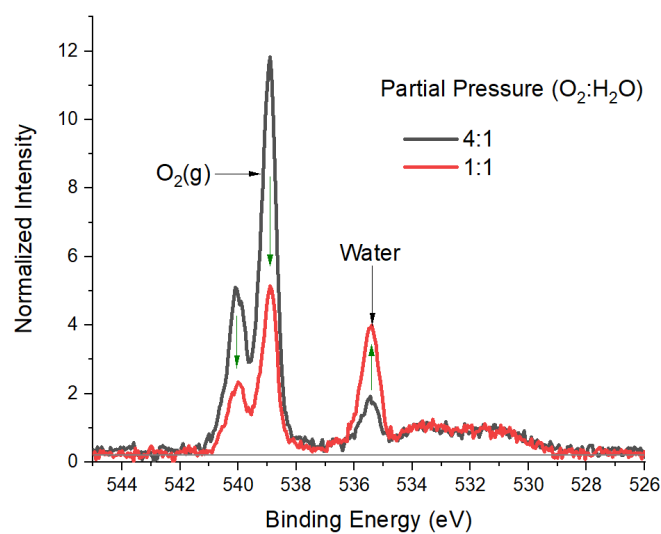


Figure 5.10: NAP-XPS spectra for FeAc-N-C measured at two partial pressure ratios of $O_2: H_2O$.

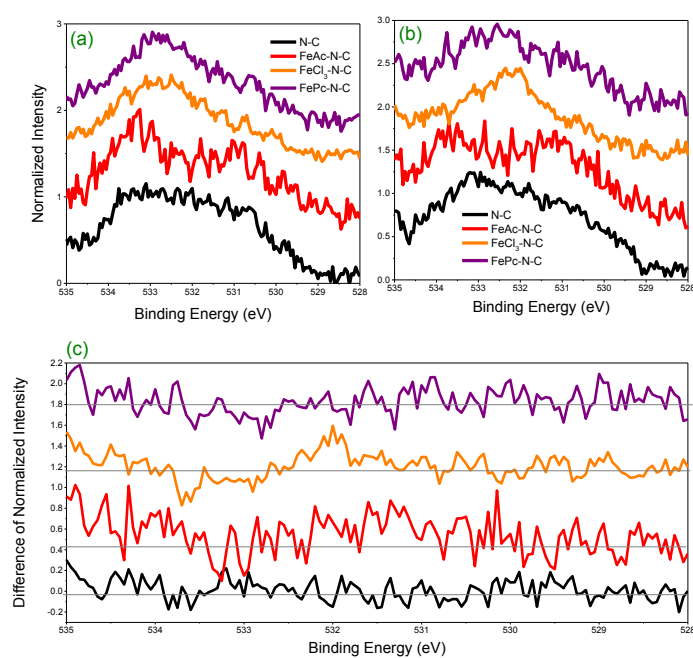


Figure 5.11: $O1s$ spectra: (a) under UHV conditions; (b) after exposure to humidified O_2 ; and (c) the NAP data normalized to the UHV data.

Overall, all three catalysts showed minimal interaction between oxygen or water and the carbon or nitrogen atoms in the catalyst materials, according to the normalised NAP-XPS spectra. Meanwhile, gaseous oxygen and multilayer film of physisorbed water peaks were detected in the O1s signal during exposure to humidified oxygen gas. However, the normalised NAP-XPS spectra did not clearly show any differences, apart from a questionable peak at 532 eV in the FeCl₃-N-C sample, assigned to C-O. It is therefore difficult to link these results directly to ORR-initiating oxygen adsorption steps. Despite the inconclusive nature of these null results, they do support the assertion that oxygen species are adsorbed directly on the Fe atoms, rather than the C or N atoms. Therefore, a study of the Fe 2p region may yield more conclusive results. However, due to the very low abundance of iron in these samples, this is not yet feasible.

5.4 Summary and Conclusions

In summary, in situ techniques are important in monitoring real-time changes during catalyst synthesis, and investigating the surface characteristics under operation conditions, to be able to link structural properties to performance. QMS was highly successful in determining the mechanisms of the decomposition of different iron precursors during synthesis, giving new insights into the formation of ORR active sites. It provides explanations for the observed presence of iron nanoparticles in all samples, and the increase in pore diameter and pore volume due to iron catalysed gasification of the carbon support in the cases of FeAc and FeCl₃. HT-XPS was useful for investigating changes in the chemical state of the iron precursors adsorbed on the nitrogen-doped carbon foam, and was used to confirm that Fe-N bonds decrease in abundance, but are retained in significant amounts during pyrolysis. NAP-XPS was supposed to be useful for investigating the adsorption of oxygen on the surface of electrocatalysts under fuel cell type

operating conditions (i.e. under humidified oxygen atmosphere). However, no new bonds were detected between carbon or nitrogen and the gaseous oxygen or water. As such, it is inferred that O₂ and/or H₂O mainly bind to Fe atoms in the electrocatalysts, in agreement with the expected ORR mechanisms at Fe-N₄ active centres. However, it may simply be that the resolution of this technique is not sufficient to detect the changes in the samples, or that larger changes are observed in electrochemical environment. As such, we plan to perform the more specialised technique of in situ electrochemical XPS in the near future.

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Chapter 6 In-situ Electrochemical X-ray Absorption Spectroscopy of Fe-N-C Electrocatalysts Synthesized using Different Iron Precursors

6.1 Introduction

In the previous chapters, the behavior of FeAc-, FeCl₃- and FePc-adsorbed on nitrogen-doped carbon foam was investigated using X-ray photoelectron spectroscopy (XPS). However, because the samples have relatively low Fe concentration (i.e. < 1 wt%), the resolution was too low to identify different Fe 2p bonding configurations using XPS. Therefore, changes in the iron precursor during pyrolysis or upon adsorption of oxygen species could only be inferred from the N 1s and O 1s narrow scan regions. In this Chapter, high energy X-rays generated by a synchrotron are used to perform X-ray absorption spectroscopy (XAS), which is capable of probing the bonding configurations of iron atoms at much lower concentrations than XPS. Specifically, the bonding states of Fe are investigated in the different Fe-N-C electrocatalysts in situ, during the oxygen reduction reaction (ORR), by varying the potential in N₂- and O₂-saturated acid electrolyte. These electrochemical XAS experiments give us insights into the electrochemical changes in the local structure of iron-based active sites under simulated PEFC operating conditions.

X-ray absorption spectroscopy (XAS) is a technique for investigating the local geometric and electronic structure of elements in a sample by measuring the X-ray absorption coefficient, $\mu(E)$ as a function of X-ray energy, E . Crystallinity is not a requirement, which makes it possible to probe more defective materials. This makes the technique highly suited to characterization of Fe-N-C electrocatalysts. XAS spectra can be obtained in transmission mode (for samples with

relatively high iron content) or fluorescence mode (for low concentration samples, e.g. ≤ 1 wt% Fe).

Generally, XAS spectra are separated into three regions, shown in Figure 6.1: (i) the edge region, comprising the pre-edge and rising edge; (ii) the X-ray absorption near-edge structure (XANES) region which is dominated by photoelectrons with kinetic energy of ~ 40 eV from the edge; and (iii) the extended X-ray absorption fine structure (EXAFS) region for high kinetic energy photons (~ 40 -1000 eV from the edge).¹ XANES and EXAFS are collectively classed as “X-ray absorption fine structure” (XAFS) when discussing oscillatory features above the edge. XANES is used to retrieve information on the oxidation state, the electronic structure and the local symmetry of an element (in this case Fe), whilst EXAFS is used to obtain information on the local environment (neighboring atoms, coordination numbers and bond distances).

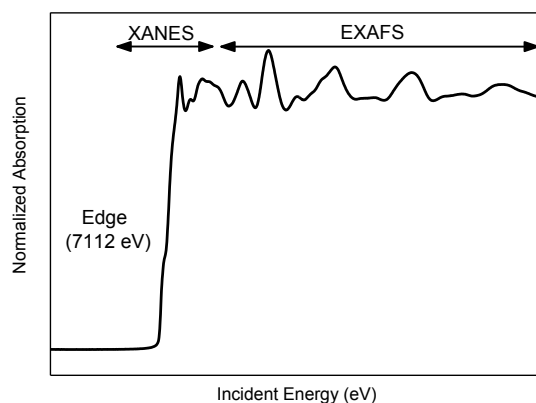


Figure 6.1: Schematic showing the XAS spectrum regions.

Since electrochemistry occurs on electrode surfaces, XAFS can provide information about the interaction between the active sites and adsorbates, which is difficult to otherwise obtain. Changes

in the oxidation states can be deduced from XANES, whilst changes in coordination numbers and interatomic bond distances can be deduced by analyzing from Fourier transform EXAFS (FT-EXAFS). Moreover, $\Delta\mu$ -XANES is a spectral subtraction method which can be used to obtain data normalized to either the potential or saturated gas species.²

Several groups have used in-situ electrochemical XAFS to investigate Fe-N-C electrocatalysts. For example, the technique was pioneered by Tylus et. al., who found that a dual-site comprising Fe^{2+} -N₄ and Fe/Fe_xO_y nanoparticles acted as primary and secondary active centers played for ORR in acid. Strickland et al. used the technique on specially prepared catalysts without Fe-N coordination, concluding that the nitrogen-doped carbon lattice was may be responsible for ORR activity in Fe-N-C electrocatalysts.³ In 2017, Zitolo et al. used electrochemical XAFS to study MOF-derived Fe-N-C electrocatalysts reportedly free of crystalline iron species, attributing the activity of Fe-N-C electrocatalysts to atomically-dispersed Fe-N_{2/4} moieties, but that the activity was also reliant on the properties of the support.⁴ A comprehensive cross-laboratory study used the technique to probe many different Fe-N-C materials fabricated using different protocols and precursors,⁵ concluding that the active site in most Fe-N-C materials is a non-planar Fe-N₄ motif embedded in the carbon matrix, irrespective of the synthesis method. Here, we apply electrochemical XAFS to our unique Fe-N-C electrocatalysts in order to probe the effect of changing the Fe precursor on the ORR mechanism.

6.2 Experimental

All XAFS measurements were performed at the Kyushu Synchrotron Light Research Center (SAGA Light Source, Japan). Working electrodes were prepared using FeAc-N-C(900-NH₃-Aw); FeCl₃-N-C(900-NH₃-Aw); and FePc-N-C(900-NH₃-Aw) electrocatalysts known herein as FeAc-N-C, FeCl₃-N-C, and FePc-N-C respectively, for clarity. Catalyst inks were prepared by mixing 5.23 mg catalyst powder in a solution of ethanol, 5 % Nafion ionomer and H₂O (with a ratio of 3:3:1). The working electrode was prepared by depositing 40 μ l of the ink onto graphite foil (100 μ m thickness) by micropipette, resulting in a loading of ~ 2 mg/cm². The ink was dried at 60 $^{\circ}$ C before the working electrode was inserted into the X-ray transparent electrochemical cell, shown in Figure 6.2. More details about the specialised cell are given in Chapter 2.5.3.

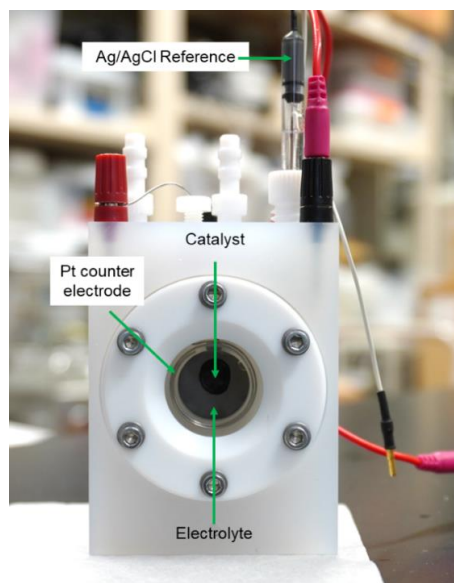


Figure 6.2: X-ray transparent PECC2 cell used in the in-situ electrochemical XAS experiments. The catalyst is deposited on a graphite foil working electrode. The counter electrode is a platinum wire, and the reference electrode is Ag/AgCl. The electrolyte is 0.1 M HClO₄.

Spectra at the Fe K-edge (7112 eV) were recorded in fluorescence mode using a silicon drift detector (SDD). The electrolyte was 0.1 M HClO₄ and N₂- or O₂-saturation was achieved by bubbling the respective gases at 5 ml min⁻¹. Chronoamperometry was used to control the voltage at the working electrode. Measurements were performed at potentials of 0.8 V_{RHE} (corresponding to the ORR onset region), and 0.2 V_{RHE} (corresponding to the mass transfer limited region). In the onset region, oxygen species are expected to be adsorbed onto the active site as e.g. O₂(g), and O*, representing the first steps of the ORR. Meanwhile, in the mass transport limited region the ORR occurs fully and efficiently, so adsorbates are rapidly converted to e.g. OH* and H₂O as the final steps of the ORR (Figure 6.3).⁶

Before measurements, the working electrodes were activated by applying potentials first in anodic direction (0.2 to 0.8 V_{RHE}, at steps of 0.2 V_{RHE}) and then in the cathodic direction at the same rate. Changes in the oxidation state and the nature of surface adsorbates were highlighted using two different “Δμ-XANES” normalization techniques. Potential-normalized Δμ-XANES were obtained by subtracting the XANES spectra recorded at 0.2 V_{RHE} from the spectra obtained at 0.8 V_{RHE}. This highlights any changes in the adsorbed species with different gases dissolved in the electrolyte (i.e. N₂ or O₂). Meanwhile, nitrogen-normalized Δμ-XANES was obtained by subtracting the XANES spectra recorded in N₂-saturated electrolyte from the XANES spectra recorded in O₂-saturated electrolyte. This highlights changes in the adsorbed species at different potentials.

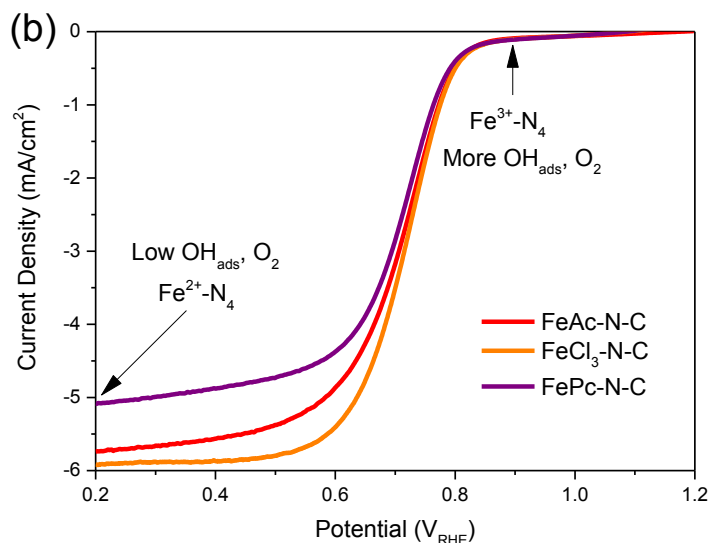


Figure 6.3: LSVs of FeAc-N-C, FeCl₃-N-C and FePc-N-C electrocatalysts, recorded using rotating ring disk electrode voltammetry in 0.1 M HClO₄. In situ electrochemical XAFS measurements are performed at 0.2 and 0.8 V_{RHE}. The expected adsorbed species at these potentials are marked on the graph.

6.3 Results and Discussion

For FeAc-N-C (Figure 6.4) there is surprisingly little difference between the XANES spectra (or 1st derivative spectra) in N₂- or O₂-saturated electrolytes. There is a much larger change in the spectra measured at different potentials, with a shift in the Fe-edge corresponding to desorption of oxygen species at 0.8 V_{RHE}.⁴ The potential-normalized $\Delta\mu$ -XANES plots (black lines) display a prominent feature at ~7125 eV, which reportedly reflects charge transfer to or from the Fe metal center to adsorbed oxygen species.^{7,8} The intensity of this feature decreases from -0.03 in N₂-saturated electrolyte, to -0.13 in O₂-saturated electrolyte. In the nitrogen-normalized $\Delta\mu$ -XANES plots (red lines) this feature is flat at 0.2 V_{RHE}, and increases to a value of +0.03 at 0.8 V_{RHE}. The

$\Delta\mu$ -XANES data thus are more dependent on changes in the potential than on the presence of O_2 in the electrolyte.^{9,8,10,11,12}

In the FT-EXAFS the largest signal at 2.0 Å is attributed to Fe-Fe bonds, indicating presence of a high proportion of carbon-encapsulated iron nanoparticles, as discussed in Chapter 4. Another peak at ~1.5 Å is attributed to Fe-N/O coordination. Fe-N and Fe-O are almost indistinguishable using this technique, but a small shift between Fe-N (1.6 Å) and Fe-O (1.5 Å) can sometimes be observed.^{13,7} There is a slight increase in the Fe-N/O peak in the presence of O_2 -saturated electrolyte compared to N_2 -saturated electrolyte, indicating some adsorption of oxygen on Fe sites in the catalyst. Between 0.8 and 0.2 V_{RHE} , this peak significantly decreases, which may indicate desorption of the oxygenated species in the mass transfer limited region, as expected.

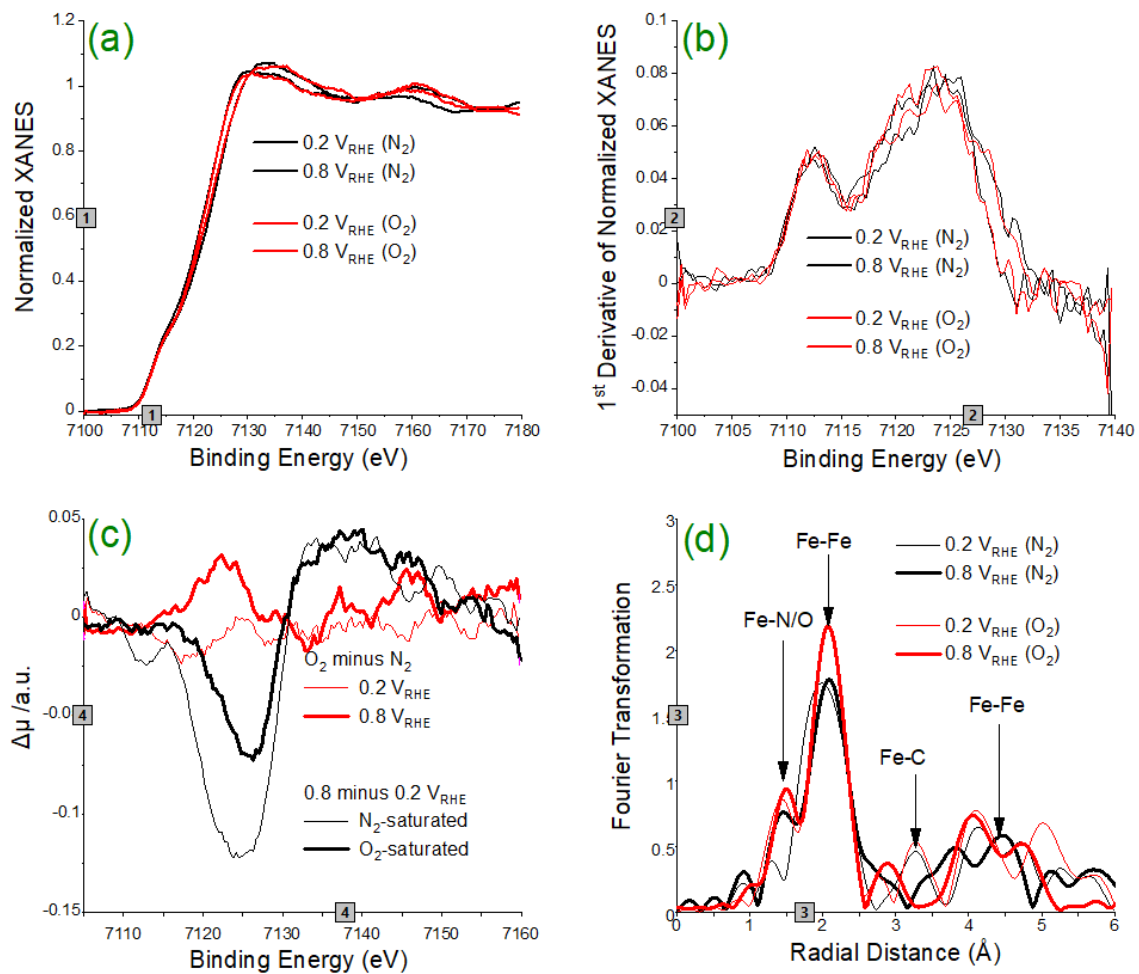


Figure 6.4: In-situ electrochemical XAS spectra of FeAc-N-C recorded in N_2 - and O_2 -saturated electrolyte at 0.2 and 0.8 V_{RHE} : (a) XANES; (b) 1st derivative XANES; (c) $\Delta\mu$ -XANES; and (d) FT-EXAFS.

For FeCl₃-N-C (Figure 6.5) the Fe-edge also shifts to lower binding energy as the potential changes from the onset region to the mass transport limited region in both N₂ and O₂-saturated electrolytes. Again, this indicates a change in oxidation state from Fe³⁺ to Fe²⁺, and is attributed to the desorption of oxygenated species. However, in contrast to the case of FeAc-N-C, there is a much greater difference between the XANES spectra in N₂- or O₂-saturated electrolytes. There is a notable increase in leading edge intensity for the XANES spectra recorded at 0.2 V_{RHE} in O₂-saturated electrolyte indicating changes in the structure of the active centres due to desorption of oxygen species.¹⁴

In the potential-normalized $\Delta\mu$ -XANES spectra (black lines), the feature at ~7126 eV increases in magnitude from -0.12 in N₂-saturated electrolyte to -0.28 in O₂-saturated electrolyte, ***showing the opposite trend to FeAc-N-C***. Understanding this difference may be the key to understanding the high ORR activity of this FeCl₃-N-C electrocatalysts. This change in the $\Delta\mu$ -XANES spectra is likely due to a stronger interaction between dissolved O₂ species and the Fe-N based active sites compared to the case of FeAc-N-C electrocatalysts, or a higher density of active sites making these changes more visible against the background. Correspondingly, the N₂-normalised $\Delta\mu$ -XANES graph has a prominent positive peak at the same binding energy, and the magnitude changes from -0.08 at 0.8 V_{RHE} to +0.1 at 0.2 V_{RHE}, corresponding to desorption of adsorbed oxygen species in the mass transfer limited region. This data shows that in the case FeCl₃-N-C there is a stronger interaction between the catalyst and O₂ in the electrolyte compared to FeAc-N-C.

In the FT-EXAFS spectra, the largest signal is again assigned to Fe-Fe, indicating the presence some iron nanoparticles after synthesis. The peak assigned to Fe-O/N at ~1.6 Å is larger here than in the case of FeAc, as discussed in Chapter 4. The intensity of this peak increases significantly in O₂-saturated electrolyte compared to N₂-saturated electrolyte, reflecting an increase in the amount

of adsorbed oxygen species (i.e. Fe-O bonds). In addition, the intensity of this Fe-N/O peak is larger at 0.8 V_{RHE} compared to 0.2 V_{RHE} , again reflecting a higher proportion of adsorbed oxygen species in the onset region, and desorption of oxygen species in the mass transfer region, as expected of an ORR active catalyst.

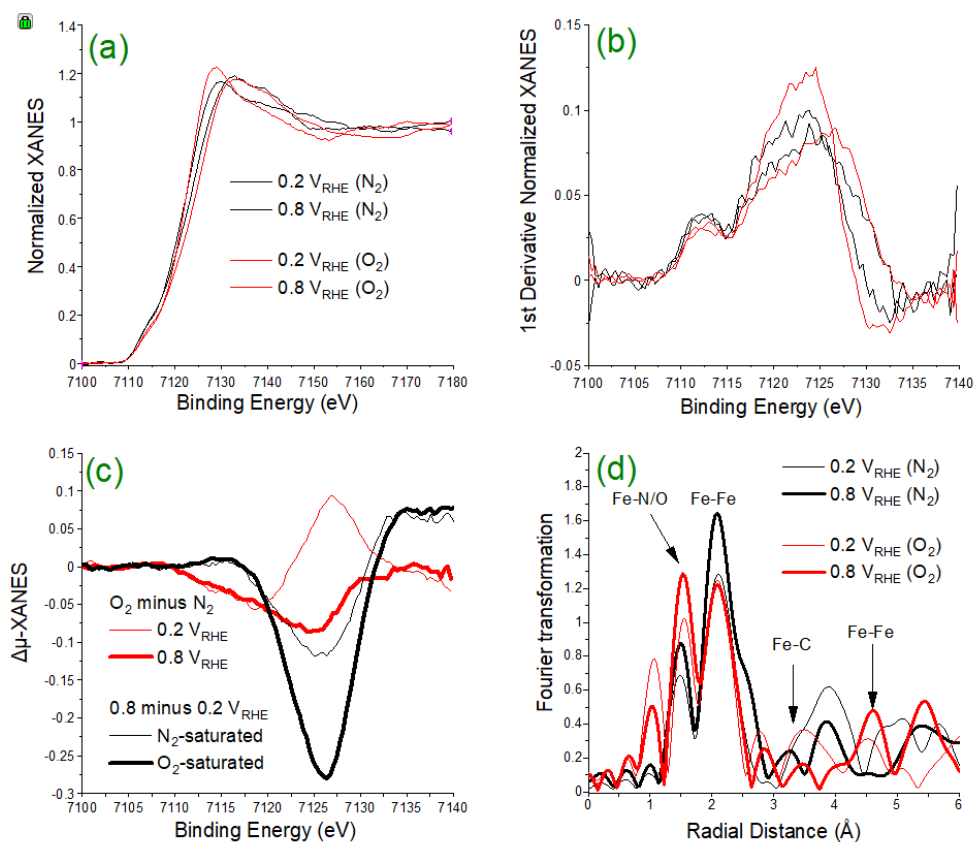


Figure 6.5: In-situ electrochemical XAS spectra of FeCl₃-N-C recorded in N₂- and O₂-saturated electrolyte at 0.2 and 0.8 V_{RHE} : (a) XANES; (b) 1st derivative XANES; (c) $\Delta\mu$ -XANES; and (d) FT-EXAFS.

Finally, for FePc-N-C (Figure 6.6), there is almost no change in the XANES spectra or the 1st derivative plots compared to the previous cases. For the potential-normalised $\Delta\mu$ -XANES data, the magnitude of the peak at 7125 eV increases from ~ 0.02 in N₂-saturated electrolyte to -0.11 in O₂-saturated electrolyte, indicating an increase in the abundance of adsorbed oxygen species. Similarly, in the nitrogen-normalized $\Delta\mu$ -XANES spectra, there is a peak with a magnitude of ~ 0.08 in the onset region at $0.8 V_{\text{RHE}}$, indicating the presence of adsorbed oxygen species, but this peak disappears in the mass transport region at $0.2 V_{\text{RHE}}$, indicating desorption of adsorbed species.

In the FT-EXAFS data, the Fe-Fe peak is proportionally lower than the other samples, as discussed in Chapter 4. In this case, there is only a very minor increase in the Fe-N/O peak with the change from N₂- to O₂-saturated electrolyte. In contrast, the peak intensity significantly decreases between the onset region at 0.8 , and the mass transport region at $0.2 V_{\text{RHE}}$, due to desorption of oxygen species.

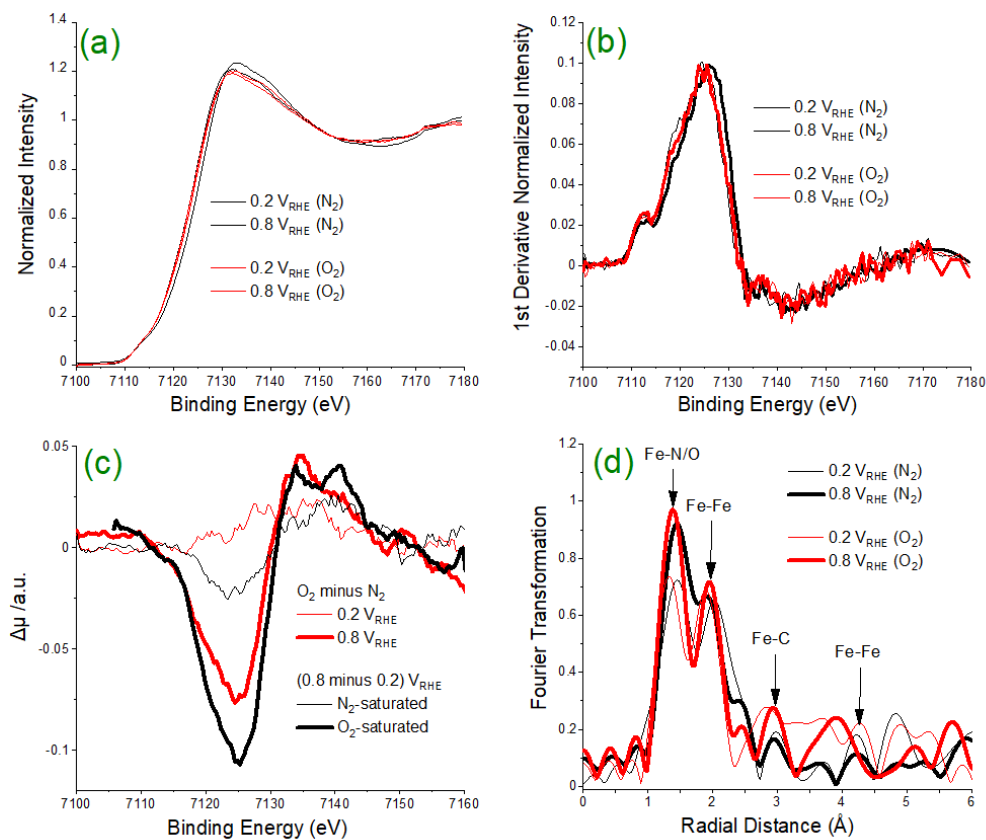


Figure 6.6: In-situ electrochemical XAS spectra of FePc-N-C recorded in N₂- and O₂-saturated electrolyte at 0.2 and 0.8 V_{RHE}: (a) XANES; (b) 1st derivative XANES; (c) $\Delta\mu$ -XANES; and (d) FT-EXAFS.

Overall, FeAc-N-C was found to undergo the smallest changes in electrochemical XAS, which indicates weak interaction between O₂ and the surface. This may be due to a lower density of active sites in this sample, due to the formation of a large proportion of iron nanoparticles, and corresponds well with the lower ORR activity measured for this sample. Meanwhile, very clear changes in the electrochemical XAS spectra were observed for FeCl₃-N-C when using N₂ or O₂ electrolyte, and when changing the potential. These changes indicated a strong interaction between O₂ and the catalyst surface, attributed to an increase in the abundance of active sites.^{8,9,10,11,12}

This data is in agreement with the fact that this catalyst had the highest recorded ORR activity. Finally, for FePc-N-C the electrochemical XAS data reveals little change between N₂- and O₂-saturated electrolytes, but significant changes when varying the potential. This unusual behavior is attributed to a high proportion of inaccessible clustered Fe-N sites outside the micropores of this catalyst, and agrees well with the fact that this catalyst had the lowest ORR activity of the samples studied here.

6.4 Summary and Conclusions

In summary, in-situ electrochemical XAS was performed on Fe-N-C electrocatalysts synthesized using different Fe precursors adsorbed on nitrogen-doped carbon foam. Measurements were performed at 0.8 V_{RHE} in the ORR onset region and 0.2 V_{RHE} in the mass transport limited region, in both N₂- and O₂-saturated electrolyte. The presence of Fe-N₄ moieties was confirmed in all three samples, with FePc-N-C having the highest abundance, followed by FeCl₃-N-C and then FeAc-N-C. All three electrocatalysts showed a potential-dependent shift in the Fe-K-edge of the XANES spectra, associated with ORR-initiating Fe²⁺/Fe³⁺ redox transitions (i.e. the adsorption of OH_{ads} and O_{ads} species at Fe-N₄ active sites). FeCl₃-N-C displayed the biggest shift, and FePc-N-C the smallest, in line with the ORR activity. A feature at 7125 eV in the Δμ-XANES plots was associated with adsorption of OH or O₂, O₂H⁻,⁹ and the formation of O_x-Fe³⁺-N₄ moieties. The changes at this binding energy were most prominent for FeCl₃-N-C and least prominent for FeAc-N-C. Finally, FT-EXAFS revealed clear changes in the proportion of Fe-N/O sites depending on the presence or absence of oxygen, and on the potential. Again, the biggest changes were observed for the FeCl₃-N-C electrocatalyst, confirming that this had the largest proportion of Fe-N₄ ORR active sites. In conclusion, FeAc-N-C contains the lowest proportion of ORR active sites; FeCl₃-

N-C contains a high proportion of Fe-N₄ sites, contributing to the highest ORR activity measured in this work; and FePc-N-C contains the highest proportion of Fe-N₄ sites but due to the inaccessibility of these sites, the ORR activity was the lowest amongst the samples tested here.

6.5 References

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Chapter 7 Summary, Conclusions and Future Outlook

In Chapter 3, we investigated how optimization of the nitrogen-doped carbon support can be used to improve the design of Fe-N-C ORR electrocatalysts. Template-free nitrogen-doped carbon foams with large surface area were developed using three different synthesis protocols. Method A was a high pressure and high temperature solvothermal technique. Method B was an ambient temperature-and-pressure solution-based technique designed to make the process cheaper, more scalable, and safer. Method C removed the requirement of metal sodium lumps, and was also an ambient temperature-and-pressure technique. Method A had relatively low yield, surface area, and porosity. Method B successfully improved the yield, surface area, porosity, and nitrogen content compared to Method A. Method C resulted in increased yield and similar nitrogen content, but lower surface area and different pore size distribution. The metal-free ORR activity of the samples was measured in order to screen the techniques for their suitability in electrochemical applications.

The results of this electrochemical screening suggested that selected samples from Method B and C were suitable for further investigation. These were decorated with FeAc, pyrolyzed in NH_3 , and acid washed. The resulting catalytic activity was comparable to that of a commercially available Fe-N-C electrocatalyst (NPC-2000), and the highest ORR activity was obtained for Fe-N-C-C(1:3)_{5,1000}. This was attributed to suitable nitrogen content, providing sufficient adsorption sites for Fe atoms; high micropore surface area, providing ample sites for Fe adsorption; the high mesopore to micropore ratio, facilitating mass diffusion. These results confirmed that careful optimization and selective design of the pore size, surface area, nitrogen content, and heating rate of carbon-based supports can result in highly active Fe-N-C catalysts.

In Chapter 4, FeAc, FeCl₃, and FePc precursors were adsorbed on carbon foam and nitrogen-doped carbon foam followed by heat-treatment at 900 °C in ammonia, and acid washing in 1 M H₂SO₄. The resulting catalysts were extensively characterized. For FeAc-N-C catalysts, there was a large microporous surface area, wide micropore diameter, and a high proportion of graphitic carbon-encapsulated iron nanoparticles coexisting with Fe-N₄ sites, leading to reasonable ORR activity. For FeCl₃-N-C there was also a large microporous surface area and wide micropore diameter, but in this case there was a lower proportion of carbon-encapsulated metallic iron, and a correspondingly higher proportion of Fe-N₄ sites, leading to high ORR activity. Meanwhile, FePc-N-C had very low microporous surface area and narrow micropore diameter, because FePc molecules (~ 1 nm) are too large to enter the micropores of the nitrogen-doped carbon support (~0.8 nm). This leads to the lowest ORR activity, despite possessing the highest proportion of Fe-N bonds. Load-cycling electrochemical durability revealed minor degradation in all three samples, probably due to iron leaching. On the other hand, start-stop durability resulted in severe carbon corrosion, suggesting the need for a more graphitized carbon support.

In Chapter 5, in situ techniques were used to monitor real-time changes during catalyst synthesis and investigate the surface characteristics under simulated operating conditions. Quadrupole mass spectroscopy (QMS) was used to successfully determine the decomposition mechanisms during synthesis, giving new insights into the formation of ORR active sites. It provided an explanation for the observed presence of iron nanoparticles in all samples, and the increase in pore diameter and pore volume due to iron catalyzed steam gasification of the carbon support in the cases of FeAc and FeCl₃. High temperature X-ray photoelectron spectroscopy (HT-XPS) was used to confirm that Fe-N are retained in significant amounts during pyrolysis. Near ambient pressure XPS

(NAP-XPS) was used to investigate the adsorption of oxygen on the surface of electrocatalysts. However, no new bonds were detected, and it was inferred that O₂ and/or H₂O mainly bind to Fe atoms in the electrocatalysts, or that the application of a potential is required to observed significant changes.

In Chapter 6, in-situ electrochemical XAS was performed to investigate the changes under applied potential and exposure to oxygen. All three electrocatalysts showed a potential-dependent shift in the Fe-edge of the XANES spectra, associated with ORR-initiating Fe²⁺/Fe³⁺ redox transitions (i.e. the adsorption of OH_{ads} and O_{ads} species at Fe-N₄ active sites). FeCl₃-N-C displayed the biggest shift, and FePc-N-C the smallest, in line with the ORR activity. A feature at 7125 eV in the Δμ-XANES plots was associated with adsorption of OH or O₂, O₂H⁻,⁹ and the formation of O_x-Fe³⁺-N₄ moieties. The changes at this binding energy were most prominent for FeCl₃-N-C and least prominent for FeAc-N-C. Finally, FT-EXAFS revealed clear changes in the proportion of Fe-N/O sites depending on the presence or absence of oxygen, and on the potential. Again, the biggest changes were observed for the FeCl₃-N-C electrocatalyst, confirming that this had the largest proportion of Fe-N₄ ORR active sites.

Overall, these results provided significant new insights into the formation mechanisms of Fe-N-C electrocatalysts by the use of a relatively stable support material, i.e. nitrogen-doped carbon foam. This allowed changes in the nature of the adsorbed iron precursor and its interaction with the support to be observed much more clearly. In particular, it is concluded that a combination of large microporous surface area, suitable porosity, and a high proportion of accessible Fe-N sites residing in the micropores is beneficial in creating highly active Fe-N-C electrocatalysts.

For future outlook, the use of FeAc and FeCl₃ precursors will be important since these result in the development of microporosity via iron catalyzed steam gasification, alongside the growth of graphitic carbon. Therefore, e.g. optimization of the FeCl₃-N-C electrocatalyst by varying the initial FeCl₃ loading and the heat treatment protocols, is expected to improve both catalytic performance and durability. The use of other types of in-situ characterizations such as electrochemical XPS to investigate the behavior of adsorbed iron at various applied potentials and high temperature TEM to directly observe the formation of metal nanoparticles and graphitic carbon nanostructures during pyrolysis, will help to further understand the catalysts formation and ORR mechanisms. Finally, the suitability of these electrocatalysts in alkaline fuel cells, or as CO₂ conversion electrocatalysts is also of interest for future studies.

Appendix

*Table A3.1: Summary of the product masses for all of the samples. *The product mass of the 2nd heat treatment step is inferred from the yield – the real value is approximately half of this, since the samples were divided at this stage.*

	Initial Precursor Mass (g)	1 st Step Product Mass (g)	1 st Step Product Yield (%)	1 st Step Surface Area (m ² /g)	2 nd Step Product Yield (%)	Sample Name
Method A	16.52	0.38	2.3	533	55	N-C-A(1:9) _{10,900}
	17.39	0.80	4.6	520	68	N-C-A(1:3) _{10,900}
					66	N-C-A(1:3) _{10,1000}
	19.38	0.31	1.6	284	53	N-C-A(1:1) _{10,900}
Method B	17.45	0.96	5.5	1160	64	N-C-B(1:3) _{10,900}
					60	N-C-B(1:3) _{10,1000}
	17.54	2.00	11.4	1730	62	N-C-B(1:3) _{5,900}
					60	N-C-B(1:3) _{5,1000}
	17.39	0.80	4.6	2479	58	N-C-B(1:3) _{2,900}
					55	N-C-B(1:3) _{2,1000}

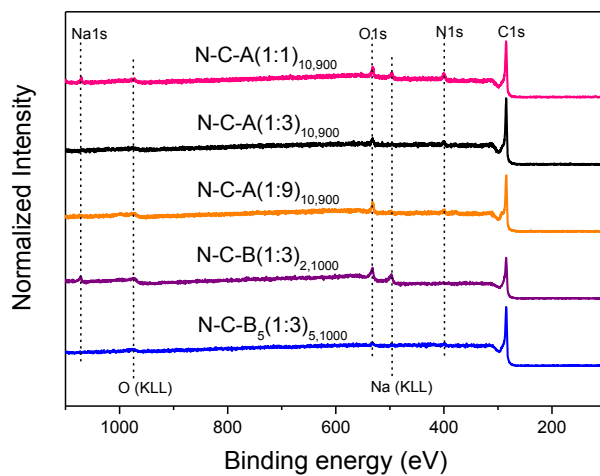


Figure A3.1: XPS wide scans of some of the nitrogen-doped carbon foams used in this study.

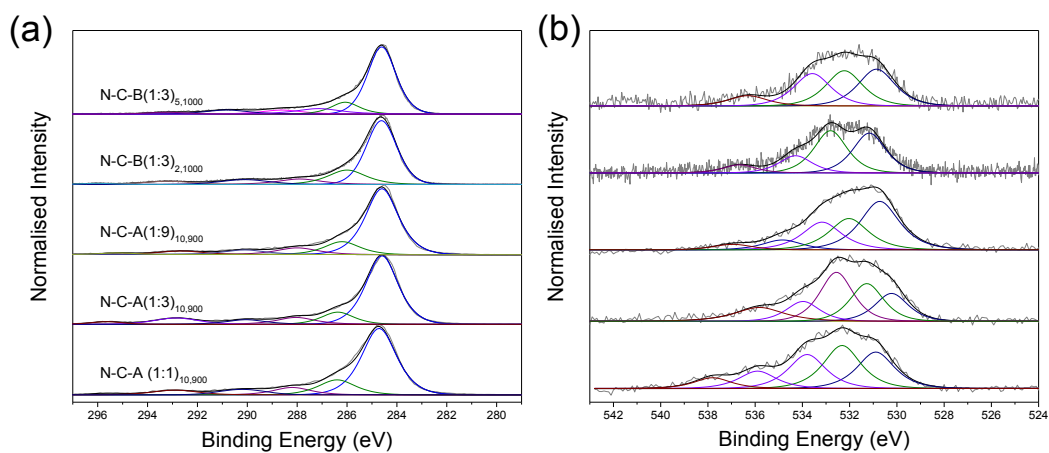


Figure A3.2: XPS narrow scan of: (a) C 1s and (b) O 1s for selected nitrogen-doped carbon foams of Method A and B.

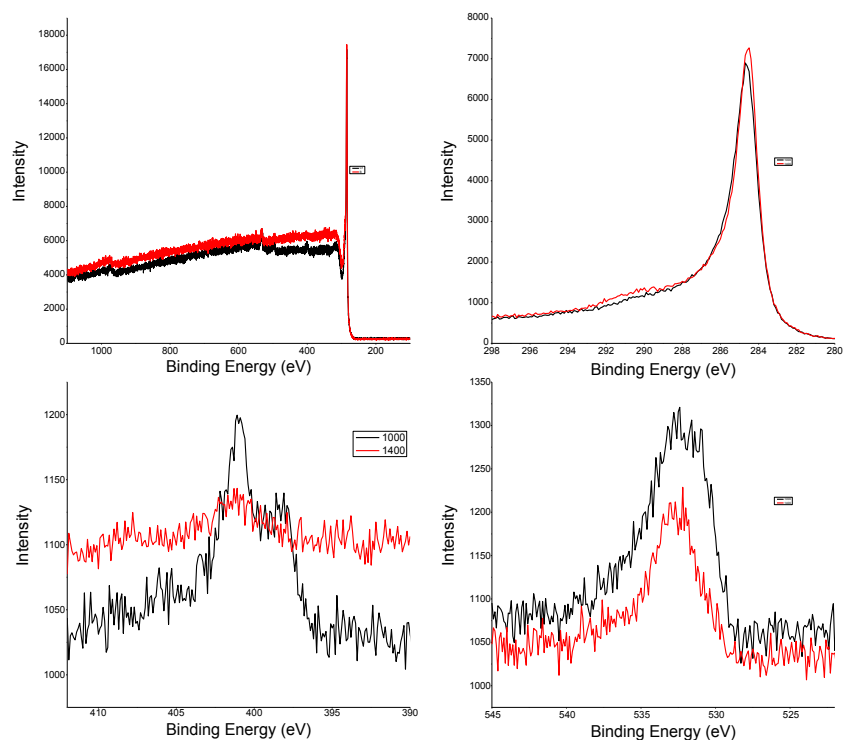


Figure A3.3: XPS: (a) wide scan and (b) narrow scan of C 1s, N 1s and O 1s Method C samples.

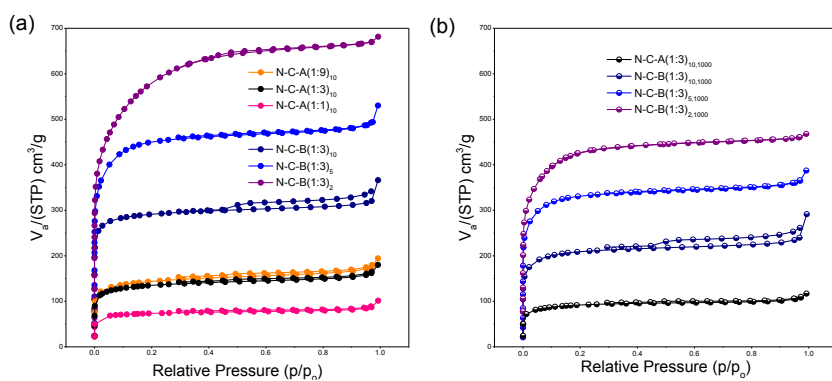


Figure A3.4: Adsorption/desorption isotherms of selected samples from Method A and B: (a) after the first structure-forming heat treatment step; and (b) after the second heat treatment at 1000 °C.

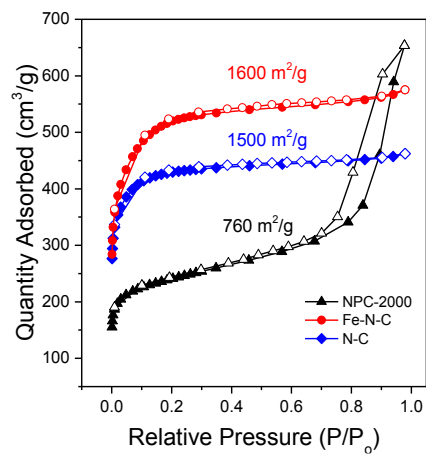


Figure A3.5: N_2 adsorption/desorption isotherms of N-C, Fe-N-C and NPC-2000 and their respective BET surface areas.

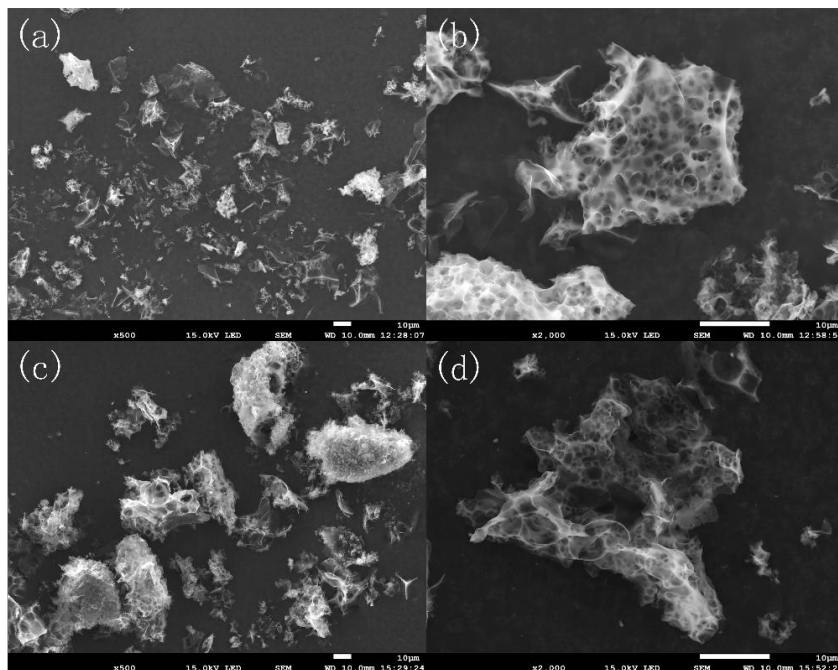


Figure A3.6: SEM images of: (a, b) N-C-A (1:3)_{10,1000}, and (b, c) N-C-B (1:3)_{10,1000} at two different magnifications.

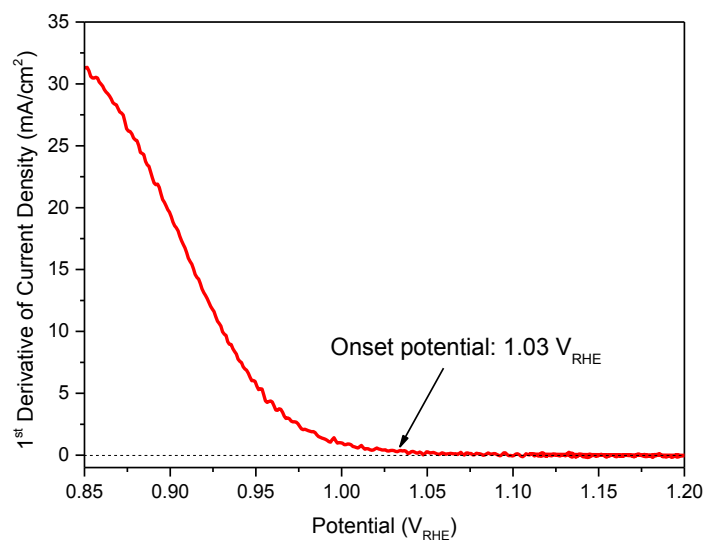


Figure A3.7: Representative first derivative of the current density in a linear sweep voltammogram (Pt/C, 1600 rpm in acid). This method was used to determine the onset potential of all samples.

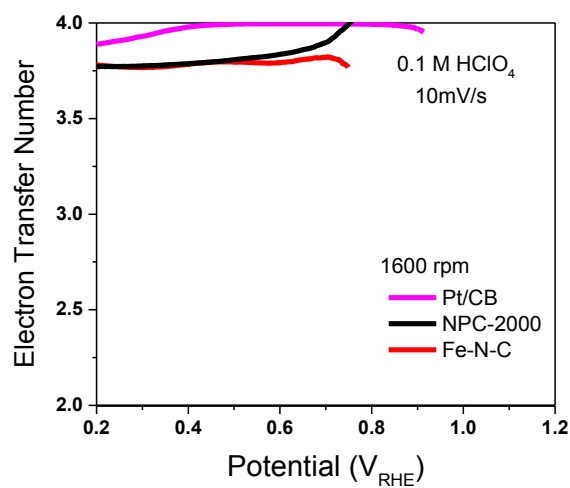


Figure A3.8: Electron transfer number of the Fe-N-C catalyst, compared with NPC-2000 (Pajarito Powder), and Pt/C.

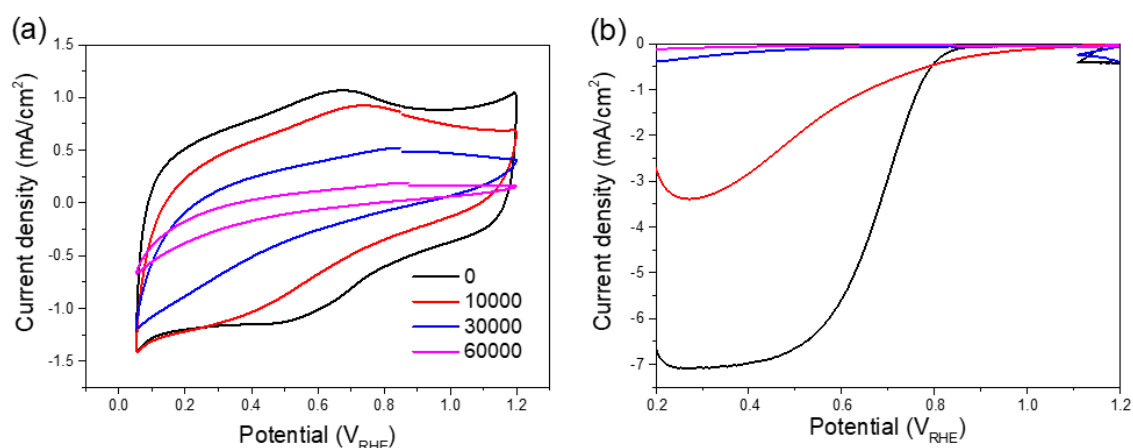


Figure A3.9: (a) Cyclic voltammograms (CVs), and (b) Linear sweep voltammograms (LSVs) of the start-stop cycles for Fe-N-C catalyst.

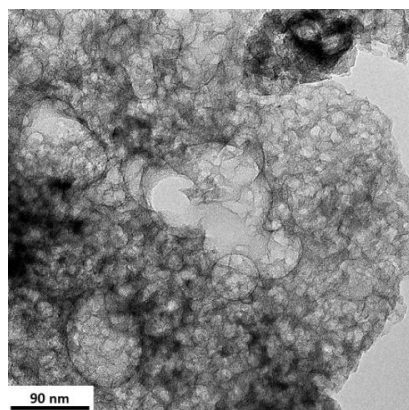


Figure A3.10: TEM image of NPC-2000

Table A3.2: Summary of the surface area and pore size distribution based on N_2 adsorption/desorption technique. A_s is the BET total specific surface area; a_1 is the total specific surface area (T-plot); a_2 is the external surface area (T-plot); $2t$ is the micropore width; $a_1 - a_2$ is the micropore surface area; V_{micro} is the micropore volume; V_{meso} is the mesopore volume, and V_{tot} is the total pore volume.

Samples	A_s (m^2/g)	(a_1) m^2/g	(a_2) m^2/g	($a_1 - a_2$) m^2/g	$2t$ (nm)		V_{micro} cm^3/g	V_{meso} (cm^3/g)	V_{tot} (cm^3/g)	V_{meso}/V_{micro}
N-C-A (1:3) _{10,900}	400	417	17	400	0.85		0.17	0.085	0.26	0.50
N-C-A	346	395	13	382	0.73		0.14	0.068	0.21	0.49

(1:9) _{10,900}										
N-C-A (1:1) _{10,900}	100	109	9	100	0.70		0.04	0.039	0.074	1.11
N-C-B (1:3) _{2,900}	1867	1866	12	1854	0.92		0.86	0.250	1.11	0.30
N-C-B (1:3) _{5,900}	1500	1386	20	1366	0.76		0.52	0.120	0.64	0.23
N-C-B (1:3) _{10,900}	1075	1234	21	1213	0.70		0.42	0.150	0.57	0.36
Fe-N-C	1600	1607	656	951	0.83		0.51	0.260	0.77	0.51
NPC-2000	760	775	256	519	1.40		0.23	0.470	0.70	2.04

Meanwhile, nitrogen-free iron-adsorbed samples were also synthesized to investigate the effect of nitrogen in the support on the final electrochemical activity. These all displayed very poor electrochemical activity, with onset potentials of 0.65 V_{RHE}, half wave potentials of 0.32 and 0.38 V_{RHE}, and the mass diffusion limited region was not reached within this potential range. The electron transfer numbers were very low (~2.5).

This shows the importance of including nitrogen in the catalyst support. One factor in the large difference in activity may be that nitrogen can act as a nucleation site for iron adsorption and the formation of FeN_{2/4} active sites. This is supported by the XAS experimental data, where the nitrogen-free carbon supports resulted in a high proportion of Fe-Fe coordination peaks, meaning that almost all the iron was metallic.

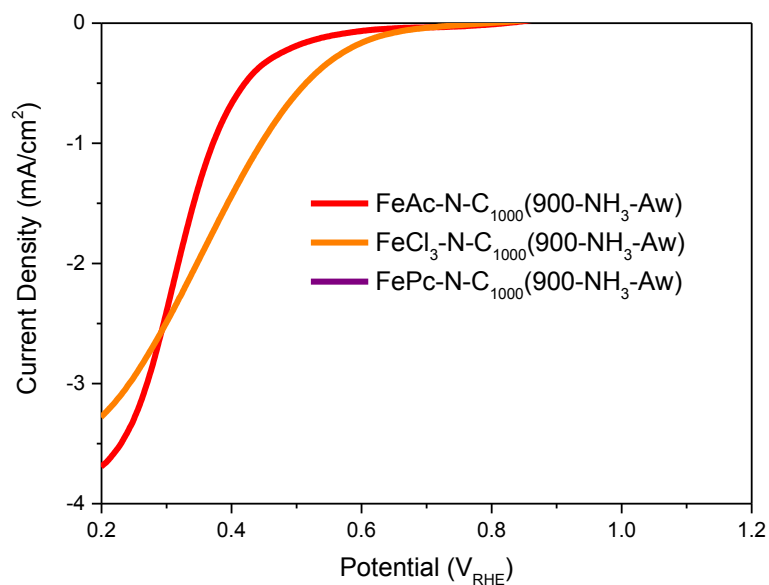


Figure A4.11: (a) Linear sweep voltammograms of: FeAc-C₁₀₀₀(900-NH₃-Aw), and FeCl₃-C₁₀₀₀(900-NH₃-Aw obtained in 0.1 M HClO₄ at 1600 rpm.

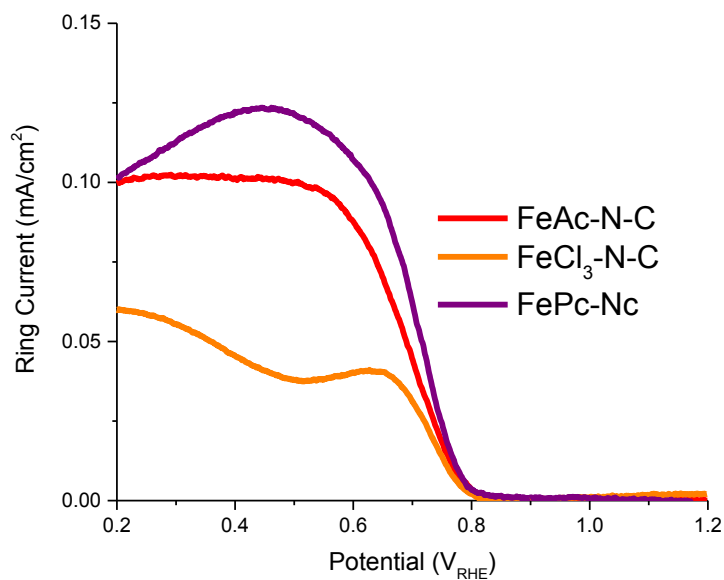


Figure A4.12: RRDE based ring currents of FeAc-N-C, FeCl₃-N-C and FePc-N-C.

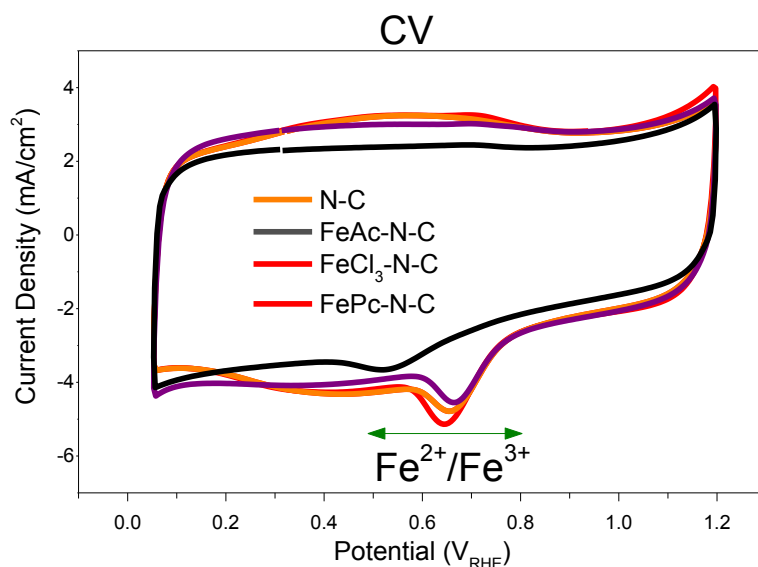


Figure A4.13: Cyclic voltammograms of N-C, FeAc-N-C, FeCl₃-N-C and FePc-N-C.

Our previous conventional XPS results for N-C (ULVAC system at Kyushu University) are compared with the results using this machine (SPECS system at Charles University), at ambient temperature and ultrahigh vacuum, in Table 1. There are only small differences between the data collected from the two systems. The slightly higher oxygen content measured by the SPECS machine may be because the sample was older at this stage and had been exposed to the ambient environment for longer, potentially adsorbing more moisture and oxygen from the air. However, overall, direct comparison between the two

data sets is justified.

Table A5.3: Comparison of elemental ratios from XPS for nitrogen-doped carbon foam measured on two different systems.

	Carbon (at%)	Nitrogen (at%)	Oxygen (at%)	Sodium (at%)
ULVAC	92.5	3.3	3.1	1.1
SPECS	90.3	4.1	5.0	0.6

Table A5.4: Summary of the relative abundance (%) of the deconvoluted peaks for C 1s spectra of N-C and FeAc-, FeCl₃-, and FePc-adsorbed-N-C samples.

Carbon		C=C (%) 284.5 eV	C-C (%) 285.5 eV	C-O/C-N (%) 286.6 eV	O=C-O (%) 288.2 eV	π - π (%) 290.7 eV
N-C	UHV	59.7	15.0	7.9	6.0	11.3
	HT-XPS	57.6	18.5	7.2	5.5	11.2
	NAP-XPS	58.0	17.5	7.1	5.8	9.5
FeAc-N-C	UHV	53.5	18.6	8.4	7.0	12.5
	HT-XPS	49.8	23.1	8.1	6.6	12.4
	NAP-XPS	52.6	23.1	7.8	6.0	10.6
FeCl ₃ -N-C	UHV	55.4	16.1	9.8	6.4	12.3
	HT-XPS	54.3	18.4	8.8	5.3	13.3
	NAP-XPS	57.0	17.2	8.7	5.0	13.3
FePc-N-C	UHV	60.3	17.4	6.9	5.8	9.6
	HT-XPS	45.1	26.4	9.6	7.2	11.6
	NAP-XPS	50.9	22.9	8.4	6.4	11.3

Table A5.5: Summary of the relative abundance (%) of the deconvoluted peaks for N 1s spectra of N-C and FeAc-, FeCl₃-, and FePc-adsorbed-N-C samples.

Nitrogen		Pyridinic (%) 398 eV	Pyrrolic/Fe- N (%) 400 eV	Graphitic (%) 401 eV	Hydrogenated- pyridinic-N (%) 403 eV	Pyridine-N- oxide (%) 404 eV
N-C	UHV	32.3	10.4	39.6	9.9	7.7
	HT-XPS	28.5	12.1	40.4	13.0	6.0
	NAP-XPS	29.4	13.2	39.3	11.0	7.1
FeAc-N-C	UHV	32.3	24.1	24.7	12.1	6.7
	HT-XPS	36.7	12.7	29.6	8.9	12.7
	NAP-XPS	37.0	14.1	28.4	8.6	11.9
FeCl ₃ -N-C	UHV	29.3	29.8	25.2	9.1	6.7
	HT-XPS	34.2	15.6	29.9	11.1	9.2
	NAP-XPS	33.2	18.0	28.0	10.1	10.9
FePc-N-C	UHV	33.0	17.1	35.8	9.8	4.4
	HT-XPS	33.4	15.0	37.1	9.5	4.9
	NAP-XPS	37.2	15.0	35.2	8.6	3.8

Table A5.6: Summary of the relative abundance (%) of the deconvoluted peaks for O 1s spectra of N-C and FeAc-, FeCl₃-, and FePc-adsorbed-N-C samples.

Oxygen		C=O (%) 531 eV	C-OH/C-O- C (%) 533 eV	Chemisorbed Oxygen (%) 535	Na KLL (%) 536 eV	Adsorbed water (%) 537 eV
N-C	UHV	33.9	42.9	20.2	3.2	0
	HT-XPS	36.6	42.3	13.5	6.7	0
	NAP-XPS	30.4	42.6	0	0	27.0
FeAc-N-C	UHV	29.7	40	22.3	8	0
	HT-XPS	34.7	13.0	52.2	0	0
	NAP-XPS	28.4	9.7	34.8	0	27.1
FeCl ₃ -N-C	UHV	22.5	41.4	24.8	5.2	6.1
	HT-XPS	15.3	38.3	28.7	6.9	10.7
	NAP-XPS	14.1	40.9	20.2	0	24.8
FePc-N-C	UHV	30.6	43.4	19.8	0	6.2
	HT-XPS	21.2	57.2	15.9	0	5.7
	NAP-XPS	17.6	33.5	17.3	0	31.6