

IMPERIAL COLLEGE LONDON
DEPARTMENT OF CHEMISTRY

**Developing high site density non-precious M-N/C catalysts
for oxygen reduction reaction in proton exchange
membrane fuel cells**

by

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Declaration of Authorship

All the works present in this thesis were carried out from 28.09.2019 to 28.09.2022 in the Department of Chemistry at Imperial College London and under the supervision of Prof. Anthony Kucernak.

I declare that I have written this thesis on my own and used no other than the named help. All the results from collaborative experiments have been clearly stated.

Signed: Mengjun Gong

Date: 2023-07-28

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Abstract

Developing high site density non-precious M-N/C catalysts for oxygen reduction reaction in proton exchange membrane fuel cells

by Mengjun Gong

Proton exchange membrane fuel cells (PEMFCs) are zero-emission power generation systems that have the potential to address the environmental issues associated with combustion engines, particularly in vehicles. However, the high cost of precious metal catalysts has hindered the commercialisation of PEMFCs. Non-precious metal-based single atom catalysts (M-N/Cs) offer a promising solution to replace precious cathode catalysts, which primarily consist of platinum group metals. Nevertheless, there are several challenges that need to be addressed to enhance the activity and stability of M-N/Cs. This thesis mainly focuses on understanding the active sites in M-N/Cs, synthesising M-N/Cs and improving the site density of M-N/Cs to achieve high-performance oxygen reduction reaction (ORR) in PEMFCs.

Seven different transition metal based M-N/Cs were synthesised using commercial zeolitic imidazolate framework-8 (ZIF-8) as a precursor. Physicochemical characterisations confirmed the formation of single atom sites. The ORR performance under different pH conditions indicated the presence of multiple types of active sites, and nitrite stripping was employed to assess the electrochemical accessible sites and the activity of different sites.

Considering that the metal-based active sites in Fe-N/C demonstrated the highest activity, efforts were made to improve the site density of Fe-N/C. Rotating ring-disk electrode (RRDE) and single cell PEMFC were performed to evaluate the ORR activity. Significantly enhancing the metal loading (around 7 wt%) and increasing the number of electrochemical accessible sites

(4.67×10^{19} site g^{-1}) greatly improved the ORR activity of Fe-N/C. Physicochemical characterisations not only confirmed the production of single atomic sites, but also indicated the role of second pyrolysis in the synthesis process.

Finally, Fe-N/Cs exhibited excellent catalytic performance on the Mukaiyama epoxidation and Baeyer-Villiger oxidation at ambient temperature and pressure. Kinetic and mechanistic studies provided evidence for the *in-situ* generation of peroxy acid and acylperoxy radicals. Furthermore, these organic oxidation processes demonstrated the presence of two distinct active sites within Fe-N/C.

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List of Publications

A number of manuscripts have been published from the content presented in this thesis and summarised as follows:

- (1) A paper on the active sites of single atom catalysts for oxygen reduction reaction as described in Chapter 3: Gong, M., Mehmood, A., Ali, B. *et al.* Oxygen reduction reaction activity in non-precious single atom (M-N/C) catalysts – contribution of metal and carbon/nitrogen framework-based sites. *ACS Catal.* **13**, 6661-6674 (2023). <https://doi.org/10.1021/acscatal.3c00356>
- (2) A paper covering the high metal loading of Fe-N/C for oxygen reduction reaction in PEMFC as detailed in Chapter 4: Mehmood, A., Gong, M., Jaouen, F. *et al.* High loading of single atomic iron sites in Fe-NC oxygen reduction catalysts for proton exchange membrane fuel cells. *Nat. Catal.* **5**, 311–323 (2022). <https://doi.org/10.1038/s41929-022-00772-9>
- (3) A paper about heterogenous epoxidation with molecular oxygen as detailed in part of Chapter 5: Gong, M., Guo, Y., Malko, D., *et al.* Using molecular oxygen and Fe-N/C heterogeneous catalysts to achieve Mukaiyama epoxidations via *in situ* produced organic peroxy acids and acylperoxy radicals. *Catal. Sci. Technol.*, **12**, 2978-2989 (2022). <https://doi.org/10.1039/D2C Y00356B>

A few papers were published as helping with the nitrite stripping to quantify the site density of single atom catalysts, which is part of work done in Chapter 3.

- (4) Barrio, J., Pedersen, A., Sarma, S., Bagger, A. Gong, M. *et al.* FeNC Oxygen Reduction Electrocatalyst with High Utilisation Penta-coordinated Sites. *Advanced Materials* **564**, 232829 (2023). <https://doi.org/10.1002/adma.202211022>
- (5) Sarma, S., Barrio, J., Bagger, A., Pedersen, A., Gong, M. *et al.* Reaching the Fundamental Limitation in CO₂ Reduction to CO with Single Atom Catalysts. *Advanced Functional Materials*, 2302468 (2023) <https://doi.org/10.1002/adfm.202302468>
- (6) Sarma, S., Barrio, J., Gong, M. *et al.* CO₂ Reduction to CO on Atomically Dispersed Fe in a C₂N-derived Electrocatalyst: Single or Dual Atom Catalyst? Just accepted: *Electrochimica Acta* (2023) <https://doi.org/10.1016/j.electacta.2023.142855>
- (7) Mehmood, A., Ali, B. Gong, M. *et al.* Development of a highly active Fe-N-C catalyst with the preferential formation of atomic iron sites for oxygen reduction in alkaline and acidic electrolytes. *J. Colloid Interface Sci.*, **596**, 148-157 (2021). <https://doi.org/10.1016/j.jcis.2021.03.081>
- (8) A paper with helping the PEMFC measurements: Wu, J., Gong, M., Zhang, W. *et al.* Simultaneously Incorporating Atomically Dispersed Co-N_x Sites with Graphitic Carbon Layer-Wrapped Co₉S₈ Nanoparticles for Oxygen Reduction in Acidic Electrolyte. *ChemElectroChem*, **10**, e202300110. (2023) <https://doi.org/10.1002/celec.202300110>

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List of Abbreviations

AAEMFC	Alkaline Anion Exchange Membrane Fuel Cell
ADF	Annular Dark-Field detector
AEM	Anion Exchange Membrane
AFC	Alkaline Fuel Cell
BET	Brunauer-Emmett-Teller
BF	Black-Field detector
BJH	Barret, John, Halenda
BPP	BiPolar Plates
BV oxidation	Baeyer-Villiger Oxidation
CA	Control Amplifier
CCM	Catalyst Coated Membrane
CE	Counter Electrode
CF	Current Follower
CHP	Combined Heat and Power
CL	Catalyst Layer
CM	CyanaMide
CTF	Covalent Triazine Framework
CV	Cyclic Voltammetry
DFT	Density Functional Theory
DOO	Degree Of Oxidation
EDS	Energy Dispersive X-ray Spectroscopy
EELS	Electron Energy Loss Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
ESA	Electrochemical Surface Area
EXAFS	Extended X-ray Absorption Fine Structure
FC	Fuel Cell
FCV	Fuel Cell Vehicle
FRA	Frequency Response Analyser
FT	Fourier Transform
FY	Fluorescence Yield
GC	Gas Chromatography
GDE	Gas Diffusion Electrode
GDL	Gas Diffusion Layer

HAADF	High-Angle Annular Dark-Field detector
HFR	High Frequency Resistance
HOR	Hydrogen Oxidation Reaction
HR	High-Resolution
IS	Isomer Shift
LCF	Linear Combination Fit
LSV	Linear Sweep Voltammetry
MCFC	Molten Carbonate Fuel Cell
MEA	Membrane Electrode Assembly
MFC	Mass Flow Controller
M-N/C / M-SAC	Metal Nitrogen doped Carbon based/ Single Atom Catalyst
MPL	MicroPorous Layer
NMR	Nuclear Magnetic Resonance
NP	NanoParticle
OCP	Open Circuit Potential
OHP	Outer Helmholtz Plane
ORR	Oxygen Reduction Reaction
PAFC	Phosphoric Acid Fuel Cell
PANI	PolyANiline
PEM	Proton Exchange Membrane
PEMFC	Polymer Electrolyte Membrane Fuel Cell
PEMFC	Proton Exchange Membrane Fuel Cell
PFSA	PolyFluoroSulfonic Acid
PM	Particulate Matter
PSD	Pore Size Distribution
PTFE	PolyTetraFluoroEthylene
QS	Quadrupole Shift
R	Resistance
RDE	Rotating Disk Electrode
RDS	Rate Determining Step
RE	Reference Electrode
RH	Relative Humidity
RHE	Reversible Hydrogen Electrode
RRDE	Rotating Ring Disk Electrode
R_s	Solution resistance
R_u	Uncompensated resistance

SAC	Single Atom Catalyst
SCCM	Standard Cubic Centimetre per Minute
SCE	Saturated Calomel Electrode
SEM	Scanning Electron Microscopy
SOFC	Solid-Oxide Fuel Cell
STEM	Scanning Transmission Electron Microscopy
TEM	Transmission Electron Microscopy
TEY	Total Electron-Yield
TOF	TurnOver Frequency
VF	Voltage Follower
WE	Working Electrode
WS	Working Sense
XANES	X-ray Absorption Near-Edge Structure
XAS	X-ray Absorption Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction
YSZ	Yttria-Stabilised Zirconia
Z	Impedance
ZAB	Zinc-Air Battery
ZIF	Zeolitic Imidazolate Framework

Physical Constants

Avogadro Constant

$$N_A = 6.022\,140\,857 \times 10^{23} \text{ mol}^{-1}$$

Ideal Gas Equation

$$R = 8.314\,4598 \text{ J K}^{-1} \text{ mol}^{-1}$$

Faraday Constant

$$F = 96\,485.3329 \text{ s A mol}^{-1}$$

Charge of Electrons

$$e = 1.60218 \times 10^{-19} \text{ C}$$

Chapter 1 Introduction

A literature overview on the background of the fuel cells and the state-of-art catalysts used in the proton exchange membrane fuel cells. Several different types of catalysts for oxygen reduction reaction have been discussed, with a particular focus on single-atom catalysts. Different preparation methods were compared and discussed in this chapter.

With the rapid development of technology, the total global energy consumption has increased over past twenty years as shown in Figure 1.1 and the energy can be generated by different sections, including renewables (orange), hydroelectricity (blue), nuclear energy (yellow) and fossil fuels, such as coal (grey), natural gas (red) and oil (green).¹ Environmental pollution and the emission of carbon dioxide have attracted people's attention for the past decades as those issues influence the daily life. Especially increasing amount of particulate matter (PM) in the urban regions, which are released during the usage of fossil fuels in combustion engines, is one of the most severe problems, because inhalation of PM triggers several diseases, such as lung cancer and acute asthma exacerbations.² Not only PM, but also other toxic gases, for example carbon monoxide (CO), nitrogen oxides (NO_x) and sulfur oxides (SO_x), and carbon dioxide (CO₂) are generated inevitably while the combustion of fossil fuel. Therefore, an environmental friendly method to generate power is highly demanded and renewable energy could be used to substitute the fossil fuel. There is a clear increasing trend in the use of renewable energy and a decline in the usage of fossil fuel as shown in Figure 1.1.¹

Fuel cells (FCs) are one of the renewable technologies to generate electricity by chemical process. Unlike internal combustion, fuel cells can generate electricity directly from the

chemical reaction instead of converting the heat energy to mechanical energy first. Complicated conversion processes in internal combustion will be inefficient and complex; fuel cells transfer the electrons from reactants through an external circuit to generate the electricity directly. More importantly, fuel cells are zero emission power generating systems. If hydrogen is used as fuel, then the only emission from the fuel cell system is water, and no toxic gases will be released during this process. Finally, the fuel cell system can generate electricity continuously with a constant operating voltage as long as the fuel is supplied. There is not any charging required, unlike batteries. Furthermore, the power generated and the capacity of fuel cells actually depend on the size of fuel cell and the size of fuel reservoir respectively.³

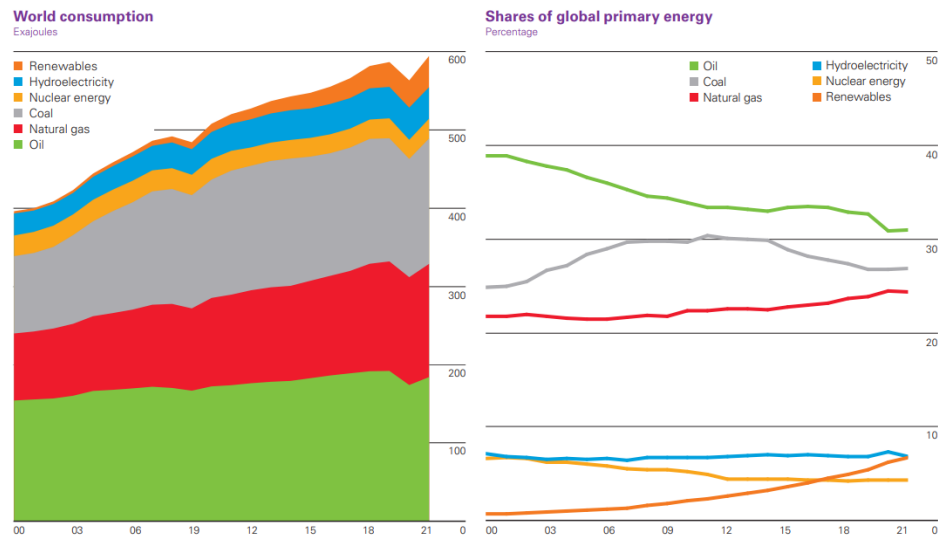


Figure 1.1 World consumption and the distribution by different sectors in past twenty years. [Taken from Ref¹]

1.1 Fuel cells

A schematic diagram of fuel cell is shown in Figure 1.2 to illustrate the operation of this system. Fuel cells directly convert the chemical energy of fuel into electricity by facilitating the flow of electrons from the anode to the cathode. The electricity generation process involves four main steps:

1. **Delivery of Reactants:** The reactants, necessary for the electrochemical reaction, are supplied to the fuel cell. To ensure efficient flow, a specialised flow structure is developed.

2. **Electrochemical Reaction:** Upon contacting the high surface area porous electrode, an electrochemical reaction takes place. At the anode, oxidation occurs, releasing electrons. Meanwhile, at the cathode, reactants accept electrons, initiating a reduction reaction. The specific reactions can vary depending on the type of fuel cell and the operating conditions.
3. **Ion and Electron Transport:** In this step, ions and electrons are transported through the electrolyte and external circuit, respectively, to facilitate the flow of electric current.
4. **Product Removal:** Finally, the resulting products are removed from the electrodes, allowing for continuous operation.

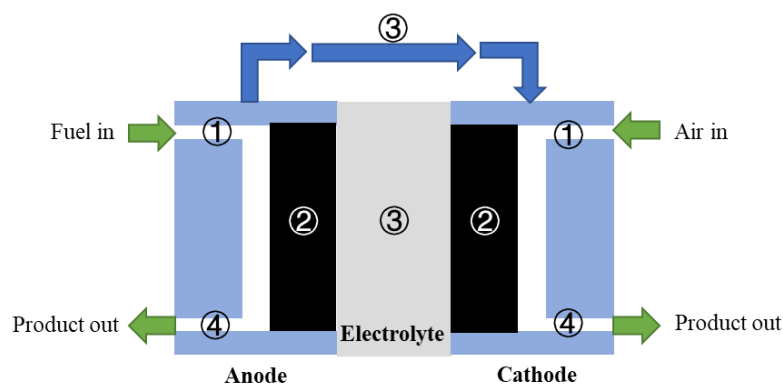


Figure 1.2 The schematic diagram of fuel cells' cross section.

There are five major types of fuel cells. Polymer electrolyte membrane fuel cells (PEMFCs) could use hydrogen or methanol as fuel and a thin polymer membrane is used as electrolyte for ion transfer. More detailed explanation about PEMFC will be discussed in next section.

For phosphoric acid fuel cells (PAFCs), hydrogen is used as fuel and liquid phosphoric acid in SiC matrix serves as the electrolyte.³ Since the melting point of phosphoric acid is 42 °C and the conductivity of phosphoric acid is poor at low temperature, the operating temperature of PAFCs is usually between 150 - 220 °C.⁴ Moreover, the electrical efficiency of PAFCs are around 40 - 50% and the combined heat and power (CHP) are around 85%; therefore, this type of fuel is already commercialised and used for stationary applications.⁴

Alkaline fuel cells (AFCs) are quite similar with PAFCs, but instead of using phosphoric acid, they use liquid potassium hydroxide as electrolyte and the ions transferred from cathode to anode are hydroxide ions.⁵ AFCs generally have better performance than acidic fuel cells, which can operate at relatively high voltage (~ 0.875 V) since the kinetics of oxygen reduction reaction (ORR) is higher in alkaline condition.³ However, pure oxygen must be used because the carbon dioxide in air reacts with the hydroxide and triggers the formation of a precipitate (K_2CO_3).⁵ The degradation of AFCs is mainly due to the adsorption of CO_2 , corrosion of carbon material by HO_2^- and flooding by water generated.⁵

Molten carbonate fuel cells (MCFCs) use molten alkali carbonates as the electrolyte; so the operating temperature of MCFCs is around $650^\circ C$.⁶ The fuels used in MCFCs can vary, including hydrogen, natural gas and even light alcohols.⁷ Moreover, the catalysts involved do not have to be precious metal, which lower the cost of catalyst.⁷ MCFCs are commercialised, but primarily used for stationary power generation.⁶ Carbon dioxide should be recirculated from the anode to cathode, which is one of the disadvantages of MCFCs.⁷ Additionally, the molten carbonate electrolyte is both energy consuming and quite corrosive.³

Solid-oxide fuel cells (SOFCs) normally used yttria-stabilised zirconia (YSZ) as electrolyte to transfer oxygen ion.⁸ This system normally operated at $600 - 1000^\circ C$ to ensure the electrolyte is liquefied, which poses a challenge in applying SOFCs to portable devices, although the power density of SOFCs is relatively high compared to others.⁹ Moreover sealing is another issue with SOFCs.¹⁰

All different fuel cells used distinct electrolytes for ion transfer and operating temperatures and a summary table of these five different fuel cells is shown in Table 1.1.

Table 1.1 Summary of major fuel cell types ³.

	PEMFC	PAFC	AFC	MCFC	SOFC
ELECTROLYTE	Polymer membrane	Liquid H_3PO_4	Liquid KOH	Molten carbonate	Ceramic
ION TRANSFERRED	H^+	H^+	OH^-	CO_3^{2-}	O^{2-}
OPERATING TEMPERATURE	60-80 °C	150-220 °C	60-250 °C	650 °C	600-1000 °C
FUEL COMPATIBILITY	H_2 , CH_3OH	H_2	H_2	H_2 , CH_4	H_2 , CH_4 , CO

1.2 Polymer Electrolyte Membrane Fuel Cells (PEMFCs)

For all different kind of fuel cells, they have very specific operating conditions that make them suitable for various fields and industries. Among them, polymer electrolyte membrane fuel cells (PEMFCs) are the most promising and suitable for transportation application due to their low operating temperature and relatively high-power density. Several commercial fuel cell cars are already available, such as BMW iX5 Hydrogen¹¹, Toyota Mirai¹², Hyundai All-New NEXO¹³. Moreover, fuel cell buses and trains are being used in several different countries.¹⁴ There are also ongoing investigation into the use of fuel cells in aircraft.¹⁵ Figure 1.3 provides a schematic diagram of two types of PEMFCs, which can operate under both acidic (right-hand side) and alkaline (left-hand side) conditions.

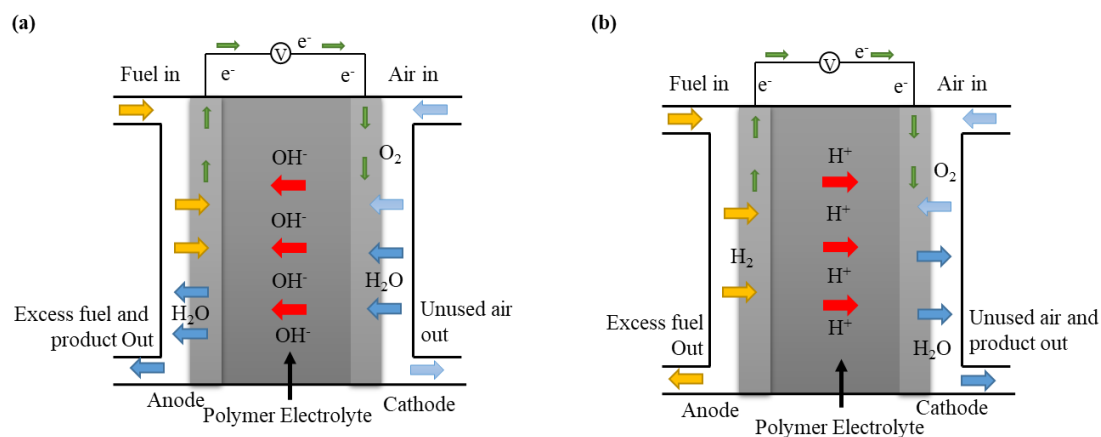
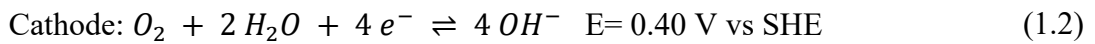
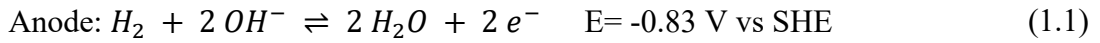


Figure 1.3 Schematic graph of two different polymer electrolyte membrane fuel cells (PEMFCs). (a) alkaline anion exchange membrane fuel cell (AAEMFC); (b) proton exchange membrane fuel cell (PEMFC).

1.2.1 Alkaline Anion Exchange Membrane Fuel Cell

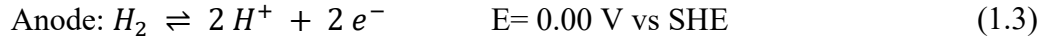
For alkaline anion exchange membrane fuel cell (AAEMFC), oxygen on the cathode is reduced to hydroxide ions, which are transferred to the anode side by polymer electrolyte. The fuel, hydrogen, is oxidised to water and the half equation is shown below:



The kinetic of the cathodic reduction reaction is higher compared with oxygen reduction reaction (ORR) under acidic conditions, so the required loading of precious metal is not too high. Many non-precious metal catalysts or metal-free nitrogen doped catalysts have shown very high activity under alkaline conditions.^{16, 17} However, the rate of the hydrogen oxidation reaction (HOR) on the anode side decreases with increasing pH, which necessitates a high loading of precious metal catalysts and increases the cost of AAEMFC significantly (approximately 100-fold lower compared to acidic conditions).¹⁸ There are also some reported non-precious metal catalysts that have demonstrated similar activity to Pt.¹⁹ Despite the cost of the catalyst not being the main reason for AAEMFCs not being commercialised yet, there is a more critical issue: the lack of commercialised stable anion exchange membrane (AEM).²⁰ The hydroxide ion conductivity is one of the most important challenges to be solved and the formation of bicarbonate or carbonate salt also presents a challenge for AEM, because there is a small amount of CO₂ present in air. In other words, using air on the cathode side will be difficult.²¹

1.2.2 Proton Exchange Membrane Fuel Cell

For proton exchange membrane fuel cell (PEMFC), the reactions on cathode and anode sides are different with AEMFC and the half-equations on both sides are shown:



The fuel cell stack consists of single cells and cooling plates, as shown in Figure 1.4 (a). A single cell is composed of a membrane electrode assembly (MEA) and bipolar plates (BPPs) as depicted in Figure 1.4 (b).²² The MEA includes two gas diffusion layers (GDLs) with microporous layers (MPLs), catalyst layers (CLs) and one proton exchange membrane (PEM). There are two different methods to prepare MEA: the gas diffusion electrode (GDE) method and the catalyst coated membrane (CCM) method.²³ In the GDE method, the catalysts for anode and cathode are coated on two GDLs, respectively, and then GDLs with catalysts are hot pressed with PEM. On the other hand, in the CCM method, the catalyst is sprayed onto the PEM first and then hot pressed with two GDLs.²³

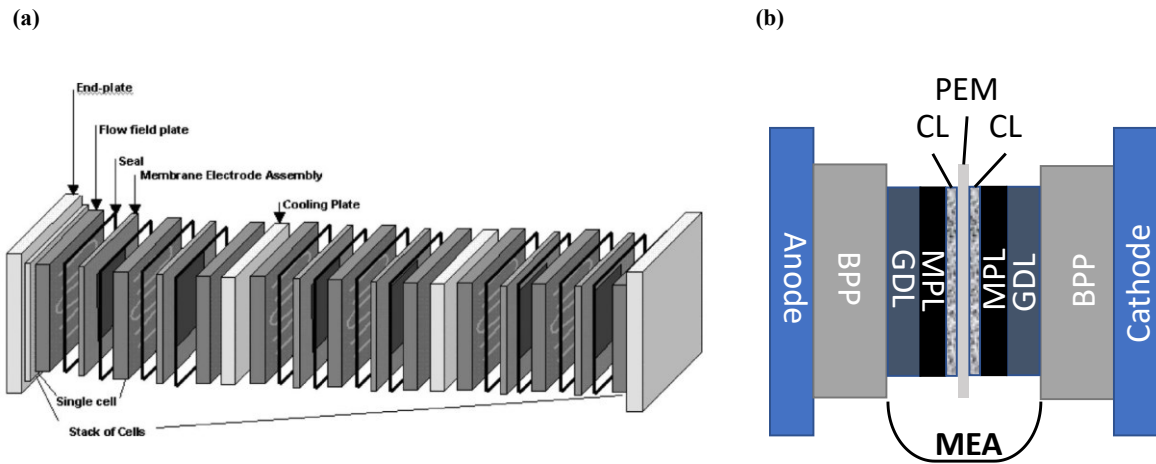


Figure 1.4 The schematic diagram of PEMFC (a) Fuel cell Stack; [Taken from Ref²⁴] (b) cross-section of a single cell.

Unlike the AAEMFC, there are several commercialised PEMs, that have shown very high proton conductivity and exhibit good electrochemical and mechanical stability.²⁵ One of the most common PEMFs is the perfluororsulfonic acid (PFSA) based membrane, and the examples of PFSA based membranes are shown in Figure 1.5. Nafion[®] is a well-known PFSA based membrane widely used in laboratory research and fuel cell stacks. It consists of two components: a hydrophobic backbone (polytetrafluoroethylene-PTFE) and a hydrophilic side

terminated with sulfonic acid group.²⁶ The PTFE component enhances mechanical strength and provides high stability under harsh conditions, such as high temperature and low pH. The sulfonic acid groups are responsible for providing proton conductivity.²⁷ In addition to Nafion[®], there are other well-known and widely used membranes, such as GORE-SELECT membrane used in MIRAI.²⁵ Currently, efforts are being made to improve the power density of PEMFC by decreasing the thickness of the membrane without compromising its mechanical and electrochemical stability, and this is an area of ongoing research.

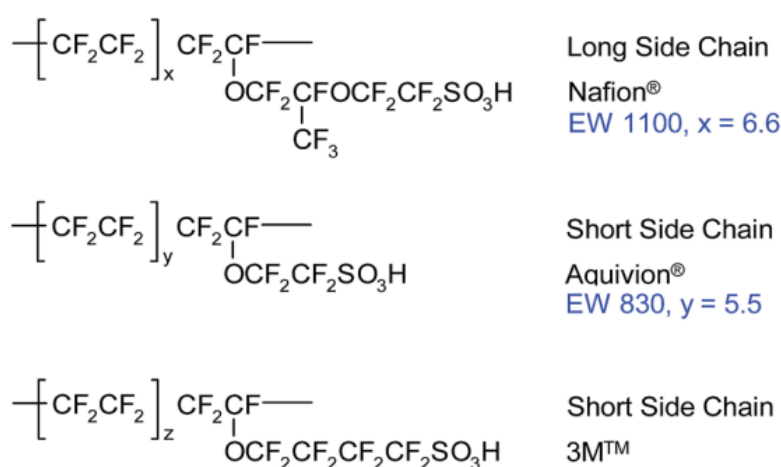


Figure 1.5 Examples of perfluorosulfonic acid (PFSA) membranes used in fuel cell.²⁷

In addition to the membrane used in PEMFCs, bipolar plates (BPPs) play a crucial role as they provide flow channels for transporting gaseous reactants to the catalyst and removing the products formed. BPPs also need to conduct electricity and thermal efficiently, high corrosion resistance, and be relatively low in cost, weight, and volume.²⁸ Most importantly, BPPs should distribute the reactants uniformly; so there are several different channel designs.³ There are still problems to be addressed, including decrease the weight volume and cost; as currently BPPs constitute around 60% of the weight and 30% of the total cost in a fuel cell stack.²⁸

Although PEMFCs have already been commercialised and the demand for FCVs kept increasing every year, the costs of fuel cell stacks remain prohibitively high. According to the reports from the Department of Energy in US²⁹ and Fuel Cell Industry challenges 2020 - 2035+

in UK³⁰, the cost of fuel cell stacks used in light-duty automotive has to decrease to around \$15 kW_{net}⁻¹, the performance at 0.8 V should be around 300 mAcm⁻² and the durability must be 8,000 hours to allow 150,000 miles of driving on a lower average-speed drive with <10% drop in rated power.²⁹ To achieve these goals, it is essential to understand the cost distribution of a fuel cell stack, which is shown in Figure 1.6. Approximately 41% of the total cost in a single fuel cell stack is attributed to the catalysts and application, primarily due to the use of scarce and precious platinum group metals and their alloys as catalysts for both HOR and ORR in the fuel cell. The global reserves of platinum group metals are around 70,000 metric tons in 2021 and more than 90% are distributed in South Africa.³¹ As a point of comparison, the global iron ore reserves in 2021 are 180 billion metric tons, which is around 2.5×10^6 higher than platinum group metals.³² Moreover, around 40% platinum group metals are used in automotives.³¹

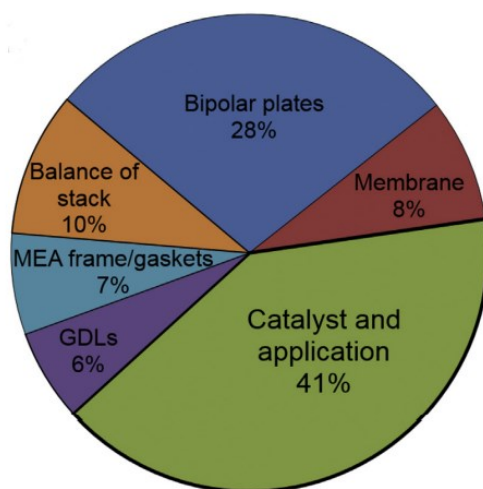


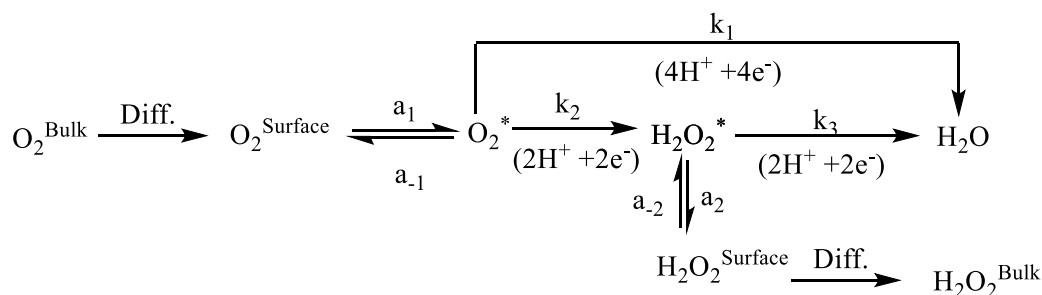
Figure 1.6 The cost of a fuel cell stack. [Taken from ref³³]

On the anode side of PEMFCs, the loading of Pt is relatively low, around 0.025 g_{Pt} cm⁻².³³ Moreover, there are still several ongoing research on reducing the loading of Pt in anode side to even μg cm⁻² by different deposition methods, such as electrospraying, plasma sputtering *etc.*³⁴⁻³⁷; so the catalysts used in anode side are not a significant concern. However, on the cathode side, the situation is different. The ORR involves a four-protons and four-electrons reduction process, which make its kinetics sluggish compared to HOR. As a result, the loading

of Pt required for ORR is around four times higher than what is used on the anode side. This poses a significant challenge, as the high Pt loading on the cathode can lead to higher costs and potential supply issues with the scarce and precious platinum group metals. Therefore, there is a pressing need to investigate potential substitutes for Pt in the ORR on the cathode side. Finding alternative catalyst materials that can offer comparable or superior performance to Pt is crucial for the development of fuel cell vehicles. These efforts aim to reduce the dependency on Pt and pave the way for more cost-effective and sustainable fuel cell technology for a wide range of applications.

1.3 Oxygen Reduction Reaction (ORR)

ORR is an important reaction not only for PEMFCs but also for other metal-air batteries, such as zinc-air^{38, 39}, lithium-air batteries, *etc.*⁴⁰⁻⁴² Therefore, it is significant to understand the mechanism of ORR and also to develop a better catalyst for ORR. Oxygen is the most abundant element in the earth's crust, and around 21% of air is composed of oxygen molecules. Oxygen is a diatomic molecule with a double bond, and the bond enthalpy of O=O is 498 kJ mol⁻¹. According to the molecular orbital theory, the ground state of oxygen molecule is triplet, which contained two unpaired electrons and this property makes triplet oxygen relatively less reactive than the singlet oxygen. The reaction with singlet oxygen is very favourable both thermodynamically and kinetically.



Scheme 1.1 General reaction scheme of oxygen reduction reaction to water.⁴³ * represents adsorbed; k and a stand for the rate constants.

The ORR is a very complicated and sluggish process since it involves four protons and four electrons. Scheme 1.1 illustrates the general and common pathways of ORR as presented in Wroblowa's publication.⁴³ Initially, bulk oxygen diffuses to the catalyst surface, where the oxygen molecule would be adsorbed on the catalyst, labelled as O_2^* . There are two possible reactions for the adsorbed oxygen: (1) a direct reduction to water (k_1), which involves four protons and four electrons; (2) a 2+2 pathway ($k_2 + k_3$), leading to the production of an intermediate, hydrogen peroxide. The desorption of hydrogen peroxide (a_2) will only happen if the rate of consumption of hydrogen peroxide (k_3) is smaller than the rate of its formation (k_2). However, the direct four-electrons reduction reaction and 2+2 two-electrons reduction reaction vary under different conditions and their overall reaction was summarised in Table 1.2.

Table 1.2 Overall equations of ORR under acidic and alkaline electrolytes.

Electrolyte	Reactions	E° VS SHE
Acidic	$\text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- \rightleftharpoons 2 \text{H}_2\text{O}$	1.23
	$\text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- \rightleftharpoons \text{H}_2\text{O}_2$	0.695
	$\text{H}_2\text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- \rightleftharpoons 2 \text{H}_2\text{O}$	1.763
Alkaline	$\text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^- \rightleftharpoons 4 \text{OH}^-$	0.401
	$\text{O}_2 + \text{H}_2\text{O} + 2 \text{e}^- \rightleftharpoons \text{OOH}^- + \text{OH}^-$	-0.065

	$OOH^- + H_2O + 2 e^- \rightleftharpoons 3 OH^-$	-0.87
--	--	-------

The detailed ORR mechanisms are very complicated and highly depended on the pH, type of catalysts and also the surface properties of electrode. For the four-electrons reduction reaction, there are two possible principle mechanisms, including dissociative and associative.⁴⁴ However, there are numerous derivatives based on those two principal mechanisms. Moreover, the dissociative mechanism has a higher energy barrier compared to the associative one since a strong O=O should be broken in the first step of dissociative mechanism. Therefore, the associative mechanism is more likely to take place both in acidic and alkaline conditions.

Acidic dissociative mechanism (four-electrons)



where * stands for the active sites of catalyst. Oxygen molecule is adsorbed on the surface of catalyst with a bond breaking of O-O in the first step as shown in Equation (1.5). Subsequently, the adsorbed atomic O* is protonated, producing OH*, which acquires another proton from the solution and then desorbs from the catalyst surface as water molecule.⁴⁵ However, for associative mechanism, the cleavage of O-O bond does not occur in the first step as shown below.

Acidic associative mechanism (four-electrons)





The diatomic oxygen molecule is adsorbed on the catalyst surface as O_2^* , which receives a proton and an electron to form OOH^* intermediate. The OOH^* intermediate accepts another proton and electron to form a water molecule, leaving an adsorbed oxygen atom O^* on the catalyst surface. The following steps are the same with Equation (1.6) and Equation (1.7).

However, there is another competing reaction leading to the formation of hydrogen peroxide, as shown in Equation (1.10), where OOH^* intermediate generates a hydrogen peroxide molecule as illustrated in Equation (1.11).

Acidic associative mechanism (two-electrons)



Moreover, the dissociative and associative mechanisms are competitive, and the energy required to break the O-O bond on the active sites will determine which pathway predominates. Several density functional theory (DFT) calculations and experimental tests have been conducted to investigate these dissociative and associative pathways. For Pt (111), it is a still ongoing discussion on which pathways dominated the ORR process.⁴⁵⁻⁴⁹ In general, it appears the dissociative process plays a more important role at high potential ranges, making the formation of hydrogen peroxide unlikely when Pt is used as catalyst. Researchers are exploring other catalysts as substitutes for precious Pt catalysts, and these alternative catalysts are discussed in the later section. Non-precious metal singlet atom catalyst is one of the most promising candidates. Consequently, numerous ORR mechanisms with non-precious metal catalysts have been proposed. In these mechanisms, it is believed that the bond-breaking of O-O on the catalyst surface is more challenging compared to Pt, leading to the dominance of the associative mechanism.⁵⁰⁻⁵²

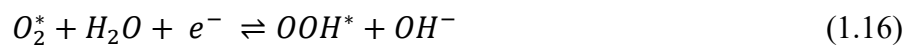
The ORR mechanism under alkaline conditions is similar to that under acidic solutions. The four-electron reduction could be separated by dissociate and associative pathway as shown below.

Alkaline dissociative mechanism (four-electrons)



Similar to the acidic dissociative mechanism, the diatomic oxygen is adsorbed on the active sites and the O-O bond is broken to generate O^* . Subsequently, a water molecule reacts with O^* to form a hydroxide ion (OH^-) and adsorbed hydroxide (OH^*), which is further reduced to hydroxide ion in the next step as shown in Equation (1.14). In contrast, the alkaline associative mechanism, which involved four electron reduction, is shown below.

Alkaline associative mechanism (four-electrons)



The adsorbed diatomic oxygen (O_2^*) interacted with a water molecule, forming hydroxide ions (OH^-) and OOH^* as shown in Equation (1.16). OOH^* is further reduced to hydroxide ions and an adsorbed oxygen atom, which will undergo reactions similar to those shown in Equation

(1.13) and Equation (1.14). Another possible reaction for OOH^* intermediate is shown in Equation (1.18).

Alkaline associative mechanism (two-electrons)



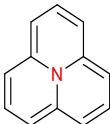
The production of hydrogen peroxide is undesirable since it can degrade the performance of PEMFC.^{53, 54} Therefore, the direct four electron reduction (dissociative mechanism) is more favourable for PEMFC. However, the dissociative mechanism has a very high energy barrier in the first step. To improve the performance of PEMFC, researchers have conducted DFT calculations to explore methods to avoid the formation of hydrogen peroxide and accelerate the bond breaking of O-O.^{50, 55}

Finally, pH has a significant effect on the ORR performance, not only for the platinum group catalysts but also for the non-precious metal single atom catalysts. The ORR performance is better under higher pH electrolytes than that of under acidic conditions. For the precious metal catalysts like Ag(111), there is almost no hydrogen peroxide generated in alkaline condition within the entire potential range.⁵⁶ However, under acidic conditions, a combination of two-electron and four-electron reductions is observed, because the interaction of $Ag-O_{2,ad}$ and $Ag-O_{ad}$ is not strong enough for O-O bond dissociation.⁵⁶

For non-precious metal catalysts with nitrogen doped carbon support (M-N/Cs), their ORR performances are also highly dependent on the pH, which could potentially involve the deprotonation / protonation of active sites.⁵⁷⁻⁶⁰ These types of catalysts are quite complicated

and potentially have more than one active sites, including the metal ions and different types of nitrogen doped carbon. Moreover, the active sites on these catalysts are not adjacent to each other; so the dissociative mechanism of ORR might be difficult to achieve. As the pH increases, the nitrogen atom will be deprotonated, potentially creating more active sites for the ORR. Consequently, the alkaline ORR performances for even metal-free nitrogen doped carbon are comparable to Pt.^{16, 17, 52} In acidic conditions, the metal centres become the main active sites, while the nitrogen is protonated.⁵⁷ Different types of nitrogen may be present in the M-N/Cs and their pK_a value are shown in Table 1.3. When the pH of electrolyte is higher than the pK_a value, then the nitrogen group will be deprotonated and become neutral as indicated in the table. At low pH conditions, the nitrogen will be protonated and protonated nitrogen might be favourable for oxygen interaction and proton transfer.⁵⁷ Although there are many literature proposed the possible active sites for M-N/Cs, there is no confirmed structure of these materials and it is very difficult to identify the active sites and also confirm their structures. The current consensus is that the atomic M-N_x, where x is the coordination number between 2 and 4.⁶¹

Table 1.3 The pK_a table of different type of nitrogen group might presented in M-N/Cs catalyst.⁵⁷

Group	Structure	pK _a ⁵⁷
Pyridinic N		6.5
Pyrrolic N		17.5
Graphitic N		-29.5

1.4 Electrokinetic and electrocatalysis

For all chemical reactions, there is a barrier that must be overcome for the reaction to take place, and this is known as activation energy (E_a). The magnitude of this barrier determines the rate of reaction and the rate constant can be calculated by Arrhenius equation as shown below: ⁶²

$$k = A e^{\left(\frac{-E_a}{RT}\right)} \quad (1.19)$$

where k stands for the rate constant of a reaction and it is crucial for the kinetic study. A is the pre-exponential factor, which indicates the frequency of collisions between reactants, R is the ideal gas constant and T is the temperature in Kelvin. The main objective of a catalyst is to provide an alternative route of reaction, which has a lower activation energy, and the interaction of catalyst and reactants stabilises the transition state. If the activation energy decreases and the temperature stays the same, the rate constant would increase and make reaction easier to take place. Similarly, the electrocatalyst also lowers the activation energy of an electrochemical redox reaction and a general electrochemical redox reaction is shown below:



where x , y and n are the stoichiometry for balanced equation. For most of cases in electrochemistry, the x and y are one. The equilibrium potential could be calculated by Nernst Equation as shown below: ^{62, 63}

$$E_e = E^\circ + \frac{RT}{nF} \ln \left(\frac{a_{\text{ox}}^x}{a_{\text{red}}^y} \right) \quad (1.21)$$

E° is the standard electrode potential under standard conditions. R and F are the ideal gas constant and Faraday constant respectively; T is temperature in Kelvin; n is the moles of electrons transferred in the redox process. a_{ox} and a_{red} represent the activities of oxidised and reduced species respectively. The current flow at any potential depends on the kinetics of electron transfer. The forward and backward current flow could be calculated by: ^{62, 63}

$$j_f = -nFk_f a_{ox}^x \quad (1.22)$$

$$j_b = nFk_b a_{red}^y \quad (1.23)$$

The reason why forward current flow has a negative sign before it is that the reduction current should be represented as negative. Once the equilibrium is reached, the forward current flow (j_f) and the background current flow (j_b) should be exactly the same. In other word, there is no net current flow within the cell and there are no overall chemical changes. The rate constants of forward and backward reaction (k_f and k_b) are related to the Arrhenius equation as shown in Equation (1.19). The potential applied can determine the rate constants as shown in Equation (1.24) and Equation (1.25).^{62, 63}

$$k_f = k_0 e^{\left(\frac{-\alpha_C nFE}{RT}\right)} \quad (1.24)$$

$$k_b = k_0 e^{\left(\frac{\alpha_A nFE}{RT}\right)} \quad (1.25)$$

k_0 is the standard rate constate at equilibrium, where the rate of forward reaction equals to the rate of backward reaction ($k_f = k_b = k_0$). α is the transfer coefficient between 0 and 1, which can be calculated by Marcus theory. For a simple electron transfer reaction, $\alpha_C + \alpha_A = 1$. Therefore, it could be also written in elimination form.

$$\eta = E - E_e \quad (1.26)$$

Overpotential (η) is the deviation of the potential from the equilibrium potential (E_e) as shown in Equation (1.26). If the applied potential of working electrode is more negative than the equilibrium potential, where η is negative, a reduction reaction would take place and a cathodic current would be observed. Vice versa, if the applied potential is more positive than the equilibrium potential, η is positive, and an oxidation reaction would occur, leading to an anodic current. When the overpotential is zero, the system is at equilibrium and the exchange current density (j_0) should be the same as j_b and $-j_f$. Therefore, the Bulter-Volmer equation was

developed to describe the relationship between the current density and the overpotential, as shown in Equation (1.27).^{62, 63}

$$j = j_0 \left[e^{\left(\frac{(1-\alpha_c) n F \eta}{RT} \right)} - e^{\left(-\frac{\alpha_c n F \eta}{RT} \right)} \right] \quad (1.27)$$

The Butler-Volmer equation is a fundamental equation in electrochemistry and provide insights into the kinetics of electrochemical reactions. At high positive overpotential, where $|j_b|$ should be much larger than $|j_f|$, the Butler-Volmer equation can be simplified to Equation (1.28).⁶³ Similarly, if the overpotential is very negative, the Butler-Volmer equation could be written as Equation (1.29).⁶³ However, if the overpotential is very small, the current density could be calculated based on Equation (1.30).⁶³

$$\text{when } |\eta| \gg 0, \log j = \log j_0 + \frac{(1-\alpha_c) n F}{2.3 RT} \eta \quad (1.28)$$

$$\text{when } |\eta| \ll 0, \log j = \log j_0 - \frac{\alpha_c n F}{2.3 RT} \eta \quad (1.29)$$

$$\text{when } |\eta| \ll \frac{RT}{\alpha_c n F} \text{ or } |\eta| \ll \frac{RT}{(1-\alpha_c) n F}, j = j_0 \frac{n F}{RT} \eta \quad (1.30)$$

Equation (1.28) and (1.29) is also known as Tafel equations ($\eta = a + b \log j$); the slope (b) and y-intercept (a) could be extracted from Tafel plot as shown in Equation (1.31).⁶²

$$a = \frac{2.3 RT}{\alpha n F} \log j_0; \text{ and } b = \frac{-2.3 RT}{\alpha n F} \quad (1.31)$$

Hence, the exchange current density (j_0) could be calculated from the Tafel slop, and the exchange current density should be related to the rate constant as shown below: ⁶²

$$j_0 = n F k_0 a_{ox}^{1-\alpha} a_{red}^{\alpha} \quad (1.32)$$

In order to increase the kinetic of an electrochemical reaction, a decrease in activation energy is required as mentioned previously and that is reason why a catalyst should be used in the reaction. However, for ORR, the mechanism is quite complicated and a heterogenous catalyst

increased the rate of reaction through several steps. Firstly, the reactants need to diffuse on the surface of catalyst and then interact with active sites of catalyst. Thirdly, there are several electron and proton transfer steps. Once the intermediate is formed, it can either desorb from the catalyst surface or further react to form the final product. Finally, the products will be desorbed from the active sites and diffuse into bulk solution. Therefore, there is a high demand to find descriptors for good ORR catalysts, which will be useful to design better catalysts in the future and prevent numerous trials and errors.

Sabatier principle states that the optimal catalyst should interact the reactants with an intermediate strength, neither too strong nor too weak.⁶⁴ If the interaction is too weak, the reactants would desorb from the active sites easily without undergoing any catalytic reaction. On the other hand, if the interaction is too strong, the desorption of products will be difficult, and the active sites could potentially get blocked. Therefore, the best catalyst should form an intermediate interaction with the reactants.⁶⁴ Sabatier principle also applies to the strength of interaction for the ORR, which is often illustrated using a graph known as the volcano plot. Two examples of volcano plots are shown in Figure 1.7. For precious metal catalysts (Figure 1.7 (a)), such as Pt (111) and Ag (111), they usually involve the dissociative mechanism with breaking an O-O bond. Therefore, a good catalyst should interact with oxygen neither too strongly nor too weakly. As shown in the graph, the Pt catalyst on the top is considered the best catalyst according to the DFT calculations.

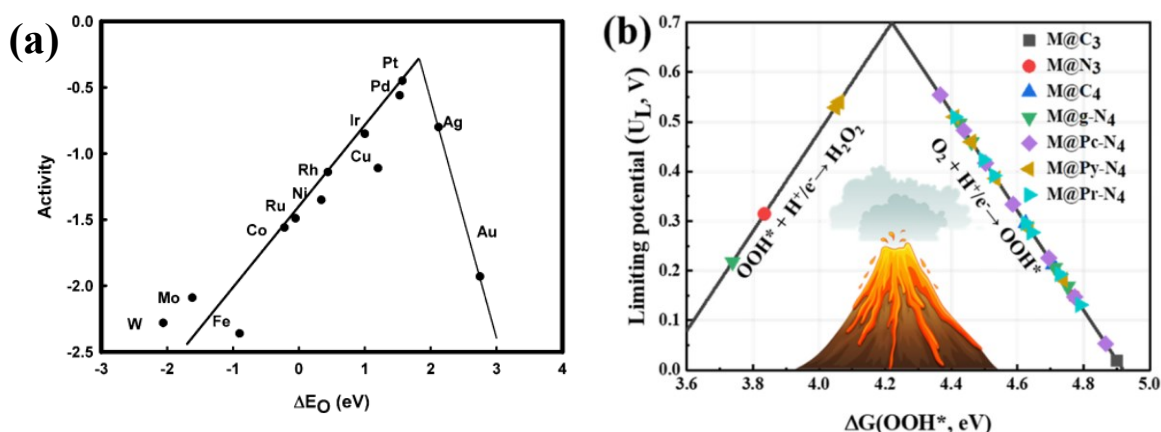


Figure 1.7 Two examples of Volcano plot for ORR. (a) A plot of electrochemical binding energy of oxygen on different metal surfaces⁶⁵; (b) Graph of electrochemical binding energy of OOH on non-precious metal single atom catalysts. [Printed with permission from ref⁵¹. Copyright © 2019, American Chemical Society]

However, for non-precious metal catalysts (Figure 1.7 (b)), the mechanism of ORR differs from that of precious metal catalysts. Although dissociative mechanism is more desirable for PEMFC, it is impossible for non-precious metal to catalyse the ORR through the dissociative pathway because there are no any adjacent active sites that would allow diatomic oxygen to attach and break the bond. As a result, the associative pathway becomes the only possible route for non-precious metal catalysts. However, there are two competitive reactions, including two electrons reduction to produce hydrogen peroxide, and four electron reduction to generate water. Therefore, the interaction with OOH is of crucial importance. Moreover, it is not only metal centres, but also nitrogen doped carbon that could potentially serve as the active sites for ORR. Hence, more studies had been conducted on the non-precious metal catalysts. In general, the interaction of active site with the reactant proves to be a good descriptor to determine the activity of catalyst. Understanding these interactions is essential for tailoring and optimising catalyst designs to improve their performance in the ORR.

1.5 Types of ORR catalysts

There are many known ORR catalysts, which have shown acceptable performances under different pH conditions. They can be categorised into three groups, including:

- 1) Platinum group metals and their alloys
- 2) Non-precious metal oxides, chalcogenides and oxynitrides
- 3) Non-precious metal single atom catalysts.

These catalysts will be discussed in the following sections.⁶⁶

1.5.1 Platinum group metals and their alloys

According to the Volcano plot shown in Figure 1.7 (a), platinum is identified as the most promising catalyst for ORR due to its intermediate interaction with oxygen. Therefore, extensive research has been done to study the catalytic ORR using platinum group catalysts and their alloys. For Pt-only catalyst, the ORR activity is found to depend on the facet and size of nanoparticles (NPs). In 0.5 M H₂SO₄ solution, Pt (111) exhibits slightly lower activity compared to Pt (100). However, a different trend is observed in 0.1 M HClO solution because ClO⁻ is weakly adsorbed and SO₄²⁻ is strongly adsorbed on Pt (111) in comparison to Pt (110). Therefore, it becomes crucial to synthesise Pt NPs with controlled facets and shapes to enhance the ORR activity under different acidic electrolytes.⁶⁷

In general, smaller NPs have a larger surface to volume ratio, which means that they present a larger number of surface sites, leading to increased mass activity if all sites are equivalent and have the same activity. However, as the particles size decreases, some facet sites might convert to edge sites, and the activities of these facet and edge sites are different.⁶⁸ Therefore, it does not necessarily mean that the smallest Pt NPs would give the best performance. According to the computational and experimental analysis, the optimum size of Pt NPs is around 2-5 nm. Further decreasing the size of Pt NPs would cause a decline in mass activity.⁶⁹ To improve the ORR performance, hollow Pt NPs had been developed and synthesised, which exhibited similar electrochemical surface areas (ESAs) with solid Pt NPs ($\sim 60 \text{ m}^2_{\text{gPt}}^{-1}$), but

five times higher mass activity per Pt mass ($1.2 \text{ mA}\mu\text{g}_{\text{Pt}}^{-1}$ for hollow Pt NP).⁷⁰ The activity of Pt-based catalysts is typically compared at $0.9 \text{ V}_{\text{vs. RHE}}$ because between $0.9 - 1.0 \text{ V}_{\text{vs. RHE}}$, Pt will be oxidised and PtO_x will cover the surface of Pt.⁷¹ Pt-enriched nanocages with facet (111) showed around 10-fold higher specific activity at $0.9 \text{ V}_{\text{vs. RHE}}$ (2.48 mAcm^{-2}) compared to Pt/C catalyst (0.25 mA cm^{-2}).⁷² M. Li *et al.* reported an ultrafine Pt nanowire with small diameters ($\sim 2.2 \text{ nm}$) and high ESA ($\sim 118 \text{ m}^2\text{g}_{\text{Pt}}^{-1}$), showing a specific activity of 11.5 mAcm^{-2} at $0.9 \text{ V}_{\text{vs. RHE}}$.⁷³ There are still numerous ongoing research to improve the ORR activity of Pt only catalysts and minimise the loading of Pt, aiming for more efficient and cost-effective catalysts for PEMFCs.

Furthermore, Pt alloyed with other metals or doped with certain elements has shown higher ORR activities than Pt metal only catalyst. In the early 1990s, S. Mukerjee *et al.* reported that the kinetics of ORR could be increased at least three times by alloying Pt with transition metal, such as Ni, Co and Mn.⁷⁴ Pt_3Ni has been widely studied due to its significantly higher performance compared to pure Pt catalysts.⁷⁵⁻⁷⁸ Various structures of Pt_3Ni have been investigated, including icosahedral⁷⁵ and octahedral^{76, 78}. One specific octahedral configuration with Mo doped Pt_3Ni exhibited a specific activity of 10.3 mAcm^{-2} and mass activity of $6.98 \text{ Amg}_{\text{Pt}}^{-1}$, demonstrating better performance and stability than Pt_3Ni catalyst without Mo doping. Moreover, DFT calculations were utilised to support the finding that the Mo-doping structure could increase the oxygen-binding energy, enhancing the catalytic activity.⁷⁶ In another study, eight $\text{Pt}_5\text{-M}$, where M represents alkaline earth metals and lanthanide group metals, were synthesised by the Chorkendorff group.⁷⁹ These catalysts demonstrated how the concentration of lanthanide elements could improve the catalytic reactivity and stability both using experimental data and also DFT calculation.⁷⁹

Other than alloying with another metal, Pt-based core-shell NPs have also shown the ability to decrease the loading of Pt while maintaining the similar ORR performances with Pt NPs. In a Pt-based core-shell structure, a thin layer of Pt or its alloys is deposited on a non-Pt NP core, and the activity and durability can be modified by the core-shell composition, size and shape.⁶⁷ Several studies have been done on these type of catalysts, including Pd, PdPt and transition metal carbide ($\text{Ti}_{0.1}\text{W}_{0.9}\text{C}$) as core with a monolayer of Pt.⁸⁰⁻⁸⁴ One of the main reasons for developing this core-shell structure is that approximately 70% of Pt in bulk of pure particles is not used during ORR reaction.⁸⁵

Indeed, the methods mentioned above have been successful in decreasing the loading of Pt for ORR and maximising the usage of Pt active sites. Impressive mass and specific activities have been reported; but the challenge lies in transferring these high performances from RDE testing to practical fuel cell applications.⁸⁶ Fuel cell operates as a two-phase system, where gaseous oxygen directly interacts with the solid catalyst. On the other hand, in RDE testing, gaseous oxygen needs to first dissolve in the aqueous electrolyte and then interact with the active sites of catalyst, creating a three-phase system. The difference in operating conditions and the complexities of the fuel cell environment can lead to variations in catalyst performance between RDE testing and real fuel cell applications. To address the issue of high-cost Pt catalysts, there is ongoing research to find alternative non-precious metal catalysts that can effectively substitute Pt.

1.5.2 Non-precious metal oxides, oxynitrides and carbonitrides

For non-precious metal catalysts, there are several different types that have been reported and, in this section, metal oxides, oxynitrides and chalcogenides will be focused on and discussed. Several metal oxides from Group IV and V, such as ZrO_2 , Co_3O_4 and Nb_2O_5 , have been studied for ORR under acidic electrolytes.⁸⁷⁻⁸⁹ Ota *et al.* proposed that the active sites for the oxygen

reduction reaction are high oxidation state surface metals with some oxygen defects.⁸⁷ However, these metal oxides face challenges due to their low conductivity and lack of adsorption site for oxygen. In order to improve the conductivity, metal oxides are supported on carbon nanotubes or carbon black. Moreover, decreasing the crystalline sizes of metal oxides could enhance the ORR performance by increasing the available active sites, surface defects and also conductivity.^{90,91} However, achieving excellent performance at $E > 0.7 \text{ V}_{\text{vs. RHE}}$, where the PEMFC is operating in a large-scale system, remains challenging for metal oxide catalysts.

Metal nitrides nanoparticles have also been synthesised and investigated for ORR.⁹²⁻⁹⁴ However, their ORR performances have been found to be even poorer than metal oxides, with an onset potential at around $0.6 \text{ V}_{\text{vs. RHE}}$.⁹² To enhance the performance of metal nitrides, researchers have explored the concept of doping nitrogen onto metal oxides, resulting in the formation of metal oxynitrides. These oxynitride are considered better candidates to substitute the Pt, as the hybridisation of O and N increased the conductivity. One method to prepare oxynitrides is to pyrolyse the catalyst under ammonia gas, which has been shown to increase the onset potential from $0.4 \text{ V}_{\text{vs. RHE}}$ to $0.8 \text{ V}_{\text{vs. RHE}}$.⁹⁵ Moreover, research by Ohnishi *et al.* revealed that pure NbN is not stable under acidic conditions, and pure NbO is not very active for ORR; niobium oxynitrides are relative more stable and active compared to pure niobium oxides and nitrides.⁹⁶ X-ray photoelectron spectroscopy (XPS) analysis indicated that catalysts with a clear N 1s peak demonstrated better performance, suggesting the importance of nitrogen in ORR, despite its instability. However, the stability of NbN catalyst could be improved by introducing oxygen, which will form niobium oxynitrides.⁹⁶

Metal carbonitrides have also been studied for ORR, particularly due to the high ORR performances demonstrated by the transition metal macrocyclic complexes. To prepared transition metal carbonitrides, researchers have utilised sputtering techniques to deposite

transition metal and carbon targets on a thin film under nitrogen atmosphere.⁹⁷⁻⁹⁹ Although the metal carbonitrides have shown improved performance compared to metal nitrides, they still fall short of Pt based catalysts in terms of ORR activity. To enhance their ORR performance, researchers have explored partially oxidised the metal carbonitrides to form a core of metal carbonitride with an oxide shell.^{100, 101} Ishihara *et al.* focused on synthesising a controlled degree of oxidation (DOO) of TaC_xN_y catalysts and comparing their ORR activities to highlight the effect of DOO.¹⁰⁰ They found that partially oxidation creates the oxygen vacancies, which act as the active sites for oxygen adsorption and electron transfer; therefore the partially oxidised TaC_xN_y catalysts exhibited better ORR activities than metal carbonitrides.¹⁰⁰

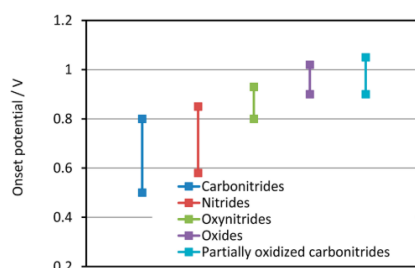


Figure 1.8 The onset potential of ORR for metal carbonitrides, nitrides, oxynitrides, oxides and partially oxidised carbonitrides in acidic electrolyte. [Printed with permission from Ref⁸⁵. Copyright © 2016, American Chemical Society]

Figure 1.8 summarises the comparison of onset potentials for various non-precious metal catalysts under acidic conditions, including non-precious metal oxides, nitrides, oxynitrides, carbonitrides and also partially oxidised carbonitrides. Among the studied catalysts, partially oxidised metal carbonitrides exhibit the most promising and active ORR performance, surpassing the other materials, including metal carbonitrides and nitrides, which demonstrate the least activity.

1.5.3 Non-precious metal single atom catalysts

The respiration of non-precious metal nitrogen doped carbon based catalyst came from the biological systems, as the transition metal macrocycles have been found to activate the oxygen. In 1964, the metal phthalocyanines, which have a similar structure with metal macrocycles,

were reported as new cathodic catalysts.¹⁰² This discovery sparked interest in exploring the potential of metal macrocycles and their derivatives as cathode catalysts. The concept of single atom catalysts (SACs) was first proposed by Qiao *et al.* in 2011. They highlighted that the dispersion of single atoms of Pt could maximise atom efficiency and also provide an excellent stability.¹⁰³ However, given the scarcity and high cost of precious metals, there has been a shift in research focus towards developing non-precious metal single atom catalysts (M-SACs / M-N/Cs) for ORR.¹⁰⁴

Catalysts could be categorised into two main types: heterogenous and homogenous catalysts. In case of homogeneous catalysis, the catalyst and reactants exist in the same physical state, allowing for efficient interactions and higher catalytic efficiency compared to heterogeneous catalysis. However, homogenous catalysts often suffer from poor stability and are challenging to separate, recycle and reuse, limiting their application. On the other hand, heterogenous catalysts offer the advantage of easy recycling, making them more economically viable and environmentally friendly. However, their catalytic efficiency is often lower due to the need for reactants to diffuse to the active sites. SACs present a unique opportunity by combining the advantages from both homogenous and heterogenous catalysts. With their high surface area, SACs can maximise the catalytic efficiency and SACs are easy to separate the single atom catalyst from reaction and reuse.¹⁰⁴

In the past decades, several different transition metals based single atom catalysts had been prepared for the ORR. These include Fe-N/Cs¹⁰⁵⁻¹¹⁴, Co-N/Cs^{106, 115-119}, Mn-N/Cs¹²⁰ *etc.* Additionally, some bimetallic SACs have been reported to exhibit high ORR performance.^{121, 122} However, one of the challenges in producing single atom catalysts lies in the high surface energy and instability of single atoms. At high temperature during pyrolysis, the agglomeration of metal atoms into nanoparticles can be easily triggered, leading to the loss of atomic

dispersion and reduced catalytic activity.¹²³ To address this challenge, different methods of preparing the non-precious metal single atom catalysts were explored, which will be discussed in the following section.

1.6 Methods of preparing the non-precious metal single atom catalysts

Over the past decades, numerous methods have been reported for preparing transition metal nitrogen doped carbon based single atom catalysts (M-SACs / M-N/Cs). These methods encompass a diverse range of techniques, including high temperature pyrolysis, ball milling, wet chemistry and atomic layer deposition methods. M-N/Cs catalysts exhibited different ORR performances under acidic and alkaline conditions. In this section, a variety of methods used to prepare M-N/Cs catalysts will be discussed, with a particular emphasis on their acidic ORR performances. The comparison of acidic and alkaline ORR performances will be detailed in the subsequent section.

1.6.1 High temperature pyrolysis method

High temperature pyrolysis is one of the most common and widely used methods for preparing M-N/Cs catalysts. Various approaches fall under this category, including template-assisted pyrolysis, metal-organic framework (MOF) pyrolysis, special metal precursor complex/mixture pyrolysis *etc.*^{104, 124} The pyrolysis process typically involves subjecting the precursor materials to high temperatures ranging from 600 to 1,000 °C. During pyrolysis, different atmosphere can be used, such as N₂, Ar, H₂ or NH₃, to create the desired M-N/Cs catalysts. These gases play a crucial role in promoting the nitrogen doping and atomic dispersion of metal species, which in turn contributes to the catalyst's enhanced ORR performance under acidic and alkaline conditions.¹²⁵

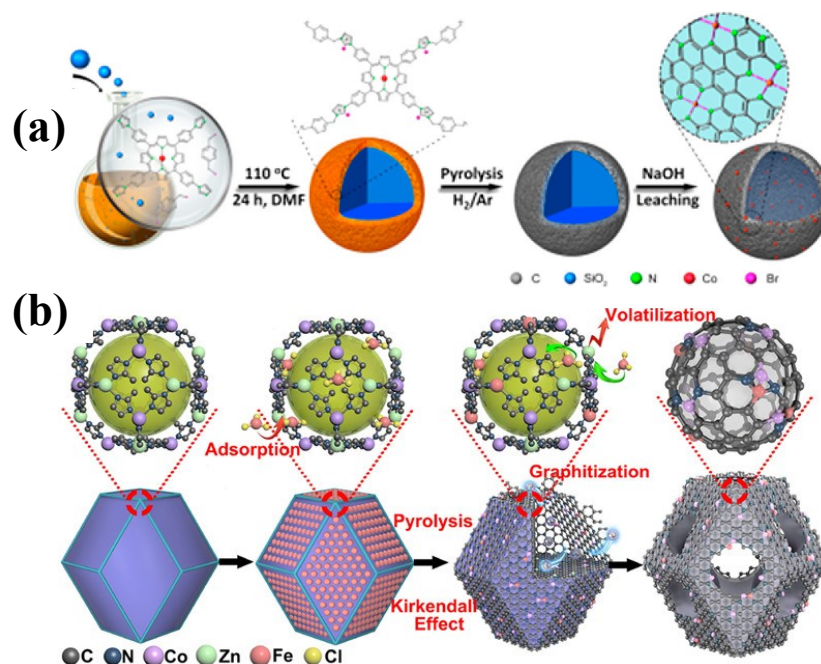


Figure 1.9 The example of (a) high temperature pyrolysis of hard-template with SiO₂ [Printed with permission from Ref¹¹⁵. Copyright © 2017, American Chemical Society]; (b) high temperature pyrolysis of ZIF-8 catalysts. [Printed with permission from Ref¹²¹. Copyright © 2017, American Chemical Society]

Template-assisted pyrolysis is a valuable approach for creating 3D porous structures with high surface areas, which significantly increases the accessible site density. Two types of templates can be utilised in this method: hard templates and soft templates. Hard templates involve using metal hydroxides or oxides as sacrificial templates or small organic molecules, metal complex or polymers as carbon precursors. Hydrofluoric acid is commonly employed to remove the hard templates, but this poses environmental and safety concerns for industrial applications. To address this, researchers have explored alternative methods. Han *et al.* synthesised a Co-based SAC (ISAS-Co/HNCS) with hollow N-doped carbon spheres and used SiO₂ as hard template, which was subsequently removed by NaOH etching and the synthesis method is shown in Figure 1.9 (a).¹¹⁵ The half-wave potential of ISAS-Co/HNCS under 0.5M H₂SO₄ is around 0.708 V_{vs. RHE}, which is comparable with the commercial Pt/C ($E_{1/2} = 0.773$ V_{vs. RHE})¹¹⁵. On the other hand, soft templates are another option for preparing the M-N/C catalysts, such as surfactant-assisted pyrolysis. In 2018, Yang *et al.* synthesised SA-Fe/NG¹⁰⁷ and CoN₄/NG¹¹⁶ using water-soluble surfactant F127. Soft templates generally offer easier removal compared

to hard templates. While hard templates can provide more stable and well-defined structures, their removal processes can be complicated and harsh, involving strong acids/alkaline or organic solvents. Soft templates offer a more accessible and convenient approach for catalyst preparation, making them a preferred option in some cases.¹²⁴

MOFs are 3D crystal frameworks composed of functionalised organic linkers and metal ions or clusters.¹²⁶ MOF-derived materials are known for their porous structures with high surface areas and nanoscale cavities, which allow small molecules to pass; and those properties would be helpful to give an attracting ORR performance.¹²⁷ Therefore, the MOF-derived catalysts for ORR have been extensively studied in recent years. Zeolitic imidazolate frameworks (ZIFs), especially ZIF-8 and ZIF-67, are the most common precursors used because they are easy to prepare and show very high ORR performances.¹²⁴ In 2017, Zhang *et al.* synthesised Fe doped ZIF crystals with controlled particle sizes (20-1000 nm) to study the effect of particles size on ORR performance.¹⁰⁸ They found that 50 nm was the optimal size for ORR and they further investigated the effect of pyrolysis temperature.¹⁰⁸ They observed that 800 °C was an important temperature because at this point, new bonds between Fe, N and C were formed and the iron was reduced from +3 to +2 oxidation state.¹⁰⁸ One concern with Fe-based material is their potential degradation through the Fenton reaction, where Fe^{2+} reacts with the hydrogen peroxide, generating hydroxide and hydroperoxyl radicals. Apart from Fe-based materials, Co doped materials derived from ZIF-8 have also been studied because Co is more stable under H_2O_2 and the Fenton reaction is slower with Co. He *et al.* developed a method to prepare Co-N₄ sites using ZIF-8 as a precursor and they identified 700 °C as the crucial temperature for Co binding with nitrogen.¹¹⁷ Researchers have also explored bimetallic dual sites catalysts. Wang *et al.* synthesised a Fe-Co dual sites catalyst from Zn/Co bimetallic MOF (as shown in Figure 1.9 (b)).¹²¹ And the half-wave potential of this dual sites catalyst is around 0.86 V_{vs. RHE} and it showed a high durability as the dual sites accelerate the bonding breaking of O-O and favour

the four-electron reduction reaction.¹²¹ Using ZIFs as precursors for ORR catalysts is currently a popular research topic due to their ability to control particle size effectively and provide high surface areas and porous volumes. However, commercial ZIFs can be expensive and self-synthesised ZIF may require large quantities of organic solvents, which may not be desirable for industrial applications.¹²⁴

Pyrolysing metal-containing complexes and precursors are another viable method to prepare M-N/Cs. Polyaniline (PANI) and cyanamide (CM) are examples of precursors that have been used for synthesising single atom catalysts.¹¹¹ The (CM+PANI)-Fe-C catalyst, for instance, demonstrated very high surface area ($\sim 1,600 \text{ m}^2\text{g}^{-1}$) and excellent ORR performance under 0.5M H_2SO_4 electrolyte ($E_{1/2} = 0.80 \text{ V}_{\text{vs. RHE}}$).¹¹¹ However, it is important to note that the process of preparing these precursors can be tedious and may not be suitable for large-scale industrial applications.

High temperature pyrolysis is a very promising method for generating single atom sites with high ORR performances. However, the problem is that the active sites are difficult to define after pyrolysis as there will be many different types of sites generated. Moreover, high temperature pyrolysis also tends to produce complex species, including $\text{M}(0)$ and MO_x nanoparticles, which are not as active as single atom sites for ORR. Furthermore, increasing the MN_4 sites are highly demanded to increase the ORR performance as they are widely accepted as one of the active sites in single atom catalyst. However, agglomeration of metal ions/ atoms into nanoparticles will happen at high temperature.¹²⁴

1.6.2 Ball milling method

Ball milling is a mechanochemical method with high energy, which is sufficient to overcome the E_a required for synthesising the catalysts.¹²⁸ There are numerous benefits to use ball milling in a chemical reaction because ball milling is a simple operation with relatively low operating

costs and does not require a large quantity of solvent during the reaction.¹²⁸ Therefore, using ball milling for catalyst preparation is very environmental-friendly. There are several papers reported that ball milling could be used for synthesising ZIF-8 and an example synthetic scheme is shown in Figure 1.10.



Figure 1.10 Example of preparing Co-doped ZIF precursor by ball milling method. [Printed with permission from Ref¹²⁹. Copyright © 2019, Elsevier Ltd.]

Mn(OAc)₂·4H₂O was used to prepare Mn doped ZIF-8 by ball milling, which exhibited a high ORR performance under both acidic and alkaline conditions. ($E_{1/2} = 0.8 \text{ V}_{\text{vs. RHE}}$ in 0.1 M HClO₄)¹²⁰ Similarly, an Fe-doped ZIF-8 was synthesised by ball milling with 2-methylimidazole and it showed a half-wave potential of 0.782 V_{vs. RHE} under 0.1 M HClO₄.¹⁰⁵ Other metal based ZIFs could be prepared in a similar way as well, such as Cu¹³⁰ and Co¹²⁹ based catalysts; however, these materials were not used for studying the ORR reactions. For all research mentioned above, ball milling was utilised for the preparation of transition metal doped ZIF-8 precursor, but high temperature pyrolysis is still required to form the M-N₄ sites.

1.6.3 Wet Chemistry Method

Wet chemical methods including hydrothermal, impregnation, co-precipitation and sol-gel *etc.* are commonly used for synthesising the precursors for SACs and an example is shown in Figure 1.11.^{104, 124} Poly(*o*-phenylenediamine) and ZnCl₂ are used to prepare Zn-N-C and Fe-N-C can be synthesised in a similar method.¹¹² These catalysts demonstrated ultrahigh loading of Zn as single atom sited and relatively good performance in RDE both under acidic and alkaline

conditions. Co-SAC catalyst is synthesised from the carbon molecular sieve (CMS) (shown in Figure 1.11), which is a 3D structure with adjustable porosity and ultra-high electrical conductivity.¹¹⁹ Although the synthesis method could be easily achieved in industry, the use of solvents is one of the problems need to be addressed. It is unavoidable to use large quantity of undesirable solvent or reagent for etching the materials. Moreover, high temperature pyrolysis is still required to carbonise the material and to achieve high conductivity.

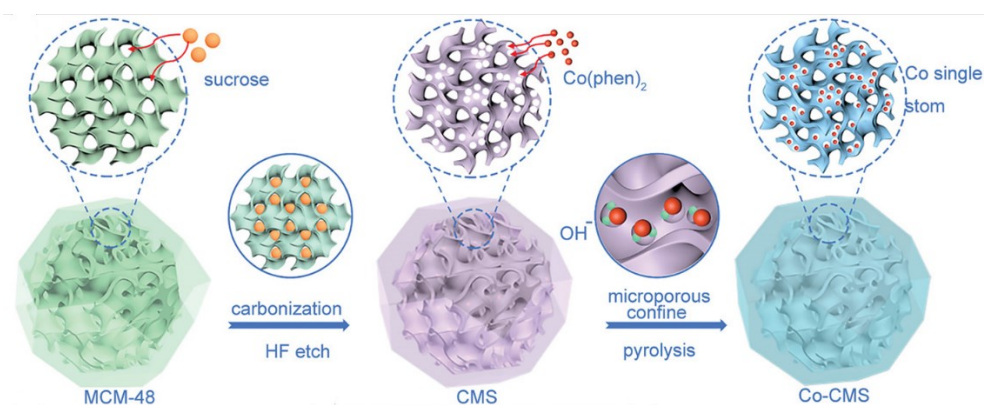


Figure 1.11 Example scheme of preparing M-N/C catalyst via wet chemistry methods. [Printed with permission from ref ¹¹⁹ Copyright © 2022, Wiley-VCH GmbH]

1.6.4 Atomic layer deposition method

Atomic layer deposition (ALD) is a technique to deposit the vapour of metal or metal oxide on a solid surface (growing film) as single atom sites or nanoparticle clusters. Unlike other method, ALD did not require thermal pyrolysis at the end.¹³¹ It is a precise way to control the size of particles and a promising and powerful technique to prepare SACs.¹³² In 2013, Zhang *et al.* reported a new method to prepare single atom niobium in graphitic layer by atomic layer deposition.¹³³ They studied the ORR performance and also conducted DFT calculations of this new Nb-in-C material, showing that the rearrangement of d-band electrons is more favourable for the dissociation mechanism.¹³³ Although it is a promising method to prepare SACs with controlled size, it has not gained much attraction in industry and not a lot of research had been done in this field due to several disadvantages. Firstly, ALD is a very expensive technique.

Moreover, the deposition process is very slow, leading to long processing time for depositing the SACs on a support. Additionally, extreme conditions are required for ALD, including under vacuum and also high temperatures.^{104, 124} These drawbacks have limited the widespread adoption of ALD for preparing SACs in practical applications.

1.6.5 Summary of different methods

There are many different methods reported to prepare SACs; however, they all have their own advantages and disadvantages as discussed above. The summary of pros and cons for each method is shown in Table 1.4. Additionally, ball milling and wet chemistry methods required high temperature pyrolysis afterward, as they can only provide the precursor. In the case of high temperature pyrolysis, there will not be any tedious synthesis process required before pyrolysis.

Table 1.4 Summary of different methods for preparing SACs, advantages and disadvantages of different methods.

<i>Method</i>	<i>Advantages</i>	<i>Disadvantages</i>
<i>High temperature pyrolysis</i>	1) High surface area with high porous volume 2) Controlled particle size 3) Promising high ORR activity	1) Tedious process 2) Strong acid/alkaline or large amount of solvent is required
<i>Ball milling</i>	1) Low cost of preparing catalyst 2) Favourable for large-scale production	1) Tedious process 2) Low purity 3) Time-consuming
<i>Wet Chemistry</i>	1) Easily apply in mass production 2) High performance in RDE and metal-air battery	1) Tedious process 2) Undesirable solvents and reagents are inevitable
<i>Atomic layer deposition</i>	1) Precise control of particle size and prevent formation of clusters	2) High cost 3) Slow deposition rate 4) Vacuum and high temperature environment

1.7 The ORR activity of M-N/Cs in different pH electrolytes

As mentioned in previous section, the mechanism of ORR highly depends on the pH of electrolytes used and different types of nitrogen have their unique pK_a value (shown in Table 1.3), which potentially influence the active sites for ORR in M-N/Cs. Therefore, in this section, a comparison of catalytic performance in various pH electrolytes will be presented and discussed. While there has not been a lot of research focused on the ORR performance in different pH conditions, it is crucial to understand the reasons why ORR performances depend on the pH as it could provide more detailed information about the active sites of M-N/Cs and ORR mechanism.

In alkaline conditions (0.1 M KOH), metal-free nitrogen doped carbon (N/Cs) have shown higher ORR performance than Pt/C.¹³⁴⁻¹³⁶ Behan *et al.* claimed that the ratio of graphitic-N (N_G) and pyridinic-N (N_P) can influence the mechanism and a N_G/N_P ratio of one favours the four electron reduction pathway.¹³⁵ Some metal-doped M-N/Cs (M=Fe, Co *etc.*) also have demonstrated very high ORR performance under alkaline conditions.^{106, 110, 137} However, it is really challenging to determine whether the high ORR activity is solely contributed by the M-N_x or if the N/C framework itself plays a role. Therefore, it is necessary to compare the alkaline ORR of M-N/Cs with the same structure N/Cs. However, maintaining the N/Cs scaffold is difficult, as the synthetic process might be altered with and without metal doping, making direct comparison challenging.

In acidic conditions, such as 0.1 M HClO₄ and 0.5 M H₂SO₄, only M-N/Cs showed reasonable performances. It is consensus that there is a significant disparity in ORR activities between acidic and alkaline conditions. Under alkaline conditions, it is common to observe E_{1/2} value around 0.90 V_{vs. RHE} even with metal-free N/Cs. However, in acidic electrolytes, M-N/Cs could barely achieve E_{1/2} around 0.80 V_{vs. RHE}. Only a few papers have discussed the acidic ORR

performance of N/Cs and compared it with activities in alkaline electrolytes.¹³⁸⁻¹⁴⁰ This difference in ORR activity under various pH conditions potentially indicates that the active sites in N/Cs are more active under alkaline condition; and the active sites in N/Cs only make a small contribution to acidic ORR. Therefore, it is crucial to consider the N/C framework activity when evaluating the performance of M-N/Cs in acidic conditions.

Only a few of papers tested the same M-N/Cs under both acidic and alkaline conditions to investigate the potential active sites of catalysts.^{57, 120, 141-144} Most studies have mainly focused on the catalytic performance without delving into the potential active sites of ORR in M-N/Cs, especially concerning the contribution of N/C framework in acidic ORR performance. Rojas-Carbonell *et al.* reported the pK_a of different types of nitrogen, which are potential active sites and test the ORR performance of Fe-N/C under 13 different pH electrolytes.⁵⁷ They found out that the key pH for changing the ORR mechanism is 10.5, as the rate of ORR below pH 10.5 is limited by the proton-coupled electron transfer. However, in alkaline conditions, the outer Helmholtz plane (OHP) mechanism is more likely to happen.⁵⁷ Malko *et al.* also studied the kinetic isotopic effect on ORR in both acidic and alkaline conditions.¹⁴⁴ The outer-sphere mechanism is more likely to happen at high pH, and in acidic conditions, the inner-sphere reaction plays a major role.¹⁴⁴

1.8 Proposal and structure of the thesis

The main objective of this work is to understand the active sites of non-precious metal single atom catalysts (M-N/Cs) and to optimise the synthesis of M-N/C in order to improve the catalytic performance in both RDE and PEMFC for ORR. To achieve this goal, there are several problems that should be solved and understood:

The first challenge is to prepare M-N/C catalyst with high metal content as single atom sites, as the current consensus in the literature is that single atom sites are the major active sites for

acidic oxygen reduction reaction. However, increasing the metal loading during synthesis raises the chance of forming metal nanoparticles or carbides.^{44, 85, 104, 124, 145} Therefore, it is important to find a way to prepare high metal content catalyst with all M-N/C sites. Transmetalation of zinc from pyrolysed ZIF-8 precursor potentially can solve the problem of forming other nanoparticles as the pyrolysed ZIF-8 had well-defined Zn-N_x sites.¹¹⁴ The formation of single atom sites could be identified by several characterisation techniques, including STEM, XAS *etc.* Moreover, the nitrogen adsorption analysis, XPS and TEM would be useful to understand the materials.

The second problem to be solved is understanding the active sites. Since the structure of catalysts could not be confirmed and this type of catalyst potentially contains more than one active site. To study the active sites, different metal centres with the same nitrogen doped carbon framework should be useful as it could be used to deconvolute the intrinsic activity contributed from the nitrogen doped carbon framework. Moreover, XPS can provide more information about the types of nitrogen, which can be correlated to the intrinsic activity. Nitrite stripping is an electrochemical method to quantify the sites density of single atom catalysts.¹⁴⁶ Nitrite stripping of different metals with the same nitrogen doped carbon catalysts could also help in deconvoluting the contribution of different active sites.

The most well-known and promising non-precious metal catalysts is Fe centre based materials. Therefore, further optimisations on increasing the metal content as single atom sites were investigated to improve the ORR activity and the optimised catalysts were tested both in RDE and in PEMFC. Since the testing condition of PEMFC is different with RDE, where a liquid electrolyte is used, the catalytic activities in PEMFC and RDE are slightly different.

Finally, this kind of catalyst has a great affinity to activate the molecular oxygen. Iron based phthalocyanine catalyst showed high activity in the epoxidation of alkene.¹⁴⁷ An heterogenous

Fe-N/C single atom catalyst, called Fe-ODAN, showed both high activity on ORR and epoxidation of alkenes with molecular oxygen.¹⁴⁸ Understanding the mechanism of heterogenous epoxidation with molecular oxygen would provide more information about the active sites of this single atom catalyst. Moreover, it is beneficial for organic synthesis as heterogenous catalysis is easier for recycling and reuse compared to homogenous catalysis. Further studies on the single atom catalyst heterogenous oxidation reaction have also been conducted during my PhD.

The thesis comprises three independent research works focused on the single atom catalysts in both electrochemical field and organic synthesis. Each chapter begins with a brief introduction outlining the background and the experimental techniques employed. The results obtained are then presented and thoroughly discussed. Finally, a separate conclusion for each chapter is provided, summarising the research findings and highlighting the key concepts of each study.

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Chapter 2 Experimental Techniques

In this chapter, a comprehensive exploration of electrochemical techniques and physical characterisation methods was introduced. These methodologies play a pivotal role in the research, providing valuable insights and data.

2.1 Electrochemical Techniques

2.1.1 Rotating disk electrode (RDE)

One of the most common methods to screen the electrochemical activity of catalysts is the rotating disk electrode (RDE) or rotating ring disk electrode (RRDE). RDE and RRDE allow testing the catalysts under quasi fuel cell conditions. This technique not only enables the comparison of catalytic performance among different catalysts but also provides mechanistic study and kinetic information, such as the number of electron transfers, the rate constant *etc.*¹⁻

³ Therefore, in this work, RDE and RRDE are the primary tools used for evaluating the catalysts.

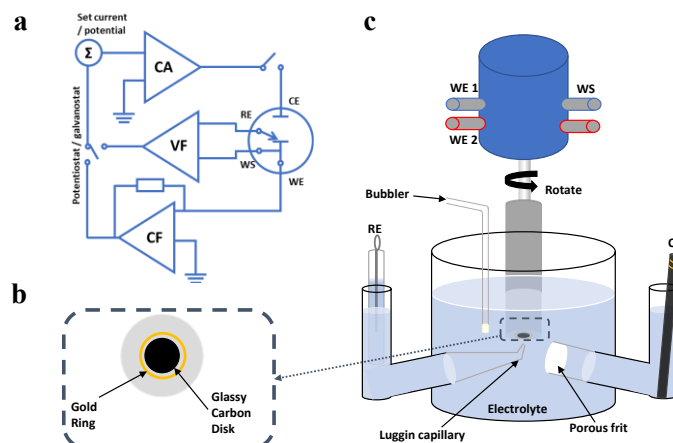


Figure 2.1 Three electrode set-up (a) schematic representation of the analog circuits of the potentiostat; (b) cross-section of the RRDE; (c) schematic diagram of three electrode set-up with an RRDE. [WE: working electrode; RE: reference electrode; WS: working sense electrode; CE: counter electrode; CA: Control amplifier; VF: voltage follower; CF: current follower.]

As shown in Figure 2.1 (c), a three-electrode cell is normally used for evaluating the performance of catalysts and in this system, it contains a reference electrode (RE), a counter electrode (CE) and a working electrode (WE). A separate electronic connection to the WE is provided by the working sense (WS) electrode, which is used to compensate for voltage losses in the cabling to the WE which can be important when currents are large. The four electrodes are connected to a potentiostat as shown in Figure 2.1 (a). The voltage follower (VF) uses a high impedance and low leakage current unity gain amplifier to provide the voltage difference between the WE and RE and thus the potential across the electrochemical double layer, driving the electrochemical process. At the summation point (Σ), the measured potential difference from the VF is subtracted from the desired set potential is able to control the signals required to generate the waveform for measurement as set in the computer; the control amplifier (CA) is used to amplify the output of the summation point. The current follower (CF) maintains the WE at a virtual earth whilst converting the current flowing through the WE to a voltage scaled by an appropriate factor to enable easy detection. The current is passed between the WE and CE. As the VF has a very high impedance, a negligible current passed through the RE. The potential applied is monitored between WE and RE.¹

For RDE, the WE should be the glassy carbon disk electrode and for RRDE, there are two WEs involved, where glassy carbon disk is the WE1 and the gold ring is the WE2 as displayed in Figure 2.1 (b). When RRDE is connected, a bipotentiostat will be used to collect the currents (i_d and i_r).² One of the benefits for using a three-compartment cell is that the solution resistance (R_s) could be minimised by placing the RE close to WE via a Luggin-Haber-capillary as shown in Figure 2.1 (c). However, there are still some uncompensated resistances (R_u), which cannot be removed due to the gap between the RE and WE. The WE should be at least $2d$ away from the capillary, where d is the diameter of the tip in order to avoid “shielding” (i.e. perturbation of the measured potential).² For all measurements in this work, the CE used was glassy carbon rod and it is separated by a porous frit, which prevent the species formed near CE from influencing the WE. The bubbler is used to purge the gases, such as oxygen, nitrogen or argon, into the electrolyte. For the RE used in this work, it will be either a reversible hydrogen electrode (RHE) or a commercial saturated calomel electrode (SCE). The potential of RHE will not shift with the pH of electrolyte and the potential of SCE could be converted to potential versus RHE by the Equation (2.1):

$$E(vs. RHE) = E(vs. SCE) + E^\circ(SCE) + 0.0591 \times pH \quad (2.1)$$

where the standard electrode potential of SCE should be 0.244 V.

There are three processes that take place for transporting the reactants to electrode, including diffusion, migration and convection.² Migration is neglected as there is an excess of supporting electrolyte. Therefore, only the diffusion and convection would be considered.² The measurement with a quiescent electrolyte could only be used for short timescale measurements (< 30 s) as the convection could be negligible; however, for long timescale measurements, the unstirred solutions are prone to convective interference from thermal gradients, making it difficult to obtain any kinetic information. Therefore, forced convection is normally used in

electrochemistry to enhance the mass transport and the most well-known technique is RDE/ RRDE as the electrode is rotating the electrolyte at frequency f and with angular velocity $\omega = 2\pi f(\text{s}^{-1})$.² The discussion of flow patterns in RDE/ RRDE is carried out in cylindrical polar coordination as shown in Figure 2.2 (a).¹ Figure 2.2 (b) and (c) are the vector representation of the flow velocities and schematic resultant streamlines of RDE respectively, where the surface of electrode is defined as $y = 0$.

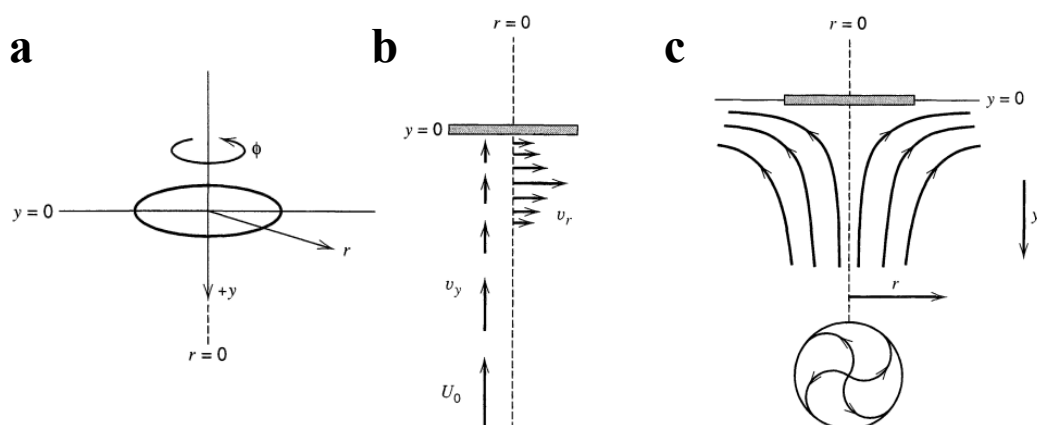


Figure 2.2 (a) Cylindrical polar coordinates for the RDE; (b) Vector representation of fluid velocities near a rotating disk; (c) schematic resultant streamlines.²

Even though there is a forced convection, the solution near the electrode still appears relatively stagnant and this is known as the hydrodynamic boundary layer δ_H , where the thickness depends on the rotation rate ω and kinematic viscosity ν . ($\delta_H = 3.6\sqrt{\nu/\omega}$)² The mass transport from the bulk solution to this stagnant layer is convection and within the stagnant layer, the mass transport of ions or molecules to the electrode surface is diffusion. The diffusion layer, δ_F , is much thinner than the stagnant layer and it also depends on the rotation rate ω . ($\delta_F \approx 0.05 \times \delta_H$). The current is controlled by the net mass transport of reactants to the surface of electrode, which is determined by the rotating rate of electrode; therefore, the current is still determined by the convection.² At the steady-state, the limiting current could be determined by the convective-diffusion equation. There are several simplifications could be made at limiting current condition, including $y = 0$, $C_R = 0$ and $\lim_{y \rightarrow \infty} C_R = C_R^*$, where C_R stands for the

concentration of reactant and C_R^* is the bulk concentration of reactant. The simplified convective-diffusion equation is shown below: ²

$$v_y \left(\frac{\partial C_R}{\partial y} \right) = D_R \frac{\partial^2 C_R}{\partial y^2} \quad (2.2)$$

where D_R is the diffusion coefficient of reactant ($\text{cm}^2 \text{ s}^{-1}$) and v_y is the velocity of fluid in y direction (cm s^{-1}). The current is the flux at the electrode surface and it could be determined by:

$$i = nFAD_R \left(\frac{\partial C_R}{\partial y} \right)_{y=0} \quad (2.3)$$

By solving the Equation (2.2) and combining with the Equation (2.3), it yields the Levich equation:

$$i_l = 0.62 nFAD_R^{2/3} \omega^{1/2} \nu^{-1/6} C_R^* \quad (2.4)$$

where n is the number of moles of electron transferred, F is the Faraday's constant (C mol^{-1}), A is the area of electrode (cm^2) and ν is the kinematic viscosity ($\text{cm}^2 \text{ s}^{-1}$). If the mass transport is efficient enough, the concentration of reactant at the electrode should equals to the concentration of bulk solution and the current measured should be determined by the kinetic of reaction only.² For an irreversible one-electron reaction, the disk current should be: ²

$$i_k = FAk_f(E)C_R^* \quad (2.5)$$

where i_k is the kinetic current in absence of any mass-transfer effects and $k_f(E)$ is the rate constant of reaction. However, the rate of a half reaction at the electrode is determined by not only the mass transport but also the sluggish kinetics of reaction. Therefore, the Koutecký-Levich equation is derived: ²

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_l} = \frac{1}{i_k} + \frac{1}{0.62 n F A D_R^{2/3} \omega^{1/2} \nu^{-1/6} C_R^*} \quad (2.6)$$

A plot of $\omega^{-1/2}$ versus i^{-1} should be a linear relationship and this graph would allow to calculate the number of moles of electron transferred and also the rate constant $k_f(E)$. The slope of the

line should be related to the diffusion coefficient D_R and also the number of electrons involved in the reaction step. The y-intercept (where $\omega^{-1/2} = 0$) should be the i_k^{-1} and the rate constant could be calculated based on i_k .

For ORR reaction, an RRDE electrode is commonly used as shown in Figure 2.1 (b), where the ring and disk electrodes are controlled independently by a bipotentiostats. In order to investigate the ORR reaction better, an I-E curve is recorded at the disk and the potential of ring electrode is hold constant (1.5 V_{vs. RHE}) to obtain information about the formation of by-product, H₂O₂. The ratio of disk current (I_d) to ring current (I_r) is known as collection efficiency (N):²

$$N = \frac{-I_r}{I_d} \quad (2.7)$$

As the reaction at ring should be the opposite of the reaction at disk electrode, there is a negative sign in the equation. In the case of ORR, the oxygen is reduced at the disk electrode, while the hydrogen peroxide is oxidised at the ring electrode; so the currents at the disk and ring should have different signs. Usually, the collection efficiency of an RRDE is determined by a redox reaction, such as Fe(CN)₆³⁻/ Fe(CN)₆⁴⁻ couple. For the ORR reaction, the yield of hydrogen peroxide could be calculated by:

$$H_2O_2(\%) = \frac{2I_r/N}{I_d + I_r/N} \times 100\% \quad (2.8)$$

2.1.2 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is a very complex and useful technique in electroanalytical chemistry.^{4, 5} Resistance (R) is measured by direct current (DC), which follows the Ohm's law:

$$R = \frac{V}{I} \quad (2.9)$$

Impedance (Z) is an electrochemical resistance measured by passing an alternating electrical current (AC) and it could be calculated by: ⁵

$$Z = \frac{V(\omega)}{i(\omega)} \quad (2.10)$$

where $V(\omega)$ is the frequency-dependent voltage, $i(\omega)$ is the frequency-dependent current and ω is the angular frequency of an oscillating sine wave. In the EIS measurement, a sinusoidal potential (or current) signal is applied and the response current (or potential) signal is recorded and analysed.⁵ One of the simplest methods is measuring the EIS at its equilibrium, open circuit potential (OCP).¹ For all experiments done in this work, the potentiostatic EIS, which applied potential signal and recorded current signal, is measured under OCP unless stated.

Frequency response analyser (FRA) is used in the potentiostat to control the frequency and amplitude of potential signal and the applied potential is: ⁴

$$E(t) = E_0 \sin(\omega t) \quad (2.11)$$

where E_0 is the amplitude of potential sine wave, t is the time and ωt represents the phase of waveform. And the output signal of current is: ⁴

$$i(t) = i_0 \sin(\omega t + \phi) \quad (2.12)$$

where ϕ stands for the phase shift or phase angle. Normally the frequency measured from around 10 kHz to around 0.1 Hz. The plot of $E(t)$ versus $i(t)$ is known as *Lissajous plot*. If the potential signal and current signal are in-phase ($\phi = 0^\circ$), then the Lissajous plot should be a line. However, if they are out of phase, a tilted oval will be observed, and a perfect circle will be seen only when $\phi = 90^\circ$.^{4, 5}

According to Euler's relationship ($\exp(j\phi) = \cos\phi + j \sin\phi$), the impedance could be rewritten as: ^{4, 5}

$$Z(\omega) = \frac{E_0 \exp(j\omega t)}{i_0 \exp(j\omega t - \phi)} = Z_0 \exp(j\phi) = Z_0(\cos\phi + j\sin\phi) = Z_{re} + jZ_{im} \quad (2.13)$$

where j is the complex number ($j^2 = -1$). Therefore, the impedance Z is consisting of two parts, including real part Z_{re} and imaginary part Z_{im} ; and the magnitude of impedance $|Z|$ could be determined by: ^{4, 5}

$$|Z| = \sqrt{(Z_{re})^2 + (Z_{im})^2} \quad (2.14)$$

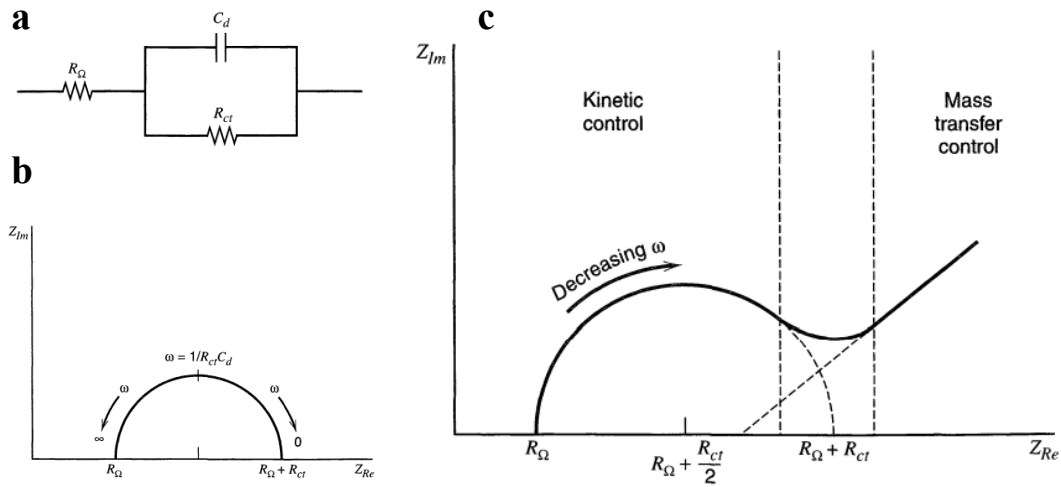


Figure 2.3 (a) Equivalent Randles circuit of a faradic half reaction; (b) Impedance plane plot for Randles circuit; (c) Impedance plot of an electrochemical system.²

In order to analyse the EIS data, circuit modelling is usually required. There are lots of different elements could be used for modelling, but for a simple system, like RDE, Randles' circuit is normally used, which is shown in Figure 2.3 (a).² R_Ω stands for the solution resistance, which is used for iR compensation; R_{ct} and C_{dl} are the charge transfer resistance and capacitance of electrochemical double-layer, respectively.² An electrochemical double-layer is formed by the negatively charged electrode as a plate and the hydrated cation as another plate. A plot of $|Z_{re}|$ versus $|Z_{im}|$, which is called Nyquist plot, is normally used for analysing the impedance and an ideal Nyquist plot of Randles circuit is shown in Figure 2.3 (b).² At high frequency ($\omega \rightarrow \infty$), the current will pass through the capacitor as the C_{dl} is smaller; however, at low frequency ($\omega \rightarrow 0$), the current will pass through the resistor R_{ct} instead.² Hence, the R_Ω and R_{ct} could be determined by the Nyquist plot.

However, the real system is slightly more complicated than the Randles circuit and a typical Nyquist plot in a real system is shown in Figure 2.3 (c).² It is separated into two regions, including kinetic control and mass transfer control.² If the R_{ct} is very large, the mass transfer only has a limited contribution, and the shape will be similar to the ideal cases (Figure 2.3 (b)).² However, if the R_{ct} is extremely small and the mass transport plays a significant role, then the Nyquist plot should be a linear plot with an angle of 45° .²

2.1.3 Cyclic Voltammetry (CV) and Linear Sweep Voltammetry (LSV)

Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) are the most widely used techniques to compare the electrochemical activities of different catalysts. LSV only scans from one potential E_1 to another E_2 at a fixed scan rate while recording the current, whereas CV sweeps between E_1 and E_2 at a fixed scan rate and the sweep is reversed once it reaches E_2 .¹ The plot of potential versus current is known as voltammogram and the scan rate can range from a few mVs^{-1} to a few hundred Vs^{-1} .¹ Typically, recording CVs over a wide range of sweep rates and potentials will be done to understand the electrochemical reactions as the appearance and disappearance of peaks, and also the amplitudes of peaks can be used to identify whether a diffusion, adsorption or coupled homogenous chemical reactions happened.¹ The difference between first and subsequent scans is normally used for mechanistic studies.¹ In order to get kinetic information, only the first scan will be used for analysing.¹

In this work, all CVs and LSVs of ORR are recorded using the RDE/RRDE setup shown in Figure 2.1 (c). Relatively low scan rates are used in order to achieve steady state performance. However, for some fast surface adsorbate reaction, the current might not be easily detected; hence, a current integrator would be introduced in such cases, especially for quantifying the site density of catalysts by nitrite stripping method, which will be discussed in Chapter 3. The charge passed in a CV could be calculated: ²

$$Q = \frac{IV}{\vec{V}} \quad (2.15)$$

where $\vec{V}$ stands for the scan rate (Vs^{-1}), I and V are the current in A and potential in V, respectively.²

A break-in process will be done before under N_2 or O_2 -saturated electrolyte to activate and clean the catalyst surface. More importantly, this process allows the catalyst surface to be properly wetted with electrolyte. The break-in CVs will be scanned until the performance stabilises and then the measurement of ORR could be carried out. Finally, a background measurement and correction will be done with the same potential range and sweeping rate as the ORR measurement, but under N_2 or Ar-saturated electrolyte to get the current for faradaic reaction. The capacitive current measure under N_2 could be used to estimate the specific surface area of the catalyst. The double-layer capacitance could be calculated by: ²

$$C_{dl} = \frac{i_{dl}}{\vec{V}} \quad (2.16)$$

where i_{dl} is the charging current of double layer. Normally, different scan rates will be used to calculate it more accurately. Then, the electrochemical specific surface area could be determined.

2.1.4 Ink preparation for the RDE measurements

For all RDE/RRDE measurements done in this work, the ink was prepared using the same composition to ensure a uniform and flat catalyst layer when deposited onto the glassy carbon electrode. 5 mg of powder catalyst was mixed with 1,038 μL of isopropanol (Sigma-Aldrich) and ultrapure water (MilliQ 18.2 $\text{M}\Omega\text{ cm}$) solution, in which they had the same volume ratio, resulting in a 0.5 wt% of ink. Then, 54 μL of 5 wt% Nafion[®] solution (Sigma-Aldrich) was added and the mass of Nafion[®] should be half of catalyst added. The ink was sonicated at least for 30 mins to achieve a homogeneous dispersion. 8.56 μL of ink was drop-casted onto the

glassy carbon (0.196 cm^2) of RDE or RRDE (Pine instruments, model AFE2M050GC and rotator model AFMSRCE) to achieve a loading of 0.2 mgcm^{-2} . The catalyst was dried with rotation around 300 rpm. Once it was dried, the catalytic performance could be tested under different electrolytes and condition. The detailed testing protocols will be discussed in the experimental sections of the following chapters.

2.1.5 Membrane Electrode Assembly (MEA)

It is indeed crucial to test the catalyst in a real operating system to evaluate their performance accurately. To achieve this, a membrane electrode assembly (MEA) is prepared for testing the catalyst in a fuel cell setup. However, due to the time-consuming nature of preparing the MEA and conducting the testing processes, only the most promising catalysts are selected for evaluation in the fuel cell system. This selective approach allows for a focused investigation of the catalysts with the highest potential for practical applications.

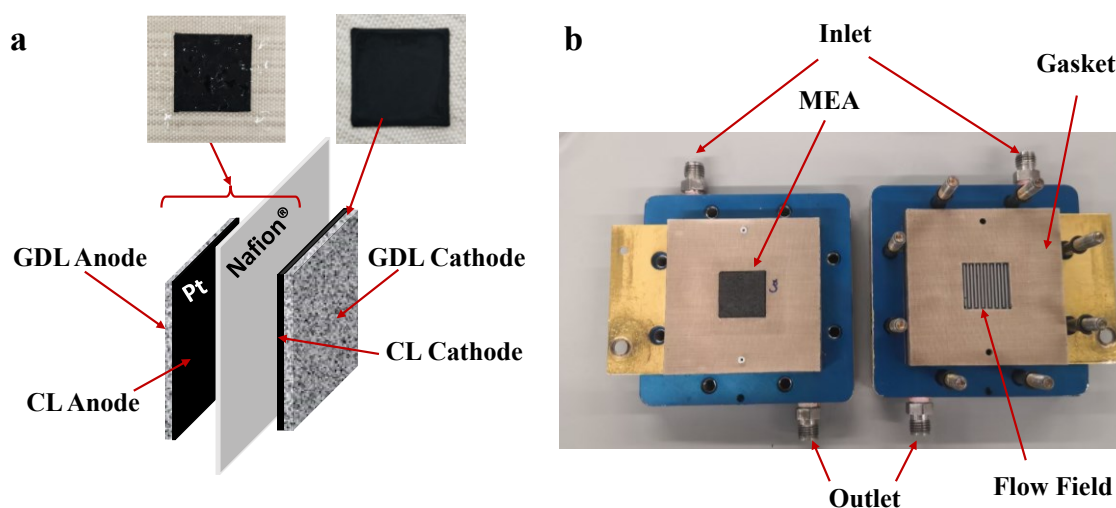


Figure 2.4 (a) Schematic diagram of MEA (GDL: gas diffusion layer; CL: catalyst layer). (b) PEMFC with MEA embedded onto the anode side (left) with gasket. Screwed the cathode and anode sides to give a completed cell.

The MEA consist of three main components, including two catalyst layers (CLs), two gas diffusion layers (GDLs) and an ion exchange membrane, as shown in Figure 2.4 (a). For the PEMFC, Nafion® 211 is commonly used as the ion exchange membrane due to its high proton conductivity and stability.⁶ In order to prepare MEA, the catalyst layer (CL) can be deposited

either on the GDL or on the membrane; also there are various methods available for ink deposition, such as spraying, drop-casting *etc.*⁶ In this PhD work, all MEAs are prepared by drop casting the catalyst onto the cathode GDL, while the anode side is a commercial Pt electrode. The MEA is obtained by hot-pressing the two electrodes and Nafion[®] membrane in the middle, ensuring that CLs come into contact with the Nafion[®] membrane as shown in Figure 2.4 (a).

The prepared MEA is then embedded into a single cell, as shown in Figure 2.4 (b). This single cell setup contains graphite bipolar plates with flow field, gas inlets, outlets, thermocouple and heaters. Glass-reinforced PTFE gaskets were used to control the MEA compression (~20 - 25 %) and also the system is sealed by screwing with a defined torque.⁶ Once the cell is fixed, it can be connected to a load cell and/or a potentiostat through the current collectors which are the gold plates.⁶ The gases, such as H₂, O₂ or air are supplied with humidification by water and the relative humidity (RH) is determined by the temperature of gases supplied and cell temperature.⁶ Moreover, the gas flow is controlled by mass flow controllers (MFCs). The gases, including unreacted reactants and products, will flow out through a condensate collection tank with a back-pressure regulator.⁶ The cell temperature is normally set to 80 °C. The high frequency resistance (HFR) is measured automatically at 1,000 Hz by the system, and this is the resistance used for iR compensation during the experiments.

2.1.6 Ink preparation for the MEA fuel cell measurements

A commercial Pt electrode (0.4 mg_{Pt}cm⁻², Alfa Aesar, Johnson Matthey, Hydrogen Reformante/Cathode) and a homemade cathode were used to make the MEA for PEMFC testing. 20 mg of powder catalyst was mixed with 220 µL of ultrapure water (MilliQ 18.2 MΩ cm) and 585 µL of isopropanol (Sigma-Aldrich), where the mass of two solvents should be 11 and 23 times of mass of catalyst respectively. Some of ink is prepared with an additional 15

wt% of Vulcan Carbon XC72R to increase the electrical conductivity and the volume of solvent will be adjusted to 258 μL of ultrapure water and 688 μL of isopropanol. The ink was sonicated for around 1 h and then 435 μL of Nafion[®] (5 wt% solution, Sigma-Aldrich) was added in. The mass of Nafion[®] should be 50 wt% of catalyst. Another 1 h of sonication was done to make sure the ink was dispersed homogenously. Then a drop casting method was used to deposit the ink onto a 5 cm^2 gas diffusion later (GDL, 29BC, SGL) at around 70 °C and the catalyst deposited GDL was dried in a vacuum oven at 70 °C for 30 mins. A pre-treated Nafion[®] 211 membrane was used to make the MEA and they were hot-pressed at 130 °C for 3 min under an applied pressure of 400 kg cm^{-2} .

2.2 Physical and analytical characterisation methods

2.2.1 Nitrogen adsorption analysis

One of the main reasons why single atom catalysts are desirable is that they normally have a very high surface area compared to bulk materials. In order to quantify the surface area and porosity of a catalyst, the Brunauer-Emmett-Teller (BET) method is widely used in the lab. This technique was developed by Stephen Brunauer, Paul Emmett and Edward Teller in 1938, and is an extension of Langmuir theory.⁷ While Langmuir theory could only apply to monolayer adsorption of gas molecules⁸, the BET theory applies to multilayer systems.⁹ There are five hypotheses were introduced in the BET theory: ⁹

1. Only one adsorbate can be adsorbed on the surface sites and all surface sites have the same adsorption energy for adsorbate. All adsorbate molecules are considered to be spherical and have a specific cross-sectional area.
2. The enthalpy of adsorption for the first layer is constant and the enthalpy of adsorption increases with number of layers.

3. Gas molecules can adsorb on a solid in layers infinitely. However, different adsorption layers will not interact each other.
4. The Langmuir theory can be applied to all layers.
5. At saturation pressure, the number of layers approaches infinity, and the enthalpy change of adsorption is the same as the enthalpy change of liquefaction.

Probing a gas, which is also known as adsorbate, to the catalysts at a low temperature could be used to calculate the surface area. Normally, nitrogen will be used at 77 K, which is the boiling point of N₂. Other probing gases, such as argon (87 K) or carbon dioxide (273 K) or even some organic vapours, could also be used.¹⁰ In order to analyse the BET surface area, a physisorption isotherm is usually used to transform it into a BET plot, which will be discussed later. Adsorption hysteresis arise when the adsorption and desorption curves do not overlap each other.¹¹ For different types of materials, there are six hysteresis loops for pore structures, which have been reported in IUPAC, and the examples of their isotherm are shown in Figure 2.5. Usually the relative pressure (p/p°) will be plotted in the x-axis, where p is the equilibrium pressure and p° stands for the saturation vapour pressure at the adsorption temperature.¹¹ For uniform mesopores, such as templated silica or mesoporous carbon, the isotherm should be H1 type.¹¹ H2 types represent more complex pore structures; silica gels and monocellular silica foams normally gave H2(a) and H2(b), respectively.¹¹ Non-rigid aggregates of plates-like particles would usually perform like H3. H5 is a very unusual type; only both open and partially blocked mesoporous material would give isotherm like H5.¹¹ For the catalysts used in this work, it is usually a H4 type material, which is micro-mesoporous carbon material.¹¹

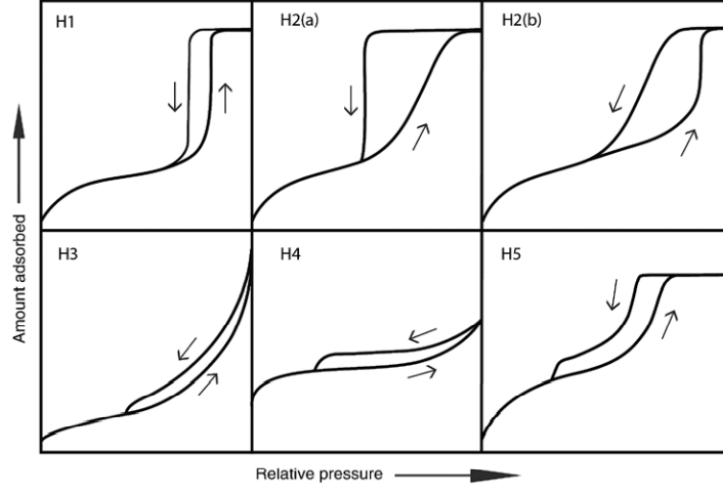


Figure 2.5 Examples of the six types of hysteresis loops ¹¹

Once the N₂ isotherm is obtained, it should be converted to a BET plot ($\frac{p/p^\circ}{n(1-p/p^\circ)}$ versus p/p°)

first to calculate the surface area and the BET equation is as follows:¹¹

$$\frac{p/p^\circ}{n(1-p/p^\circ)} = \frac{1}{n_m C} + \frac{C-1}{n_m C} (p/p^\circ) \quad (2.17)$$

where n is the specific amount adsorbed at the relative pressure p/p° , n_m is the specific monolayer capacity and C is a BET constant, which is determined by the energy of monolayer adsorption. C is exponentially related to the energy of adsorption, as shown:

$$C = \exp\left(\frac{E_1 - E_L}{RT}\right) \quad (2.18)$$

where E_1 is the energy of adsorption in the first layer and E_L is the energy of adsorption at higher layers. BET should show a linear relation within the range p/p° around 0.05 to 0.30.

Based on the linear region, the n_m and C could be determined by the slope and y-intercept.

Then the BET specific surface area could be calculated by:

$$a_s(BET) = \frac{n_m L \sigma_m}{m} \quad (2.19)$$

where $a_s(BET)$ is the BET specific area, σ_m is molecular cross-sectional area, L is the Avogadro constant and m is the mass of catalyst. Not only the BET specific surface area, but also the pore size distribution (PSD) of micro-pores (the width of pore is less than 2 nm) and meso-pores

(the width of pore is between 2 nm and 50 nm) could be determined based on the isotherm, where p/p° is in a range between 0.4 and 0.97.¹² The Barret, Joyner, Halenda (BJH) method could be used for the pore size less than 60 nm; so BJH is usually used for carbon blacks.¹² For the pore size less than 2 nm, which is the micropore, the Broekhoff-de Boer equation could be used and the t-plot could extract the micropore area.¹²

For all BET measurements done in this work, the samples were dried at 130 °C under a continuous flow of nitrogen to degas the power and also remove the physically adsorbed water on the surface. Then, a multipoint BET was used to calculate the surface area by Micromeritics Tristar II 3020 instrument.

2.2.2 Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Spectroscopy (EDS)

Scanning electron microscopy (SEM) is a convenient and powerful technique for observing the morphology of catalysts at different synthetic stages. All measurements are done under vacuum, so a vacuum pump is usually attached to the SEM machine as shown in Figure 2.6 (a). The electrons are generated by the electron gun installed in the SEM; the electron beam is focused onto the sample and accelerated by a high voltage (5 kV or 15 kV) to act as a light source. When the electron beam interacts with the sample, secondary electrons will be emitted from the substrate, backscattered electrons, X-rays, light, heat and transmitted electrons. Secondary and/or backscattered electrons are collected for the SEM's imaging. The sample tested in the SEM must be conductive; if it is non-conductive, a thin layer of metal, such as gold, should be sputtered coated onto the surface of sample. Additionally, energy dispersive X-ray spectroscopy (EDS/EDX) is often connected to the SEM as well to obtain the elemental mapping of sample. EDS is an emission spectroscopy of X-rays. The high energy electron beam would excite the electrons in the samples to an excited state, where the electrons are in a higher

energy level. However, this higher energy level is not stable and the electron tends to relax back to the ground state with an emission of X-ray. Different energy of emitted X-ray corresponds to different elements in the sample, allowing for elemental mapping.

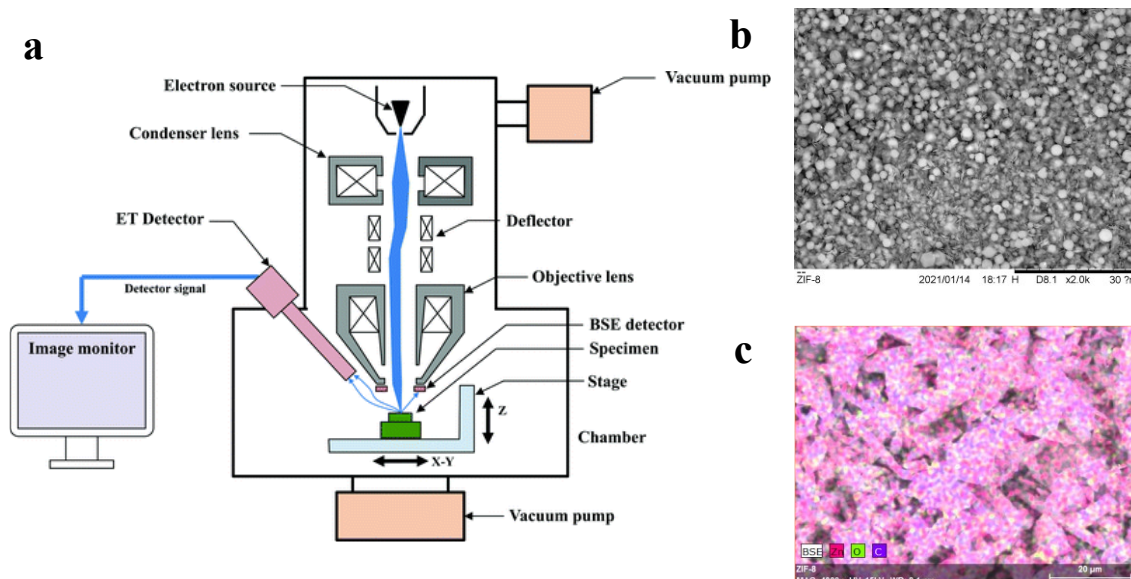


Figure 2.6 (a) Schematic diagram of scanning electron microscopy ¹³; (b) example of SEM on homemade ZIF-8 ; (c) example of EDS elemental mapping on homemade ZIF-8.

The metallic aluminium stubs, which is immobilised with carbon tape, are commonly used as a sample holder for SEM. The catalysts were deposited on the carbon tap and tested in the SEM machine. The example of SEM and EDX elemental mapping on the homemade ZIF-8 is shown in Figure 2.6 (b) and (c) respectively. Based on Figure 2.6 (b), the morphology of homemade ZIF-8 could be identified, consisting mainly of polyhedrons. The EDS elemental mapping (Figure 2.6 (c)) confirms that the elements Zn, C and O are evenly distributed in the ZIF-8 sample. All SEM and EDS images presented in this work were acquired using the Hitachi TM3030, unless stated.

2.2.3 Transmission Electron Microscopy (TEM) and Energy Dispersive X-ray Spectroscopy (EDS)

Transmission electron microscopy (TEM) is another useful microscopy that provides detailed information about the structure of materials. The schematic diagram of TEM with energy

dispersive spectroscopy (EDS) is shown in Figure 2.7 (a). Unlike SEM, the beam of electrons in TEM transmits through thin samples to form an image.¹⁴ Therefore, the sample must be very thin (approximately 100 nm in thickness) to allow the electron beam to pass through.¹⁴ The transmitted electrons are magnified and focused by electromagnetic fields onto a fluorescent screen, which is a layer of photographic film and is used as imaging device.¹⁴ The resolution of TEM is significantly higher than the optical microscopes as the electrons have a much smaller de Broglie wavelength, which allows the instrument to capture the fine details. The resulting TEM image is a 2D representation, therefore this becomes the limitation of TEM imaging as most of materials, such as the amorphous materials are 3D samples.¹⁴ Consequently, providing 3D information about the catalyst may be difficult, but TEM remains a powerful technique for investigating the crystalline domains in nanomaterials.¹⁵ Moreover, EDS is usually equipped with the TEM to provide the elemental mapping in the sample, allowing to analyse the elemental composition of the sample.

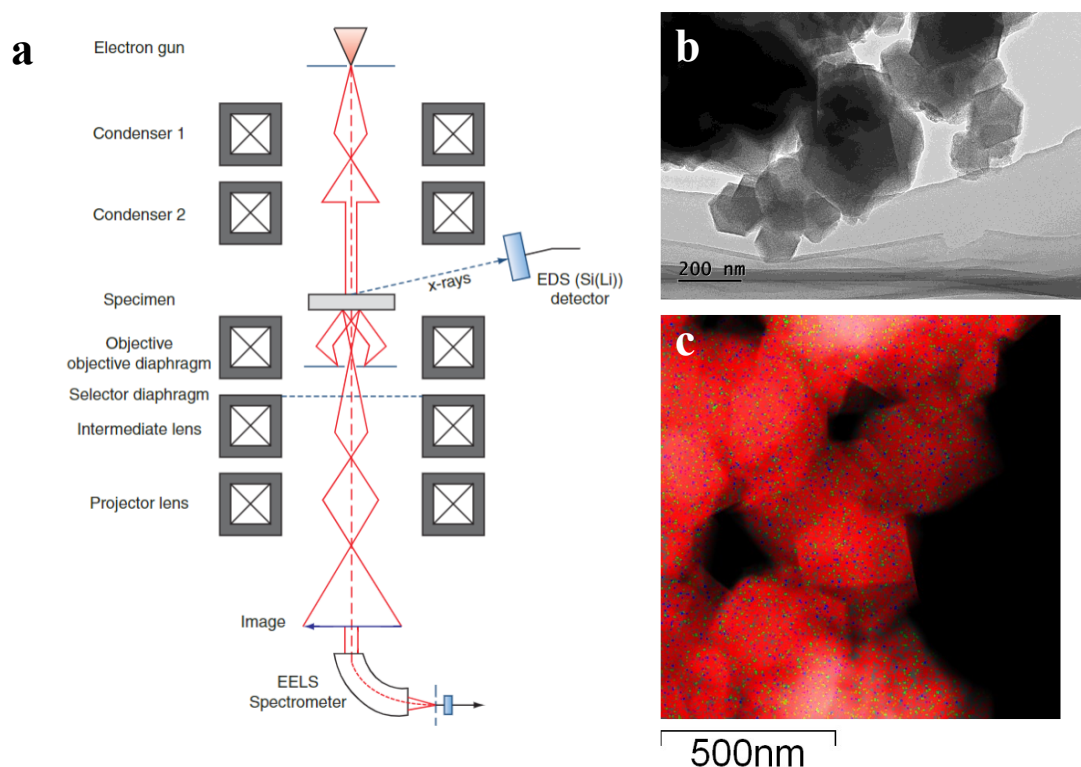


Figure 2.7 (a) Schematic diagram of transmission electron microscopy (TEM)¹⁵; (b) example of TEM image of Fe-N/C catalyst; (c) example of EDS mapping of Fe-N/C where red is Cl, blue is zinc and green is Fe.

As shown in in Figure 2.7 (b) and (c), these are representative examples of TEM and EDS elemental mapping of Fe-N/C catalyst, which will be discussed in Chapter 4. The TEM imaging and EDS elemental mapping measurements were obtained from a FEI Titan Tecnai G2 F20 and they were done by one of the collaborators in China United Test& Certification Co. ltd. (CUTC).

2.2.4 Scanning transmission electron microscopy (STEM) with electron energy loss spectroscopy (EELS)

Scanning transmission electron microscopy (STEM) is a special type of TEM. The main difference is that the electron beam is focused at large angles and converged into a fine point, which is then scanned over the sample in a raster illumination pattern.¹⁶ There are various detector can be used to obtain high-quality images, including bright-field (BF) detector, annular dark-field (ADF) detector and high-angle annular dark-field (HAADF) detector.¹⁶

Electron energy loss spectroscopy (EELS) is often combined with STEM to gain additional information, such as the local chemical environment.¹⁷ Normally the EELS could be obtained simultaneously with STEM imaging, allowing for direct correlation of spectroscopy information with the STEM image.¹⁶ Some electrons will undergo inelastic scattering, resulting in energy loss, which can be measured by an electron spectrometer.¹⁷ Inelastic scattering can be triggered by various interactions, such as photon excitation, plasmon excitation, inner shell ionisation *etc.*¹⁷ In principle, EELS is capable of providing information about atomic composition, chemical bonding and also conduction band electronic properties; and EELS works better for the low atomic numbers from carbon to 3d transition metals.¹⁷

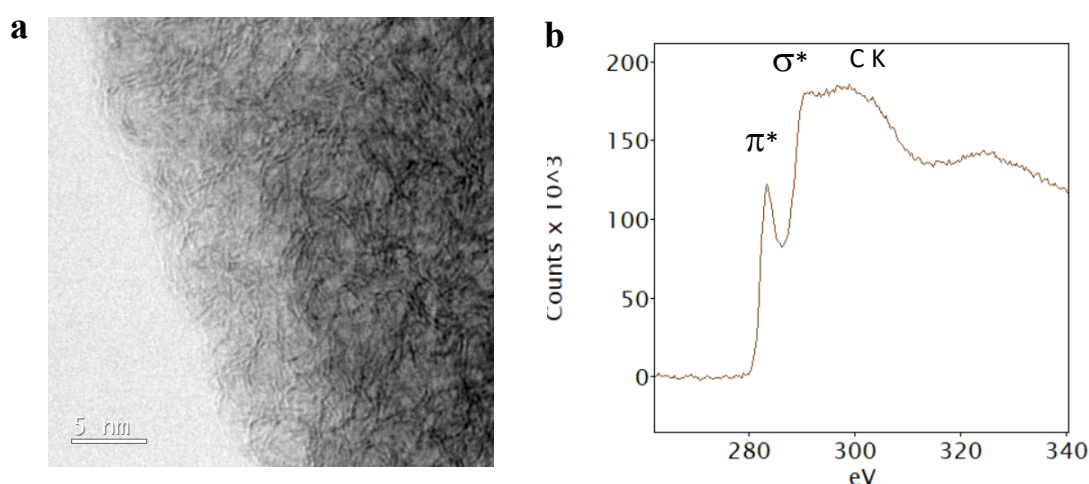


Figure 2.8 (a) Example of HR-STEM image of Fe-N/C; (b) EELS spectrum of HR-STEM of Fe-N/C.

High-resolution (HR)-STEM is a valuable technique commonly used to characterise single atom catalysts and observe the atomically dispersed metal, as exemplified in Figure 2.8 (a). Additionally, HR-STEM is often combined with EELS, as shown in Figure 2.8 (b), to gain further insights into the nature of sample. The high-resolution STEMs in Chapter 4 were obtained from Talos TEM (F200X, FEI). A probe spherical aberration-corrected STEM (Joel ARM 200 CF) was used to get the atomic resolution. All images were obtained by a collaborator in National Institute of Chemistry in Slovenia.

2.2.5 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a widely utilised technique for analysing the physical properties of the solid surfaces, including their elemental composition and bonding between atoms.¹⁸ In XPS, a well-defined energy X-ray (E_{photon}) is exposed to the surface of catalyst and the electrons from surface will be emitted if the energy is sufficient as shown in the left of Figure 2.9 (a).¹⁸ The de-excitation process can involve Auger transitions, depicted on the right side of Figure 2.9 (a).¹⁸ The kinetic energy of electron emitted (E_{kinetic}) will be measured precisely and the binding energy (E_{binding}) could be calculated as shown:¹⁸

$$E_{\text{binding}} = E_{\text{photon}} - (E_{\text{kinetic}} + \Phi) \quad (2.20)$$

where Φ stands for the work function of the instrument. The XPS instrument schematic diagram shown in Figure 2.9 (c) illustrates how the data is collected. There are three types of data can be collected, including the energy distribution spectrum, spatial distributions, which used for elemental mapping, and depth distribution, which should be less than 10 nm from the surface.¹⁸ For the energy distribution spectrum, it would provide information about the elements and also the orbitals since different elements had their specific binding energies.¹⁸ Furthermore, the chemical environment surrounding the atom can cause shifts the binding energies, providing insight into the local atomic arrangements.¹⁸ For instance, a high resolution of N 1s spectrum can be useful for analysing the different nitrogen environments in the M-N/Cs catalysts.

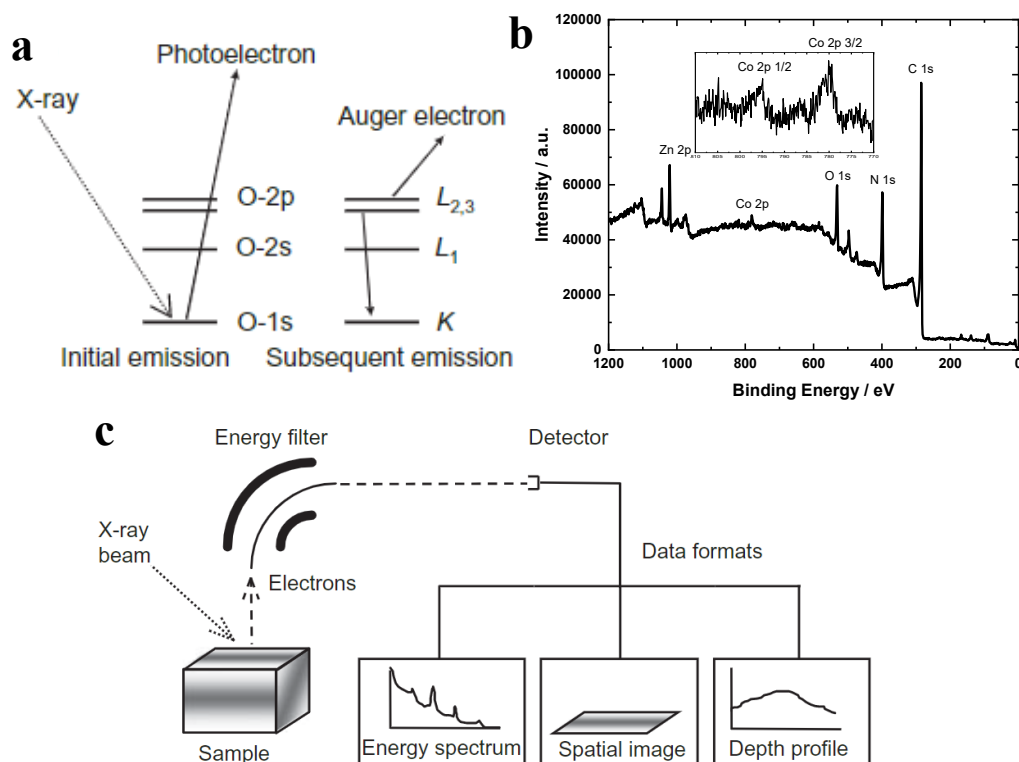


Figure 2.9 (a) Schematic diagram of the emission of photoelectron from the sample¹⁸; (b) representative example of XPS in Co-N/C; (c) schematic diagram of the XPS¹⁸.

A representative XPS spectrum is shown in Figure 2.9 (b). The x-axis in the spectrum normally will be binding energy (E_{binding}) rather than the kinetic energy (E_{kinetic}) since the E_{binding} is independent with the energy of X-ray used for excitation. The major peaks of Co-N/C had been labelled and the inset shows a high resolution spectrum of Co 2p region. The full XPS spectrum allows for the determination of the elemental composition of the catalysts' surface, and by fitting the high resolution N 1s spectrum, the amount of different types of nitrogen, such as pyrrolic and pyridinic *etc.*, can be determined. Most of the XPS measurements in this work were performed using the Thermo Scientific K-Alpha X-ray Photoelectron Spectrometer system (Al K α , 1486.6 eV) from the Harwell EPSRC National XPS Facility. More details will be provided in the experimental section of the following chapters.

2.2.6 X-ray adsorption spectroscopy (XAS)

X-ray adsorption spectroscopy (XAS) also involves exposing a sample to X-rays, but instead of generating a photoelectron as in XPS, it excites the core electron to a higher energy level.¹⁹ Just like in XPS, each element has its unique energy for exiting the core electrons.¹⁹ The absorption edge is the point where the absorption coefficient rises significantly, and the edge energy (E_0) is approximately halfway up the edge.¹⁹ XAS is particular sensitive to the molecular structure of the sample. Extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) are normally used for providing information about molecular structure, not only the number of bonds, but also the distance between two atoms in the samples.¹⁹ For most cases, K-edge is used, which involves exciting the core electrons from 1s to the unoccupied np orbitals, with a dipole $\Delta l = \pm 1$.¹⁹

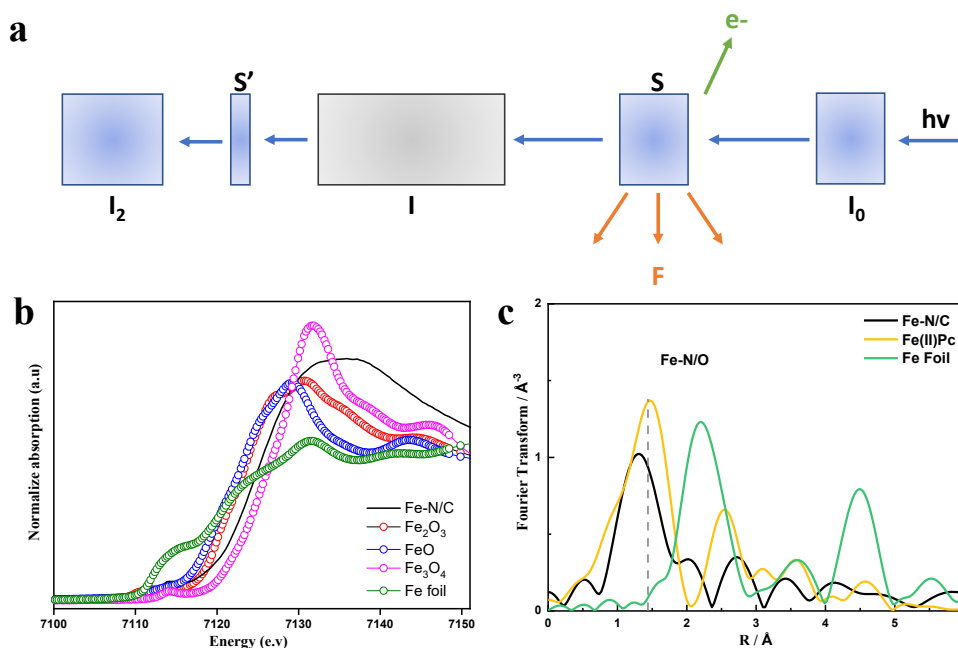


Figure 2.10 (a) Schematic diagram of XAS with the arrangement for transmission, fluorescence and electron yield measurement where S is sample, S' is the calibration foil, F is fluorescence and e^- is electron yield;¹⁹ (b) representative example of Fe K-edge XANES of Fe-N/C; (c) representative example of EXAFS of Fe-N/C.

There are three different modes that commonly used in the XAS, including transmission, fluorescence yield (FY) and total electron-yield (TEY) measurements a shown in Figure 2.10

(a).¹⁹ The measurement could be determined by either one mode individually or combined. In the transmission mode, the X-ray beam passes through the sample, and the measurement involves comparing the initial intensity (I_0) of the X-ray, the transmitted intensity (I) after passing through the sample, and the transmitted intensity for standard (S') used for the energy calibration.¹⁹ Fluorescence (I_f) and total electron-yield (I_e) could also be detected and they detect the decay products when the core-hole is refilled.²⁰ For solution sample, transmission is more commonly seen and for powder sample, fluorescence is normally used. TEY could determine the structure deeper and get more information about the structure.²⁰

Figure 2.10 (b) shows a representative graph of Fe K-Edge XANES of Fe-N/C catalyst, which will be discussed in Chapter 3 and Chapter 4. XANES is an region where can be used for chemical information as an indicator of local site symmetry and orbital occupancy.¹⁹ The oxidation state of an element can be determined based on the position of peaks. The EXAFS spectrum is usually Fourier Transformed (FT) and an example of Fe K-Edge EXAFS is shown in Figure 2.10 (c). The fitting of EXAFS could determine the bond length between the element tested and surrounding elements. In this work, it will be used to ascertain the interatomic distance of M to surrounding elements (N or C). Moreover, the EXAFS fitting can determine the coordination number of M to N or C. This could confirm whether a single atom $M-N_x$ formed successfully or not. The measurement details will be provided in the experimental section of following chapters.

2.2.7 X-ray diffraction (XRD)

In order to determine the phase of crystalline material, x-ray diffraction (XRD) is one of the most common and convenient techniques used in the research. The machine will provide X-rays to the surface of samples and these X-rays are diffracted by the atoms in the structure.²¹

The direction of the beam diffracted could be used to calculate the spacing between atomic plans based on the Bragg's Law:²¹

$$n\lambda = 2d \sin \theta \quad (2.21)$$

where n is the diffraction order, λ is the wavelength of the x-ray, d is the crystal plane separation and θ is the angle between the crystal plan and the incident beam as shown in Figure 2.11 (a). When analysing powder samples, all possible diffraction directions of the lattice should be recorded due to their random orientation. The 2θ positions in the XRD pattern can be used to calculate the spacing between crystals or atoms in the material. The intensity of peaks is related to the amount of molecules in that specific crystallographic phase. Furthermore, the width of peaks is inversely proportional to the crystal size. A broad peak indicates either a very small crystal size or the presence of amorphous material in the sample.

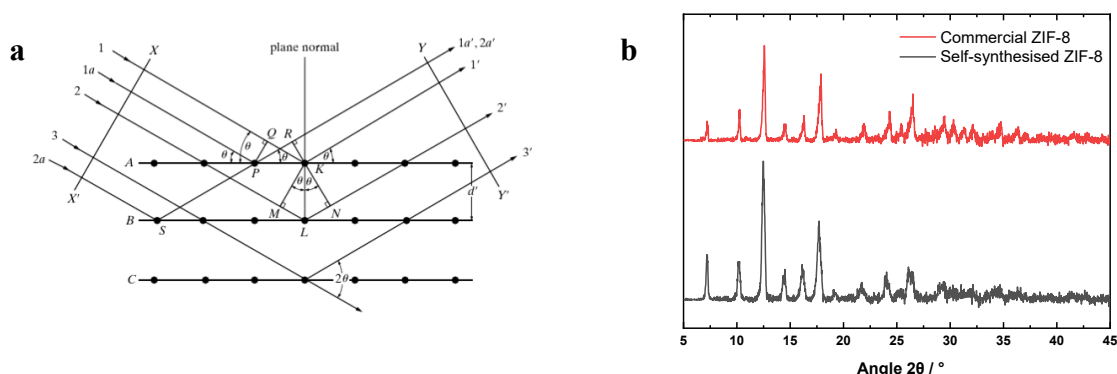


Figure 2.11 (a) The schematic diagram of the diffraction of x-rays by a crystal;²¹ (b) representative example of commercial ZIF-8 and self-synthesised ZIF-8.

A representative example of both commercial and homemade ZIF-8 is shown in Figure 2.11 (b). A comparison with the commercial ZIF-8 is useful to verify whether the homemade ZIF-8 has the same structure and crystallinity as the commercial one. All the XRD measurements are gained on a Bruker AXS D2 Diffractometer with a Cu-K α radiation.

2.3 Reference

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Chapter 3 Oxygen reduction reaction activity in non-precious metal catalysts- contribution of metal and carbon-based sites*

A detailed synthetic procedure for M-N/C catalysts was introduced. Seven different metal-based materials were successfully prepared with single atom sites, as proven by XAS. Furthermore, the similarity in physical properties, such as surface areas, pore size distributions and nitrogen functionality, suggested that the M-N/C catalysts had the same framework structure, and the only difference was in metal centres. The oxygen reduction reaction and nitrite stripping of all catalysts were tested and discussed in this chapter. Comparing the performance of different metal-based catalysts, the presences of two active sites was noticed and a hypothesis equation for predicting the catalytic performance based on the number of metal surface sites was introduced.

3.1 Introduction

Synthesising different metal based single atom catalysts (SACs) is highly demanding due to their remarkable catalytic performance in both organic¹⁻⁴ and electrochemical processes⁵⁻⁹. However, there are still several problems that need to be studied and solved. Firstly, as mentioned in Section 1.5.3 (Chapter 1), it is extremely challenging to prepare a single atom catalyst because the metal ions tend to agglomerate together, leading to the formation of nanoparticles, metal carbides, or metal nitrides *etc.* Secondly, the identification of active sites in SACs is a complex task as the structures of catalysts cannot be definitively confirmed after pyrolysis, which appears to be an unavoidable step in the preparation of SACs. Finally, the

* Parts of this chapter have been published in the paper: “Oxygen reduction reaction activity in non-precious single atom (M-N/C) catalysts – contribution of metal and carbon/nitrogen framework-based sites” of which I am the first author.

quantification of site density and the turnover frequency (TOF) of different sites are significant for a comprehensive understanding and for designing more efficient SACs.

In order to gain a better understanding and design more effective catalysts, methods for calculating the site density are being investigated. For non-precious metal SACs, several quantification methods have been reported, including the *cryo* sorption of CO gas^{10, 11} and also some other ionic or gaseous probes, such as hydrogen sulphide¹², cyanide¹³, and thiocyanide¹⁴. Unlike platinum group metal catalysts, non-precious metal SACs do not interact with CO at room temperature. Therefore, the *cryo* sorption of CO had to be done at a very low temperature (around -80 °C) and this method is an *ex-situ* quantification as the site density is calculated based on the CO uptake. It is not a convenient method for other researchers and the correlation between the site density and corresponding electrochemical activity is difficult to establish. For other probing gases or ionic solutions, the catalytic activity could not be recovered after poisoning and this leads to inaccurate quantification of active sites since not all the sites, which interacts with probing molecules or ions, are available for the electrochemical reaction. Therefore, those *ex-situ* methods tend to overestimate the number of electrochemical accessible sites. In 2016, D. Malko *et al.* reported nitrite ion, NO gas and hydroxylamine were able to interact with iron based SAC, leading to a significant decline in ORR.¹⁵ An *in-situ* quantification method to calculate the site density of M-N/Cs, called nitrite stripping, was developed based on the interaction of nitrite ion.^{15, 16} This method allows for the full recovery of catalytic performance after poisoning, enabling a more accurate determination of the relationship between site densities and ORR activities. Nitrite stripping offers a major advantage over other *ex-situ* methods as it provides a more reliable measure of the electrochemically active sites in the SACs, facilitating a deeper understanding of their catalytic performance. The details of the nitrite stripping method will be discussed in this chapter.

As discussed in Section 1.7 (Chapter 1), the ORR performances of M-N/Cs depend on the pH of electrolytes and the presence of more than one active site has been proposed in the literature.¹⁷⁻²² Preparing different metal based SACs with the same carbon-nitrogen framework would be useful to understand the role of metal centres and gain insights into the active sites. In Section 1.6 (Chapter 1), several different methods for preparing SACs were discussed and a wide range of metal based SACs has been reported in recent times. Some promising universal methods have been developed, which can produce M-N_x sites by using different metal based precursors during synthesis.^{3, 23, 24} Although these methods could successfully generate single atom sites, the physical characterisations of the resulting M-N/Cs, such as BET surface area, nitrogen content and also the amount of different types of nitrogen, vary significantly from each other. Therefore, this indicates the structures of M-N/C are not exactly the same and metal plays an important role during synthesis.

In this chapter, the intention is to prepare various metal based SACs using the same nitrogen-doped carbon scaffold. This approach enables the deconvolution of activity contributed by the framework and facilitates the understanding of active sites in M-N/C catalysts. The ORR will be examined under three different pH conditions (acidic, near-neutral, and alkaline), and the determination of active site density will allow for the correlation of the relationship between site density and ORR activity.

3.2 Experimental

3.2.1 Preparation of catalysts

There are three main steps for preparing the single atom catalysts (M-N/Cs). Firstly, ZIF-8 (100% tradename Basolite[®] Z1200) was pyrolysed at 900 °C for 1 hour in a tube furnace (Carbolite) under flowing Ar gas (99.99%, BIP plus-X47S, Air products) and the heating rate of the tube furnace was 3 °C min⁻¹ to generate a Zn-N/C. Then the catalysts were leached with

2 M H₂SO₄ (95%, VWR) overnight at 80 °C to remove Zn and create a nitrogen doped carbon ((Zn)-N/C) precursor. Then, 100 mg of nitrogen doped carbon precursor and 25 mg of non-precious metal salts as listed in Table 3.1 were mixed in 100 mL methanol (VWR) and the mixture was heated under reflux for 8 hours.

Table 3.1 Non-precious metal salts used for preparing the M-N/Cs.

Chemicals	Brand	Purity
FeCl ₂ ·4H ₂ O	Honey Fluka	99.0%
CoCl ₂ ·6 H ₂ O	Fluka Analytical	≥ 98.0%
NiCl ₂ ·6 H ₂ O	Sigma-Aldrich	≥99.0%
MnCl ₂ ·4 H ₂ O	Sigma-Aldrich	≥ 98.0%
SnCl ₄ ·5 H ₂ O	Sigma-Aldrich	98.0%
SbCl ₃	Sigma-Aldrich	≥99.0%
Bi(NO ₃) ₃ ·5 H ₂ O	Sigma-Aldrich	99.999%

The powder catalyst was washed with 1 L of DI water (MilliQ 18.2 MΩ cm) twice and then leached with 1 L of 0.5 M H₂SO₄ overnight at room temperature with stirring to remove the physically adsorbed metal nanoparticles. Afterward, the catalyst was washed with 1 L of DI water three times to remove the residual acid and dried under vacuum at 80 °C overnight. Finally, the catalyst was pyrolysed at 900 °C under 5% H₂/N₂ (BOC) for 1 h and the heating rate was 3 °C min⁻¹.

3.2.2 Physicochemical Characterisations

All physicochemical characterisations were obtained by the same method as in Section 2.2 (Chapter 2) unless stated. BET surface area, pore size distribution and pore volume of all catalysts were determined by the same methods as in Section 2.2.1 (Chapter 2). High-purity nitrogen gas (BIP Plus, 99.99998%) was used during analysis and high-purity helium gas (BIP, 99.9999%) was used for the free-space measurement. Transmission electron microscopy (TEM) was obtained from an FEI Titan Tecnai G2 F20 in China United Test & Certification Co. ltd.

(CUTC). X-ray absorption spectroscopy (XAS) at transition metal K-edges was measured at the 10C beamline of the Pohang Accelerator Laboratory (PAL) in fluorescence mode. As references, XAS of metallic foils and metal phthalocyanines were also measured for energy calibration. X-ray absorption near-edge structure (XANES) and Fourier transformation (FT) of the extended X-ray absorption fine structure (EXAFS) spectra were processed using Athena software. The extracted EXAFS signal, $\chi(k)$, was weighted by k^3 to emphasize the high-energy oscillations and then Fourier-transformed (FT) in the k -range of 3.0 - 11.0 Å⁻¹. Note that the FT magnitude plots of EXAFS spectra were not phase corrected and as such the real bond length should be ~ 0.4 Å longer than shown in the plots. Inductively coupled plasma mass spectrometry (ICP-MS) was taken by Agilent ICP-MS 7900.

3.2.3 Nitrite Stripping

The ink for electrochemical measurement was prepared in the same method mentioned in Section 2.1.4 (Chapter 2) and the electrochemical cell used for measurement is shown in Section 2.1.1 (Chapter 2). A potentiostat (Autolab, model PGSTAT20) was used for current and potential control and the rotating speed was 1600 rpm for all measurements, which was controlled by PINE Research. Current integrator must be introduced in the nitrite stripping method as the reduction of NO is surface electrochemical process, which means the reaction happen on the catalyst. The current might be recorded incorrectly if only staircase voltammetry is used.

Glassy carbon and saturated calomel electrode (Sentek) were used as the counter electrode and the reference electrode respectively. Sodium acetate (99%, Sigma-Aldrich), glacial acetic acid (AnalR Normapur, VWR) and ultrapure water (MilliQ 18.2 MΩ cm) were used to prepare 0.5 M acetate buffer electrolyte solution with pH 5.2, which was confirmed by a pH meter (Thermo Scientific, Orion Versastar). Ultrapure nitrogen (BIP Plus, 99.99998%) and oxygen (Ultra Pure

Plus, 99.9998%) were utilised in this experiment. Method used in this chapter is modified based on Malko *et al*'s previous publication.¹⁶

The detailed nitrite stripping methods are shown in Figure 3.1 and all electrochemical potentials are listed versus the RHE potential scale. The catalyst was electrochemically cleaned and activated under both nitrogen and oxygen two times and the potential range, scan rate, and the number of scans are shown in the green box. Then the catalyst was ready for the unpoisoned measurement. There are three main steps for the measurement step, including an ORR measurement, a nitrogen pre-baseline and also a nitrogen baseline measurement as shown in the blue box. Normally, a nitrogen background was measured after this in order to correct the ORR background. Then, a poisoning step, which is not an electrochemical step, was done by immersing the electrode in 0.125 M NaNO₂ solution (Sigma-Aldrich, ≥ 99.0%) for 5 minutes with a rotating rate at 300 rpm, allowing the nitrite ion interacts with the catalyst. Then the electrode was cleaned in DI water for 1 minute to remove the physically adsorbed nitrite ions and the electrode was immersed in the pH 5.2 buffer electrolyte to stabilise the NO interaction with the catalyst.¹⁵ Finally, the catalyst was cleaned by DI water again for 1 minute. The catalyst should be poisoned by nitrite successfully. After poisoning, the measuring step was repeated to get the poisoned ORR and nitrogen pre-baseline and baseline.

The potential of nitrogen baseline should be able to reduce the NO interacted with the catalyst. The recovered measurement was done to confirm the initial performance of catalyst was re-established. A second poison would be carried out to calculate the stripping charge more accurately. However, for the second poisoning, the ORR performance would not be recorded. Only the nitrogen pre-baseline and baseline were tested. According to the difference between poisoned and recovered baseline region of nitrogen CV, the stripping charge (Q_{strip}) could be calculated by:¹⁶

$$Q_{strip} [C g^{-1}] = \frac{Area[AV]}{scan\ rate[Vs^{-1}] \times Catalyst\ Loading[g]} \quad (3.1)$$

where area is calculated by the differences in baseline nitrogen CV between poisoned and recovery scan, scan rate should be 10 mVs⁻¹ and the catalyst loading are 0.0392 g. Based on the Q_{strip} calculated, the gravimetric site density (MSD) and site density (SD) could be determined by: ¹⁶

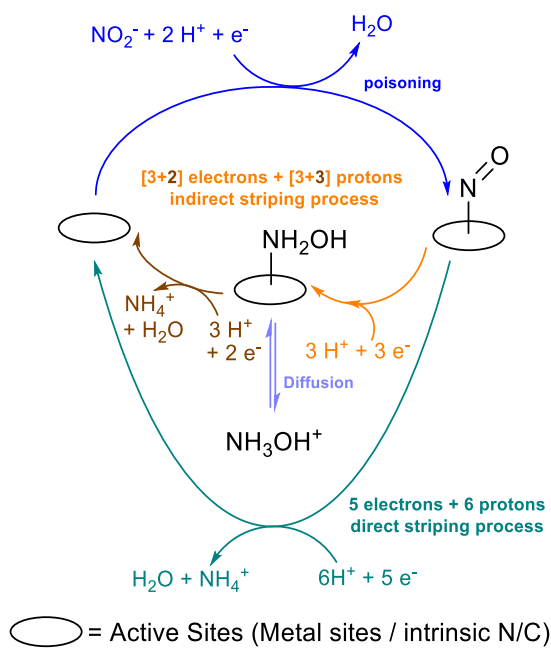
$$MSD[mol\ g^{-1}] = \frac{Q_{strip}[C\ g^{-1}]}{n_{strip} \times F[C\ mol^{-1}]} \quad (3.2)$$

$$SD[sites\ g^{-1}] = \frac{Q_{strip}[C\ g^{-1}] \times N_A[mol^{-1}]}{n_{strip} \times F[C\ mol^{-1}]} \quad (3.3)$$

where F stands for the Faraday constant and n_{strip} is the number of electrons involved in the reduction of one nitrosyl adsorbed on the metal centres. The value of n_{strip} reported for the reduction step could vary between 3 and 5 leading to different final products such as hydroxylamine or ammonium ion as shown in Scheme 3.1.²⁶ Ammonium ions were more likely to be produced as previously reported. Therefore, a n_{strip} value of 5 was used in the following calculation.^{16, 27} The turnover frequency (TOF) could be calculated based on the MSD as shown in: ¹⁶

$$TOF [s^{-1}] = \frac{\Delta i_k[Ag^{-1}]}{F [A\ s\ mol^{-1}] \times MSD[mol\ g^{-1}]} \quad (3.4)$$

where Δi_k is the change in kinetic current between poisoned and unpoisoned ORR.



Scheme 3.1 Schematic diagram of nitrite stripping. Blue: poisoning step, green: 5 electrons and 6 protons direct reductions process, orange: [3+2] electrons and [3+3] protons indirect stripping process. [Printed with permission from ref²⁵]

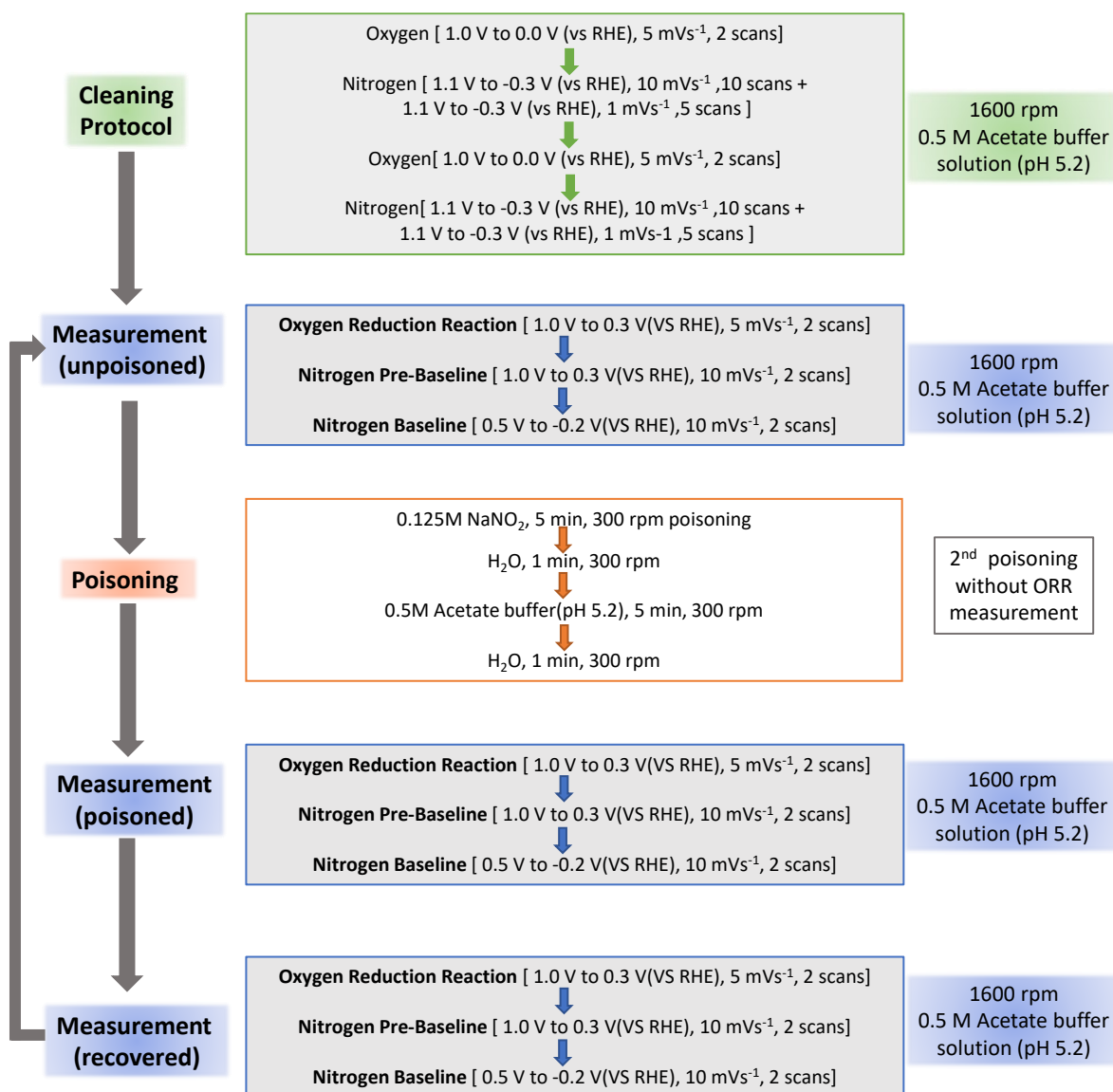


Figure 3.1 The protocols of nitrite stripping. [Printed with permission from ref²⁵]

3.2.4 Oxygen Reduction Reaction

The ink for electrochemical measurement was prepared in the same method mentioned in Section 2.1.4 (Chapter 2) and the electrochemical cell used for measurement is shown in Section 2.1.1 (Chapter 2). A Ring Rotating Disk Electrode (Pine Instruments, model AFE6R1AU with glassy carbon as a disk with a concentric gold ring and rotator model AFMSRCE) was used as the working electrode. Reversible hydrogen electrode (RHE) and glassy carbon were used as reference and counter electrode respectively. For ORR measurement, 0.5 M sulfuric acid (VWR, 95.0%) and 0.1 M KOH (VWR, 85.3%) were

prepared by ultrapure water (MilliQ 18.2 MΩcm) and used as electrolyte. Ultrapure oxygen (Ultra Pure Plus, 99.9998%) and nitrogen gases (BIP Plus 99.99998%) were used in the measurements, which were taken in the potentiostat (Autolab, model PGSTAT20) and all measurements were taken under rotating 1,600 rpm unless stated.

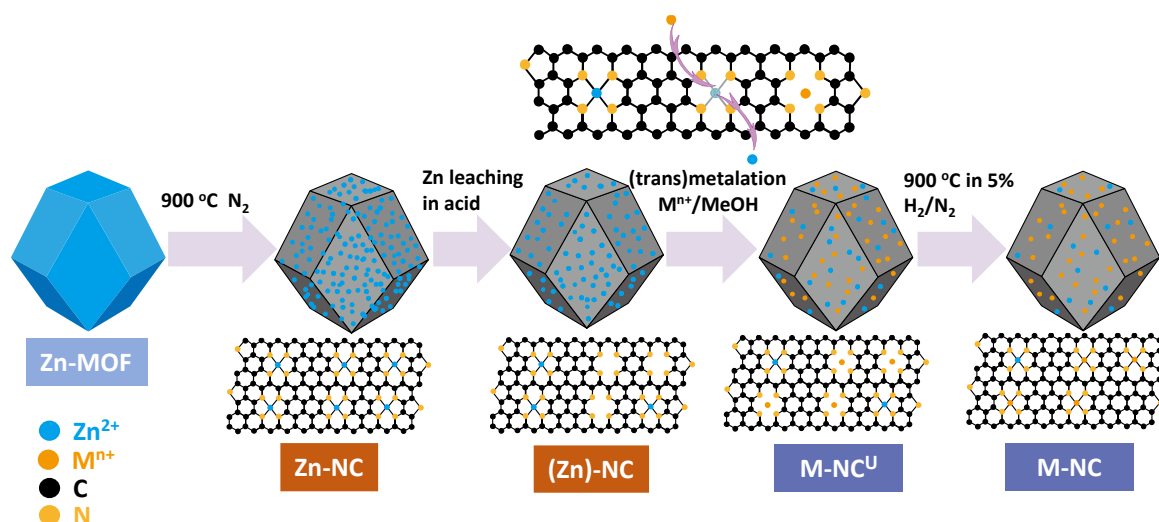
The dried catalyst was first activated in O₂-saturated electrolyte by CV between 0.00 and 1.00 V_{vs. RHE} with a scan rate of 10 mV s⁻¹. After 3 cycles, the ORR performance should be stable and the catalyst should be wetted properly. Then the ORR polarisation was taken by linear sweep voltammetry (LSV) from 1.00 V_{vs. RHE} to 0.00 V_{vs. RHE} with a scan rate of 5 mV s⁻¹, and the ring current was recorded under 1.50 V_{vs. RHE} to calculate the yield of H₂O₂ by Equation (2.8) as shown in Chapter 2. Subsequently, the nitrogen background was measured by LSV under N₂-saturated electrolyte with the same potential range and scan rate as the ORR done under O₂ condition. Ohmic resistances were determined by electrochemical impedance spectroscopy (EIS) for the iR composition.

3.3 Result and Discussion

3.3.1 Physical Characterisations of M-N/Cs

The M-N/C catalysts were prepared from pyrolysed zeolitic imidazolate framework-8 (ZIF-8), which was used as a Zn-N/C template as shown in Scheme 3.2. After first pyrolysis, there were around 25wt% of zinc present in the catalyst and most of zinc were removed in 2 M sulfuric acid at room temperature, generating some empty N/C sites. Then the (Zn)-N/C catalyst was refluxed with a metal chloride solution in methanol to coordinate the metal. There are two possible pathways for doping the metal into the N/C framework, including direct metalation into the vacant N/C sites and transmetalation by exchanging the residual Zn with the desired metal. The M-N/C^U was acid leached in 0.5 M sulfuric acid overnight to remove the adsorbed metal ions and followed by water washing to remove the residual acid. Finally, the catalyst was

pyrolysed again at 900 °C to active the M-N/C. The major advantage of this synthetic method is that the N/C scaffold should be nearly identical, and this would be helpful to investigate the contribution of different metal centres and also average out the activity from N/C framework, which had not been done before.



Scheme 3.2 Synthetic scheme of M-N/C catalyst from ZIF-8 via (trans)metalation. [Printed with permission from ref²⁵]

Seven different metal M-N/Cs were prepared using this method and a reference (Zn)-N/C was obtained without any (trans)metalation and pyrolysed twice. The transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) images of these M-N/Cs are shown in Figure 3.2. For all M-N/Cs, TEM images showed the morphology of catalyst is polyhedron, similar to the ZIF-8 precursor. Furthermore, the particle size of M-N/Cs is around 400 nm and is similar with that of ZIF-8. EDS elemental mapping of metals in M-N/Cs suggested the metal are evenly distributed in the catalyst without forming any visible clusters or nanoparticles. Due to the low metal loading in the catalyst, some of the elemental mapping are not very distinct. ICP-MS was a more reliable technique to determine the metal loading in the M-N/Cs since all other methods could only detect the metal on the surface of catalyst. Leaching with aqua regia overnight would dissolve all metals, including those on the surface and buried within the catalyst, in the solution and the percentage of metal is shown in Table 3.3. For Ni-N/C, Mn-N/C and Bi-N/C, the active metal loading was relatively low (< 0.50 wt%),

while for Co-N/C, Sn-N/C, Sb-N/C and Fe-N/C, the active metal loadings were in the range of 0.50 – 7.10 wt%. Therefore, both ICP-MS and EDS confirmed that the seven different metals were successfully doped into the catalyst.

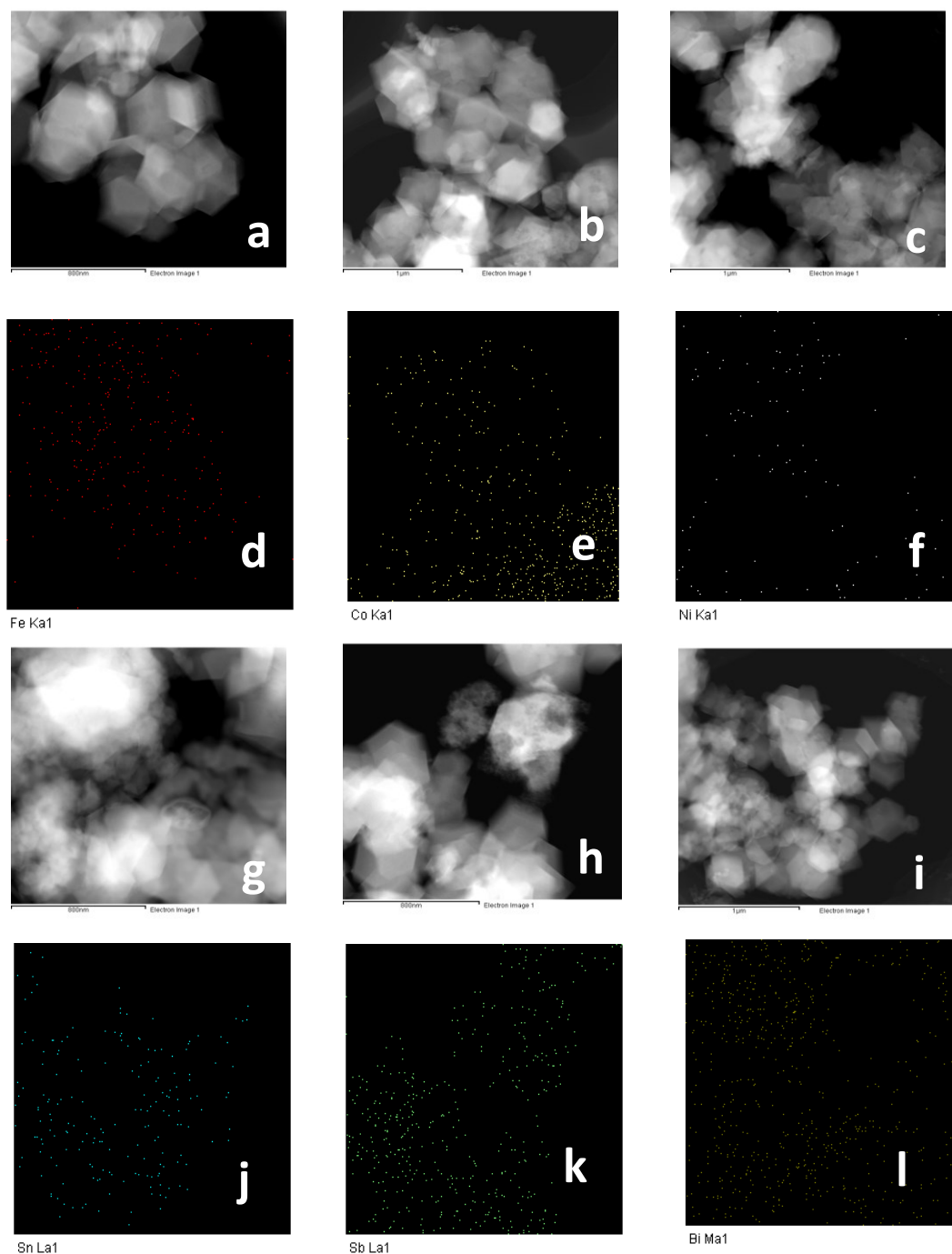


Figure 3.2 Transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) element mapping of M-N/Cs. (a)&(d) Fe-N/C; (b)&(e) Co-N/C; (c)&(f) Ni-N/C; (g)&(j) Sn-N/C; (h)&(k) Sb-N/C; (i)&(l) Bi-N/C. [Printed with permission from ref²⁵]

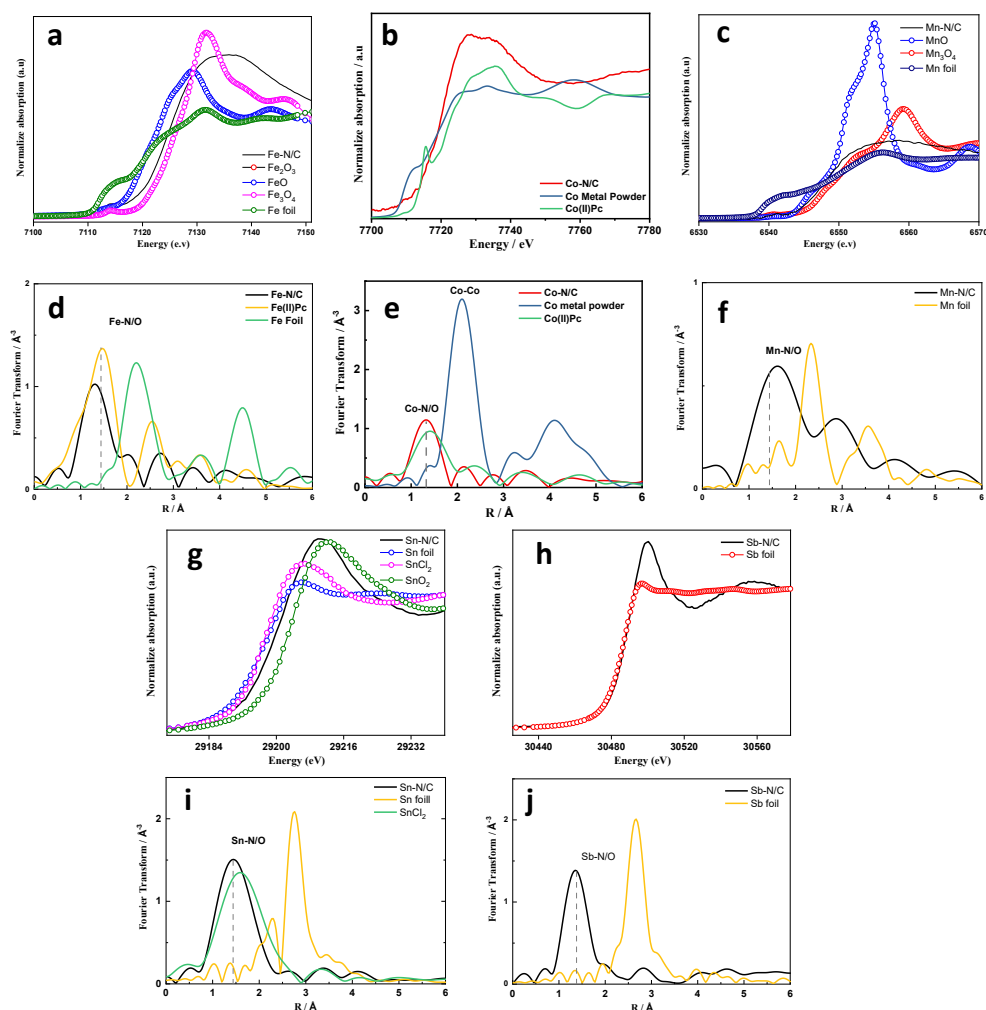


Figure 3.3 X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) of M-N/Cs (a)&(d) Fe-N/C; (b)&(e) Co-N/C; (c)&(f) Mn-N/C; (g)&(i) Sn-N/C; (h)&(j) Sb-N/C. [Printed with permission from ref²⁵]

In order to confirm the formation of single atom site, X-ray absorption spectroscopy (XAS) measurements were taken to analyse the coordination environments. X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) of M-N/Cs are shown in Figure 3.3. XANES should be able to provide the valence oxidation state of metal ions. Although the oxidation of salts used for (trans)metalation is known, the oxidation state in the M-N/C catalysts could potentially change during the second high temperature pyrolysis. For Co-N/C, the edge peak at $\sim 7,730$ eV indicates the presence of Co(II) in the catalyst, which is the same as the salt.²⁸ EXAFS of M-N/Cs provides the information about the type of bonds forming with the metal centre. All catalysts had a peak at around $1.4 \text{ \AA}$ (labelled as dash line

in the graphs), corresponding to a M-N/O coordination.^{3, 28} The fitting of EXAFS could also be used to calculate the coordination number and bond strength, which will be discussed in Chapter 4. The formation of M-N/O and the absence of an M-M peak in the EXAFS indicate the formation of single atom sites without generating any metal nanoparticles or metal carbides *etc.*

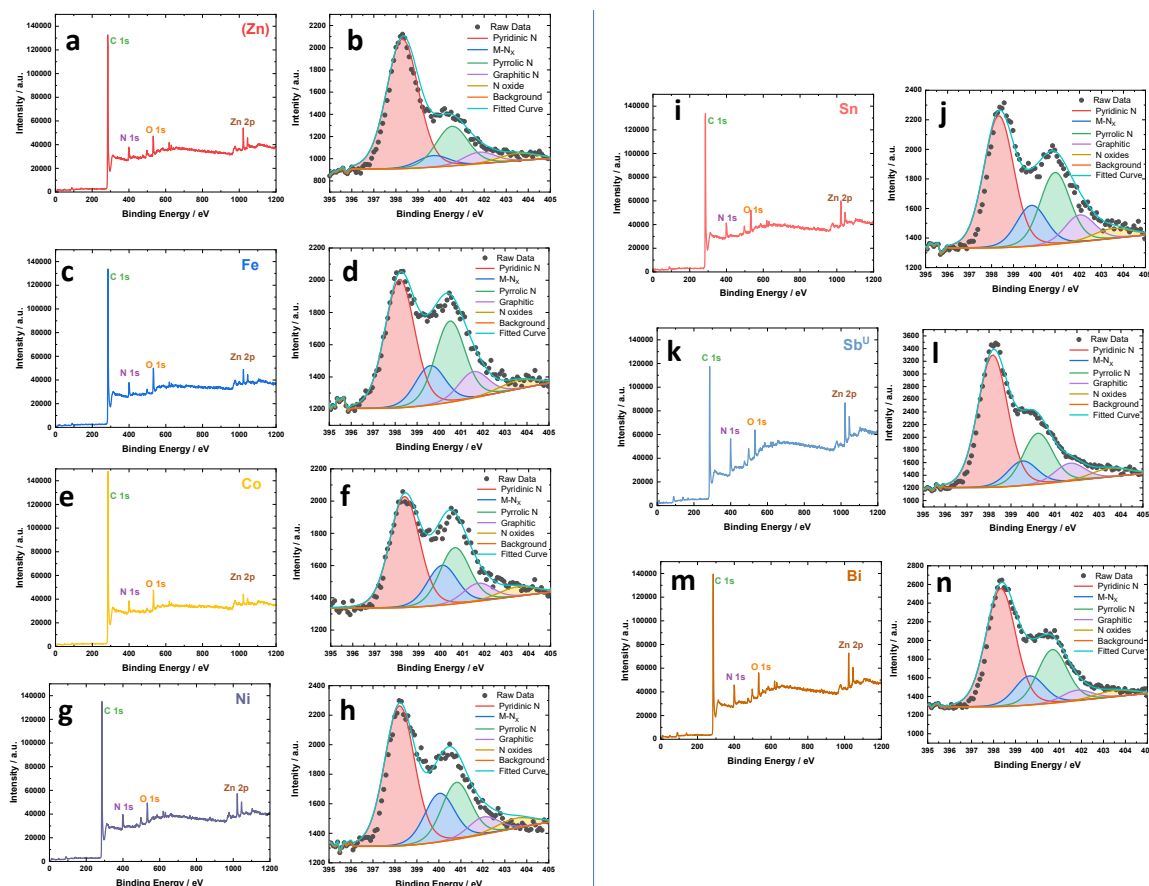


Figure 3.4 X-ray photoelectron spectroscopy of M-N/Cs. (a), (c), (e), (g), (i), (k) and (m) are the survey XPS spectra of (Zn)-N/C, Fe-N/C, Co-N/C, Ni-N/C, Sn-N/C, Sb-N/C and Bi-N/C catalysts respectively; (b), (d), (f), (h), (j), (l) and (n) are the high-resolution N 1s XPS spectra of (Zn)-N/C, Fe-N/C, Co-N/C, Ni-N/C, Sn-N/C, Sb-N/C and Bi-N/C catalysts, respectively. [Printed with permission from ref²⁵]

X-ray photoelectron spectroscopy (XPS) analysis of M-N/Cs are shown in Figure 3.4, including the survey XPS spectra and high-resolution N 1s spectra. The area under each peak is proportional to the amount of that element in the catalyst. In the survey scan, clear C 1s, N 1s and O 1s peaks are observed, indicating that the catalysts predominantly consist of these elements. As the loading of metal is not high and only surface metal could be detected, the

metal peaks in the XPS spectra are not obvious. However, there is a Zn 2p peak shown in the survey spectra because the acid leaching and pyrolysis did not remove all of the Zn from the catalysts. For all catalysts prepared, there are small amount of Zn left in the catalysts. Furthermore, there will be a noticeable mass loss during the second pyrolysis, which is due to the loss of zinc and also nitrogen. The latter could be noticed by a comparison to the survey XPS spectrum of the unactivated catalyst. Finally, the nitrogen peak would provide valuable insights into the catalysts because it is associated with two potential active sites: M-N and N/C, both of which are linked to nitrogen. Therefore, the high-resolution N 1s was analysed for all M-N/Cs.

There are five different bonding configurations of nitrogen are broadly found in these types of catalysts, including pyridinic N (398.3 eV), M-N_x (399.7 eV), pyrrolic N (400.6 eV), graphitic N (401.7 eV) and N oxides (403.5 eV).²⁹ For all catalysts, the analysis and fitting of peaks were performed in CasaXPS and the amount of different types of nitrogen environments are shown in Figure 3.4. Most of nitrogen (around 90%) are pyridinic N, M-N_x and pyrrolic N in M-N/Cs; and only small amount of graphitic N and nitrogen oxides are presented in the catalyst. Moreover, the amount of pyridinic nitrogen in the unactivated catalyst (Sb^U) is much higher than other activated catalysts, which suggested the loss in nitrogen during second pyrolysis is dominated by the pyridinic nitrogen.

Table 3.2 The percentages of different types of nitrogen in M-N/Cs. Based on the XPS analysis [U stands for the unactivated catalyst, which means the catalyst was not pyrolysed under 5% of H₂/N₂ again]. [Printed with permission from ref²⁵]

Catalyst / at%	Pyridinic N	M-N	Pyrrolic N	Graphitic N	N oxides
(Zn)-N/C	48.56	7.3	29.53	9.76	4.85
Fe-N/C	44.82	13.75	28.38	9.24	3.8
Co-N/C	46.84	16.81	23.77	7.61	4.97
Ni-N/C	51.06	17.73	20.29	6.38	4.54
Sn-N/C	46.44	14.37	25.3	9.5	4.39
Sb-N/C ^U	55.95	10.4	21.59	7.54	4.52
Bi-N/C	53.86	13.29	24.46	4.79	3.59

Finally, the Brunauer-Emmett-Teller (BET) measurements were taken for all M-N/Cs and the plotted graphs are shown in Figure 3.5. The nitrogen isotherms of all catalysts are similar with type I / H4 and the surface areas for all catalysts are between 1,000 and 1,150 m² g⁻¹. The micropore volumes are 0.36 - 0.40 cm³g⁻¹.

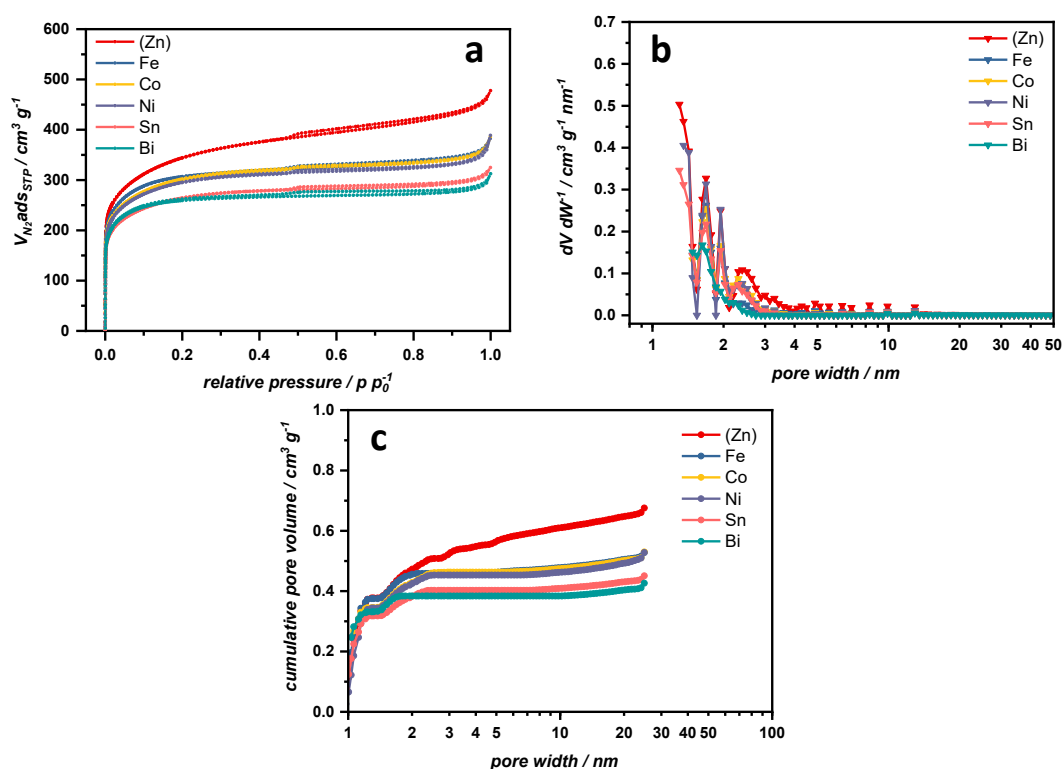


Figure 3.5 BET of M-N/Cs (a) N₂ adsorption and desorption isotherms; (b) cumulative pore volumes; (c) pore size distribution profiles. [Printed with permission from ref²⁵]

For all physical characterisation spectra, they showed very similar results among all M-N/Cs, including morphology, BET surface area, amount of different types of nitrogen *etc.* It indicates that all M-N/Cs have a nearly identical nitrogen/carbon framework and the only difference among catalysts is the metal doped. Therefore, it is beneficial to study the electrochemical activities contributed by framework and metal centres separately and would give a better understanding on this type of catalysts in terms of different active sites and catalytic activities.

3.3.2 Oxygen Reduction Activity under different pHs (acidic, near-neutral and alkaline)

The oxygen reduction reaction activities were measured by RRDE in 0.5 M H₂SO₄ and 0.1 M KOH. The ring current was measured at 1.5 V_{vs.RHE} to make sure all hydrogen peroxide generated is oxidised completely. The ORR linear sweep voltammetry (LSV) and hydrogen peroxide yields are shown in Figure 3.6. The ORR activities and % H₂O₂ yields of unactivated catalysts, M-N/C^Us, were also tested as shown in Figure 3.6 (a) and (b) as a reference. The half-wave potential ($E_{1/2}$) is significantly improved after the second pyrolysis; especially for Fe-N/C and Co-N/C. Furthermore, the % H₂O₂ yields decrease after the second pyrolysis. As the activated catalyst had much better performances in acidic electrolyte, the ORR of activated catalysts M-N/Cs were conducted only. In alkaline conditions, most of catalysts had already reached the limiting current at 0.8 V_{vs. RHE}; however, they showed poor activities in acidic electrolytes at the same potential. The hydrogen peroxide yields in alkaline conditions were always less than 25%; clustering around 20% yield. Although the second pyrolysis had lowered the hydrogen peroxide yield in acidic condition, the yields of hydrogen peroxide were still in a range of 10 - 35%. Hydrogen peroxide yield was not measured in near neutral conditions as only RDE was used for near-neutral conditions.

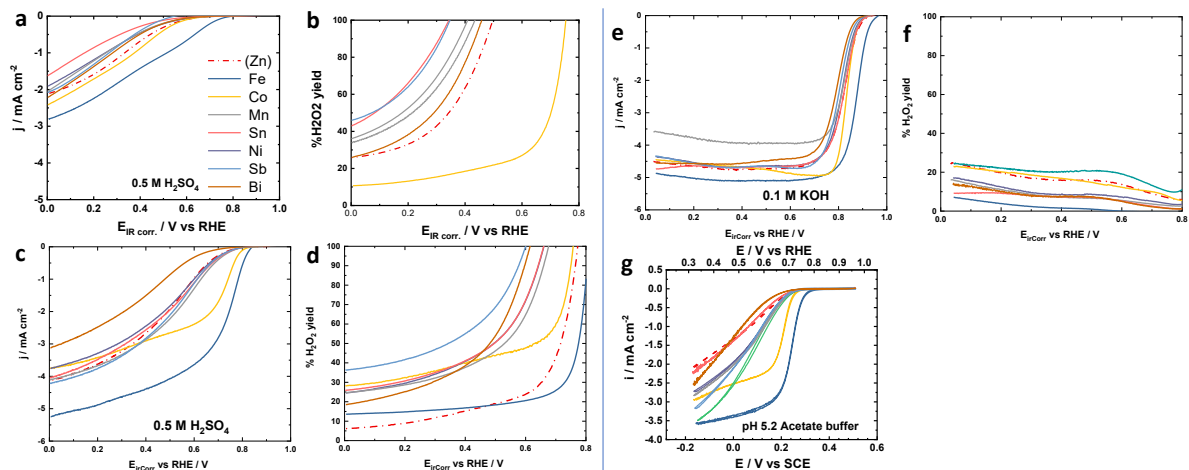


Figure 3.6 Oxygen Reduction Reaction (ORR) performances (a) M-N/C^{Us} in 0.5 M H₂SO₄; (c) M-N/Cs in 0.5 M H₂SO₄; (e) M-N/Cs in 0.1 M KOH; (g) M-N/Cs in pH 5.2 acetate buffer. and %H₂O₂ yield of (b) M-N/C^{Us} in 0.5 M H₂SO₄; (d) M-N/Cs in 0.5 M H₂SO₄; (f) M-N/Cs in 0.1 M KOH. All measurements were done with 1,600 rpm rotation and scanning rate 5 mVs⁻¹. [Printed with permission from ref²⁵]

In order to understand the catalytic activity and mechanism better, Tafel plots under different pHs are plotted as shown in Figure 3.7 (a), (b) and (c). The mass transport to and within the catalyst would influence the analysis; so a kinetic mass activity was used in Tafel plot, which was determined by:

$$\frac{1}{j} = \frac{1}{j_{\text{kinetic}}} + \frac{1}{j_{\text{limiting}}} \quad (3.5)$$

where j is the experimentally measured current density, j_{limiting} is the diffusion-limiting current, and j_{kinetic} is the kinetic current density. For all Tafel plots under different pH conditions, a line with 45 mV decade⁻¹ was drawn as a reference for comparison of activity. In general, only iron and cobalt based catalysts showed significant improvements in the ORR activity; bismuth based catalyst gave a poorer performance. All other metal based materials had very similar activity and clustered together. In acidic conditions, there was not a well-defined Tafel slope shown for the iron and cobalt based catalysts; and for the other catalysts, including bismuth, they seem to give a higher Tafel slope close to 150 mV decade⁻¹ compared to cobalt and iron based catalysts. In near-neutral conditions (pH = 5.2), the trends were very similar to the acidic conditions. Cobalt and iron based catalysts showed a well-defined Tafel slope with 45 mV decade⁻¹. Having the similar Tafel slope means that the number of electrons involved in the

rate determine step (rds) is the same, which suggests that the mechanism of acidic and near-neutral ORR is similar. For alkaline conditions, the improvement of iron based and cobalt based catalysts was not extremely obvious and the activity of Co-N/C was slightly overlapped with the cluster at high potential region (0.9 - 0.85 $V_{\text{vs. RHE}}$). Moreover, the Tafel slope of Fe-N/C and Co-N/C is also close to 45 mV decade^{-1} . For the other catalysts, there was not a clear Tafel region suggesting that there is a continuous change in rds with the potentials. A reference line with 60 mV decade^{-1} slope is shown in the alkaline Tafel plot; for alkaline ORR, it seems all catalysts required a small overpotential to accelerate the reduction in high potential region.

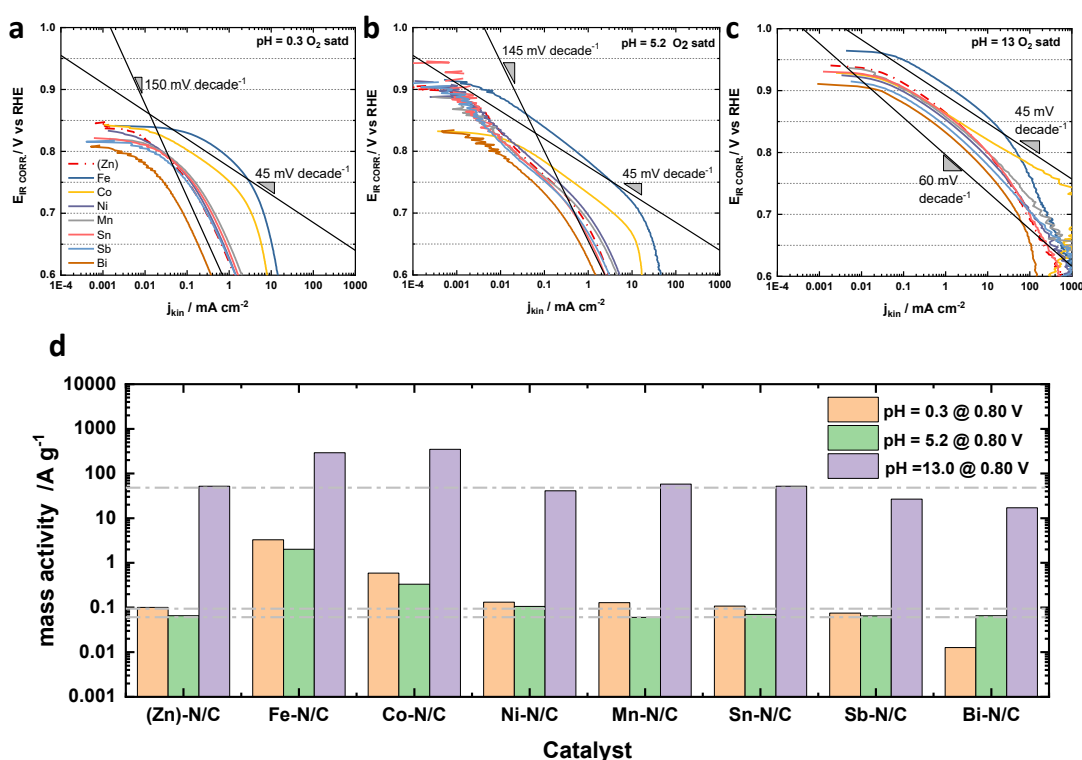


Figure 3.7 Tafel plot of ORR measured (a) in 0.5 M H_2SO_4 ; (b) in 0.5 M acetate buffer solution (pH=5.2); (c) 0.1 M KOH (pH=13.0); (d) Comparison of mass activity in different electrolytes at 0.80 V_{RHE} under different pHs. For all measurements, the scan rate was 5 mV s^{-1} with a rotation speed of 1,600 rpm and the catalyst loading were 0.2 mg cm^{-2} . [Printed with permission from ref²⁵]

The comparison of kinetic mass activity at 0.8 $V_{\text{vs. RHE}}$ is shown in Figure 3.7(d). The mass activity in alkaline medium is around 1,000-fold higher than the mass activity in acidic and near-neutral conditions at the same overpotential. As mentioned previously, all M-N/Cs, except Fe-N/C, Co-N/C and Bi-N/C, had very similar activities, which close to the mass activity of

(Zn)-N/C. Therefore, three reference lines (grey dashed line) were shown in the Figure 3.7 (d), which are the mass activity of (Zn)-N/C under different conditions. In acidic conditions, the activity of iron, cobalt and bismuth based catalysts was 30-fold higher, 5-fold higher and 10 times lower than that of (Zn)-N/C respectively; and 0.1 A g^{-1} is believed to be the *framework* mass activity in pH 0.3 electrolyte, contributed by the nitrogen doped carbon framework. For near-neutral conditions, a similar trend was also observed and the *framework* mass activity is around 0.08 A g^{-1} . In pH 13.0 electrolyte, the mass activity of iron and cobalt based catalysts only around 6 times higher than the *framework* mass activity, which is around 50 A g^{-1} .

Comparing the *framework* mass activity under different pH conditions, the nitrogen doped carbon is more active in alkaline conditions than in acidic conditions. Several papers have reported metal-free N/C exhibited high ORR catalytic activity and the main active site is attributed to pyridinic nitrogen.^{30, 31} As shown in Table 3.2, M-N/Cs are enrich of pyridinic nitrogen; therefore, the *framework* mass activity under alkaline condition is relatively high. Furthermore, the pK_a of pyridinic nitrogen is around 6.5 and the nitrogen will be protonated under acidic conditions, which potentially decrease the framework activity at low pH conditions. Finally, metal centre seems play a more important role under acidic and near-neutral conditions; so the mechanism of ORR should depend on the pH and different active sites had their distinct activities, which will be discussed in next section.

3.3.3 Nitrite stripping

The nitrite stripping of M-N/Cs was used to study the active sites of catalyst and there are three representative examples shown in Figure 3.8 including the (Zn)-N/C, Fe-N/C and Co-N/C. The calculated total number of site density by nitrite stripping is shown in Table 3.3. In Figure 3.8 (a), (c) and (g), ORR performance lost especially at the high potential region (around $0.7 \text{ V}_{\text{vs. RHE}}$) when the catalyst was poisoned by nitrite and the poisoned activity was shown in the red

line. Not all of the ORR activity had been lost, indicating some active sites were not blocked by NO. The ORR performance could be fully recovered after nitrite stripping, suggesting that the electrochemical assessable sites could be determined. Except Fe-N/C and Co-N/C, all other catalysts had very similar nitrite stripping reduction peak and site density; hence, only (Zn)-N/C was shown as an example. The metal contents in M-N/Cs varied depending on the specific metal centres employed; but all, except Fe-N/C and Co-N/C, had very similar site densities and also ORR activities under different pH conditions as discussed above. Therefore, the NO not only probed the metal centre (M-N_x), but also attached to the nitrogen doped carbon site (N/C). Compared the NO reduction CVs among M-N/Cs as shown in Figure 3.8 (b), (e) and (h), most of the catalysts, except Fe-N/C and Co-N/C, did not have a clear reduction peak and the reduction take place over a range of potential. However, for the Fe-N/C and Co-N/C, the reduction took place at 0.05 V_{vs. RHE} and -0.15 V_{vs. RHE}, respectively. The shift in reduction potential also indicated that NO interacted with the metal centres. Finally, the Tafel plots of unpoisoned ORR activity and poisoned ORR activity, as shown in Figure 3.8 (c), (f) and (i), allow to calculate the TOF_{total} by Equation (3.4) as shown in Table 3.3.

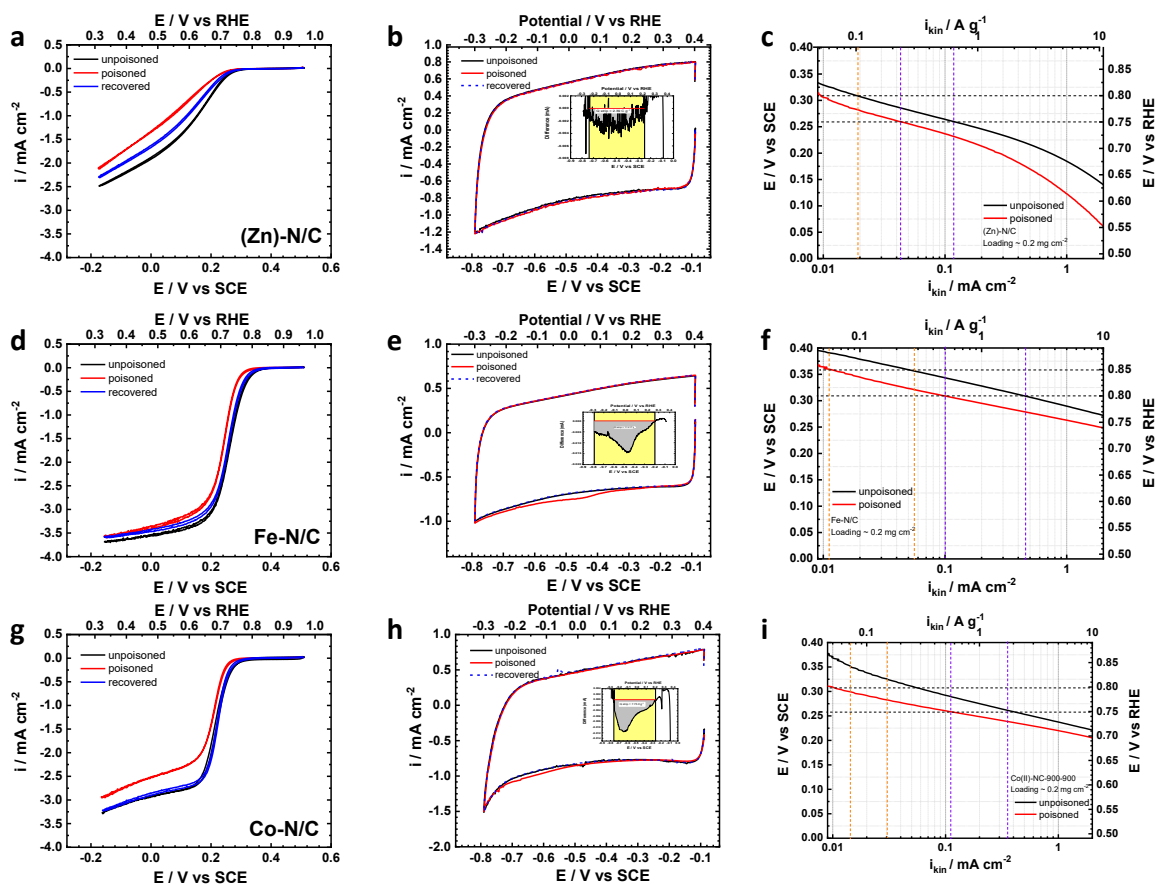


Figure 3.8 ORR activity of (a) (Zn)-N/C, (d) Fe-N/C and (g) Co-N/C; Baseline CV scans of (b) (Zn)-N/C, (e) Fe-N/C and (h) Co-N/C; Kinetic ORR activities of (c) (Zn)-N/C, (f) Fe-N/C and (i) Co-N/C. Black line stands for the unpoisoned measurement, red line is the poisoned activity and blue line is the recovered activity after nitrite reduction. [Printed with permission from ref²⁵]

As a wide range of M-N/Cs were prepared, the **framework** site density could be determined by averaging the stripping charge of all M-N/Cs, except Fe-N/C and Co-N/C. The average stripping charge contributed by the framework is $3.9 \pm 0.9 \text{ C g}^{-1}$, which suggested the **framework** site density to be $4.9 \times 10^{18} \text{ sites g}^{-1}$. In Figure 3.8 (a), there are still around 40 % of original activity remained after poisoning, which suggested not all framework sites are poisoned by nitrite solution. If the framework sites are all the same, the total number of **framework** sites should be $7.8 \times 10^{18} \text{ sites g}^{-1}$.

Table 3.3 The site density, ICP-MS metal content, site utilisation and TOF_{total} of M-N/C catalysts. [Printed with permission from ref²³]

Catalyst	ICP(metal) / wt%	Total site density / 10 ¹⁹ sites g ⁻¹	Metal site utilisation / %	TOF _{total} (0.75 V _{RHE})
(Zn)-N/C	8.50	0.30	0.38	0.83
Fe-N/C	7.10	1.42	1.85	3.34
Co-N/C	0.54	0.97	17.5	0.79
Ni-N/C	0.13	0.51	38.5	0.67
Mn-N/C	0.18	0.62	31.59	0.37
Sn-N/C	0.83	0.37	8.67	0.61
Sb-N/C	3.14	0.62	4.01	0.24
Bi-N/C	0.02	0.62	1083*	0.16

*This abnormality in calculation of metal site utilisation for Bi-N/C is due to low ICP metal content, but high site density. It also indicates that the nitrite stripping is likely happening at N/C framework sites.

The significant differences between Fe-N/C or Co-N/C and other M-N/Cs in both ORR activities and site densities allow to deconvolute the contribution of **framework** sites (N/C) and **metal** sites (M-N_x). However, it is also important to know whether the activity of different sites is the same or not. In other words, the relationship between site density and turnover frequency should be investigated. In order to understand this, a meta-analysis of nitrite stripping with various different catalysts, which are produced by distinct institutes and the nitrite stripping of those catalysts were tested in the Kucernak Group.³²⁻³⁴ The graph of TOF *versus* site density at different potential is shown in Figure 3.9 (a). The relationship could be written in a power expression as shown in Equation (3.6).

$$SD = k \times TOF^{\alpha} \quad (3.6)$$

where k is a constant and α is the fitting parameter. If α is -1, the site density and turnover frequency are inversely related, which means the increasing the site density will trigger a decrease in turnover frequency proportionally. However, based on the fitting, there was not a clear relationship between the SD and turnover frequency and the fitting was very poor at all

different potentials, including 0.80, 0.85 and 0.90 V_{vs. RHE}. The coefficient of determination (R^2) was even less than 0.5; therefore, site density and turnover frequency are independent. It is indeed intriguing that we do not observe a common turnover frequency for all catalysts, which one might expect if there was only one active site.

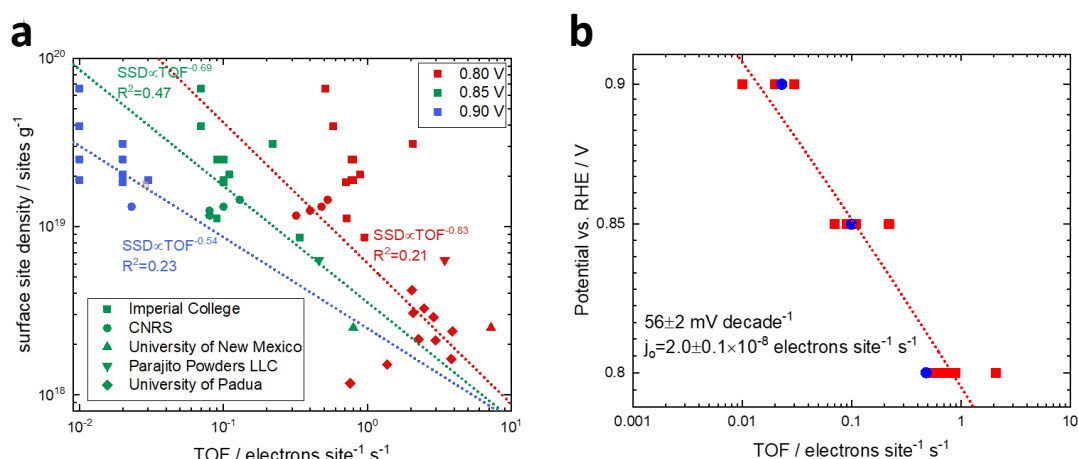


Figure 3.9 Analysis of site density and TOF of Fe-N/C catalysts produced through different methods and institutes (a) the relationship of site density and TOF data for 38 catalysts produced in different laboratories and data published in³²⁻³⁴; (b) Tafel slope and exchange current density of 10 best catalysts (i.e. those which show activity at 0.90 V_{vs. RHE}). [Printed with permission from ref²⁵]

However, if the very active catalysts, which had some performance at 0.9 V_{vs. RHE}, are considered in more detail, it is interesting to notice that they had a very similar Tafel slope (56 ± 2 mV decade⁻¹) as shown in Figure 3.9 (b). This potentially indicates that there is a common active site which dominates the activity in the high potential region and these active sites are believed to be M-N_x. The hypothesis about the active sites in M-N/Cs is that only two identified active sites (including **framework** N/C sites and metal based M-N_x sites) presented in this type of catalysts and each of the active sites has a distinct different contribution to the ORR kinetic mass activity under different conditions (potential and pH of electrolyte); therefore, the kinetic mass activity could be calculated by Equation (3.7):

$$j_{mass,total}^k(E, pH) = j_{mass,metal}^k(E, pH) + j_{mass,framework}^k(E, pH) \quad (3.7)$$

where $j_{mass,total}^k$ is the kinetic mass activity of catalyst, $j_{mass,metal}^k$ and $j_{mass,framework}^k$ are the kinetic mass activity contributed by metal based active sites and framework sites respectively. The mass activity of each component could be determined by its respective site densities (SDs) and turnover frequencies (TOFs) as shown in Equation (3.8) and (3.9).

$$j_{mass,metal}^k(E, pH) = SD_{metal} \times TOF_{metal}(E, pH) \quad (3.8)$$

$$j_{mass,framework}^k(E, pH) = SD_{framework} \times TOF_{framework}(E, pH) \quad (3.9)$$

Total kinetic mass activity of M-N/Cs for ORR is determined by four parameters, including two site densities and two turnover frequencies corresponding to each site. There is a key assumption had made for Equation (3.8) and (3.9), which is the site density of **framework** and metal based sites is independent to the pH of electrolyte and the potential. All changes in the mass activity under different potential and pH attribute to the change in turnover frequency of active sites. $j_{mass,framework}^k$ is calculated by averaging the performance of M-N/Cs, expect Fe-N/C and Co-N/C and the $j_{mass,metal}^k$ is determined by subtracting the total mass activity of Fe-N/C and Co-N/C with the $j_{mass,framework}^k$. Similarly, the $SD_{framework}$ and SD_{metal} could be determined. $TOF_{framework}$ and TOF_{metal} were calculated by Equation (3.8) and (3.9) as the site density and kinetic mass activity were known. All calculated values were reported in Table 3.4.

Framework sites, which are poisoned by nitrite, are around 4.9×10^{18} sites g^{-1} and this type of sites has a very small contribution for ORR activity under acidic and near-neutral conditions as the TOFs of framework sites are lower than five even at 0.7 V_{vs. RHE}. However, the TOFs under alkaline condition are around 200-fold higher than under acidic or near-neutral conditions. Therefore, it indicates the pH of electrolyte is a crucial factor for the activity of oxygen reduction reaction. For metal active sites (Fe-N_x and Co-N_x), they are more active than

the framework sites as the TOFs of metal sites are higher than that of framework sites under the same condition.

Table 3.4 Site density and turnover frequency of framework and metal sites at different potential and electrolytes. [Printed with permission from ref²³]

Sites	Site density/ 10 ¹⁸ sites g ⁻¹	TOF _{pH 0.3}			TOF _{pH 5.2}			TOF _{pH 13.0}		
		0.70 V	0.75 V	0.80 V	0.70 V	0.75 V	0.80 V	0.70 V	0.75 V	0.80 V
Framework	4.88	1.98	0.70	0.12	3.30	0.72	0.08	614.2	186.6	45.11
Fe-N _x	9.35	21.5	9.81	2.14	49.5	13.4	1.31	541.9*	322.8*	171.8
Co-N _x	4.79	19.9	5.93	0.65	20.7	2.65	0.35	1530*	3033*	408.2

* This value is extrapolated from the Tafel slope as shown in the main manuscript. As the Co-N/C and Fe-N/C have already reached the limiting currents at 0.80 V, therefore, the value looks extremely high especially for the Co-N/C.

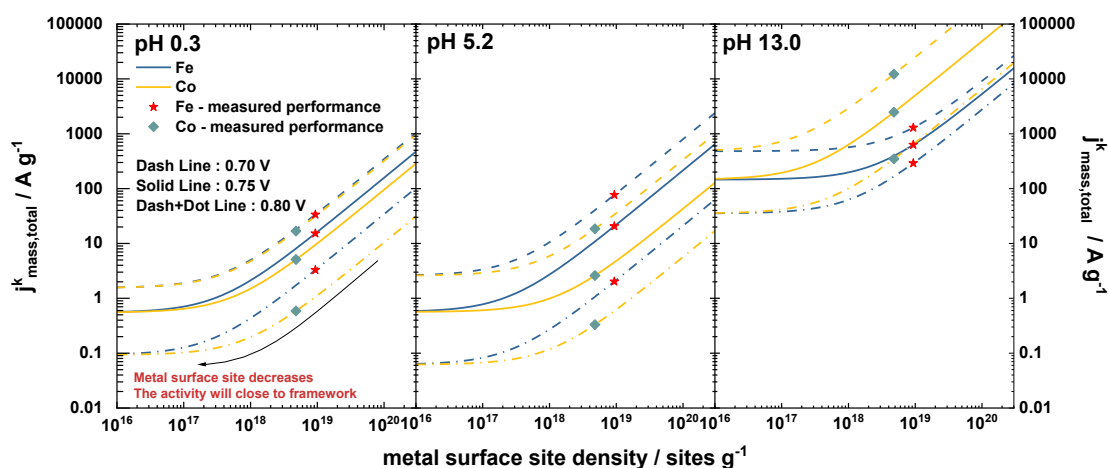


Figure 3.10 Total kinetic mass activity predicted according to the number of metal surface site density for M-N/Cs under different electrolytes and potentials. Stars are the measured Fe-N/C performance in this work and rhombuses stands for the measured Co-N/C result. [Printed with permission from ref²⁵]

The calculated $TOF_{framework}$ and TOF_{metal} would allow an estimation of the kinetic mass activity of M-N/C (M = Fe, Co) under different conditions by Equation (3.7) as the number of framework sites should be constant and the only variable is the site density of metal surface sites. Therefore, the kinetic mass activity of M-N/C (M = Fe, Co) was fully depended on the number of metal surface site density and a graph of metal surface site density *versus* kinetic mass activity is shown in Figure 3.10. As shown in the graph, if the metal site density in the catalyst is very low, then the kinetic mass activity of Fe-N/C and Co-N/C will be the same,

which is the *framework* activity. $\text{TOF}_{\text{Fe-N}}$ and $\text{TOF}_{\text{Co-N}}$ are different; hence, the differences between dark blue line (Fe) and pale yellow (Co) will be observed as the metal site density increases. Under acidic conditions, Fe-N_x is the most active site compared with others as the $\text{TOF}_{\text{Fe-N}}$ is the highest, which means that increasing the number of Fe-N_x sites could improve the activity significantly, especially at high potential range. This also proves that the common active site among active catalysts from different institutes (Figure 3.9 (b)) should be Fe-N_x. A similar trend has also observed for the near-neutral condition. Furthermore, the framework activity at pH 5.2 electrolyte is also similar to the activity at 0.3; however, when alkaline electrolyte was used, the framework activity increased significantly, indicating the activity of framework site depends on the pH of electrolytes. Metal sites are still more active than the framework sites as increasing the metal site density could still increase the mass activity visibly, so in order to improve the ORR performance, increasing the metal site density could be a promising way. Under alkaline condition, although the framework sites are already very active, Co-N_x still has higher TOF than others and have the best alkaline activity compared with others. It is crucial to compare the activity of different sites to design a better catalyst in the future; for acidic catalysts, increasing the metal loading would be useful and the catalysts used for alkaline condition could focus on the framework sites.

3.4 Conclusion

In this chapter, there are several important outcomes. Firstly, (trans)metalation proved to be a promising method for producing single atom catalysts without the formation of any metal clusters or nanoparticles. Seven M-N/C catalysts (M = Fe, Co, Ni, Mn, Sn, Sb and Bi) were prepared using this protocol and XAS analysis with a peak at 1.4 Å in EXAFS confirmed the presence of single atom sites. Secondly, all of catalysts had nearly identical framework N/C structures and the only differences among M-N/C were the metal centre doped and metal

loadings. Additionally, all seven M-N/C and the reference (Zn)-N/C exhibited very similar physical properties, such as BET surface area, total pore volume and nitrogen composition *etc.* This uniformity in physical properties is beneficial for understanding the active sites in these and also their contributions to ORR.

The ORR activities of all M-N/Cs, including the reference (Zn)-N/C, were tested under three pH conditions (pH 0.3, 5.2 and 13.0). Surprisingly, although the metal contents were divergent for Ni, Mn, Sn, Sb and Bi based catalysts, these catalysts had very similar ORR performances and also site densities. Furthermore, the ORR activities and site density of these catalysts were significantly lower than that of Fe-N/C and Co-N/C. This observation suggests the existence of a common **framework** site (N/C) among this type of M-N/Cs and another separate metal based active site (M-N_x). While it has been previously proposed that single atom catalysts could have more than one type of active site, this study is the first to quantify the site density of each site and its corresponding performance. According to the nitrite stripping, the site density of all catalysts was determined, and the framework site density was calculated by averaging all M-N/Cs' site densities, except Fe-N/C and Co-N/C. The **framework** site density should be around 4.89×10^{18} sites g⁻¹, and it was observed that this framework site was not very active under acidic or near-neutral conditions, as the $TOFs_{framework}$ were very low under those conditions. However, under alkaline conditions, the $TOFs_{framework}$ were quite high and the potential reason why an increasing mass activity will be seen at high pH conditions is the deprotonation of pyridinic nitrogen. Metal based active sites had higher activities compared to framework sites in general. Fe-N_x sites showed higher activity under acidic and near-neutral conditions, while Co-N_x performed better in alkaline conditions. Finally, the kinetic mass activities of Fe-N/C and Co-N/C catalyst were estimated based on the number of active sites. It was evident that increasing the metal site density could dramatically improve the ORR activity, especially under acidic conditions. On the other hand, for alkaline conditions, the focus

could be on increasing the number of framework sites, as the $\text{TOF}_{\text{framework}}$ was very high under alkaline conditions.

3.5 Possible future work

A wide range of M-N/Cs was prepared by (trans)metalation, which is a promising method to produce single atom catalysts. However, there are several things could be done in the future to improve and understand the catalyst better.

Firstly, increasing the metal contents could be done by optimising the synthetic method. Only Fe based catalyst showed a very high metal content, which suggests there are potential empty sites without metal doped in. Refluxing with excess of salt during (trans)metalation could be tried to obtain a higher metal content. However, this should be done careful to prevent the formation of any metal clusters.

Also, a different amount of iron chloride could be tried during (trans)metalation step in order to prepare Fe-N/C with varying metal content. The oxygen reduction reaction and nitrite stripping tests can be performed with these catalysts to demonstrate the correlation of between site density and ORR. More importantly, it could potentially show whether the activity of iron based sites depends on the number of sites or not.

Furthermore, the optimisation of Fe and Co-based catalysts could be pursued, as they are the most promising catalysts for ORR. Increasing the metal content, lowering the particle sites, and increasing the surface area could be explored to further improve ORR performance.

Finally, there are potential other electrochemical reaction could be explored. Ni-based catalysts appear to be excellent candidates for catalysing the carbon dioxide reduction reaction to carbon monoxide. Moreover, the single atom catalysts for nitrogen reduction reaction and nitrate reduction reactions, which are widely studied recently, could be investigated in the future.

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Chapter 4 **Platinum-free catalyst for air-breathing electrochemical device-increasing the surface density of single atom coordinated Fe sites to improve performance***

In this chapter, Fe-N/C catalyst was focused on as it showed a promising performance. The synthetic method discussed in chapter 3 was optimised in three aspects, including the choice of solvent for transmetalation, the temperature of pyrolysis and also the use of different activating agents. The loading of iron ultimately reached 7 wt% with all single atom sites and the electrochemical accessible site of the optimised catalyst exceeded previously reported value. The performance of Fe-NC was tested both in rotating ring disk electrode and in fuel cell system under hydrogen-oxygen and hydrogen-air conditions. Although the performance of Fe-N/C was extremely high compared with other non-precious metal catalyst, the stability of Fe-N/C was very poor, and this problem should be investigated and improved in the future.

4.1 Introduction

Proton exchange membrane fuel cell (PEMFC) is a zero-emission power generation system that utilise hydrogen and oxygen from air, producing only water as by-product, making it environmentally friendly, as discussed in Chapter 1. However, one of the major barriers to commercialising PEMFC is the high cost of Pt catalysts. Under acidic conditions, Fe-N/Cs and Co-N/Cs have emerged as promising alternatives to Pt on the cathode side. Much research has been dedicated to improving the oxygen reduction reaction (ORR) performance of these catalysts under acidic conditions.¹⁻³ However, the performances of non-precious metal single atom catalysts (M-N/Cs) still fall short of Pt. In Chapter 3, (trans)metalation method was introduced and successfully prepared seven different M-N/Cs (M = Fe, Co, Ni, Mn, Sn, Sb and

* Parts of this chapter have been published in the paper: “High loading of single atomic iron sites in Fe-NC oxygen reduction catalysts for proton exchange membrane fuel cells” of which I am the second author.

Bi). Their oxygen reduction reaction performances and also site densities were measured as well. Fe-N/C showed the best performance in the acidic electrolyte but is still poorer than commercial Pt catalysts. Furthermore, the study of active sites on these catalysts indicates that increasing the loading of Fe could potentially enhance the catalytic performance significantly as the turnover frequency (TOF) of Fe-N_x sites was found to be the highest.

However, increasing the metal loading in M-N/Cs is indeed challenging due to the potential formation of the metal clusters, such as metallic nanoparticles, metal carbides or metal nitrides *etc.* during high temperature pyrolysis. The blast furnace is a well-known industry method to extract iron from ore by carbon; therefore, the presence of carbon can potentially facilitate the reduction of metal ions at high temperatures.⁴ These clusters are not as active as the single atom site for ORR and the formation of those clusters will decline the conductivity of catalysts. (Trans)metalation has shown promise in preventing the formation of metal clusters, but further optimisation of the process is necessary to achieve higher metal loadings with more active sites.

Therefore, in this chapter, the focus was on optimising the synthesis of the Fe-N/C catalyst to improve its ORR performance and gain a better understanding of its structure and active sites. The presence of Fe-N₄ moieties in the catalyst was confirmed by the ⁵⁷Fe Mössbauer spectroscopy (performed at CNRS in France) and X-ray absorption spectroscopy (XAS, performed at synchrotron SOLEIL in France). The site density of catalysts was determined by nitrite stripping as discussed in Chapter 3.^{5, 6} Finally, a PEMFC containing a cathode layer composed of the synthesised catalysts was tested under hydrogen-oxygen and hydrogen-air conditions.

4.2 Experimental

4.2.1 Synthesis of Catalysts

The catalyst was prepared in a similar way as reported in Chapter 3, but several improvements were done to optimise the resultant performance. Commercial ZIF-8 (Basolite[®] Z1200, Sigma Aldrich) was pyrolysed at 900 °C under nitrogen (BOC, 99.9995%) for 1 hour with the ramping rate is 3 °C min⁻¹. After the first pyrolysis, the mass loss of the catalyst is around 50 wt% as some of the zinc vaporises (Zn boiling point 907°C) and resolidifies on the inside of the furnace tube at a cooler location. The resultant black powder contains significant amounts of nitrogen doped carbon containing Zn-N_x sites, which is labelled as Zn-NC. In order to remove Zn more efficiently, compared to previous approaches, the Zn-NC catalysts were heated under reflux in 2 M H₂SO₄ (95%, VWR) for 8 hours instead of leaching at 80 °C to get □-NC, which □ stands for the empty vacancy site generated (Zn replaced by two protons). Around 2 g of □-NC were washed with 1 L of deionised water twice after the acid leaching to remove the physically adsorbed sulfuric acid. The catalyst was ball milled at 400 rpm for 2 hours with 100 zirconia balls within a Retsch PM 100 CM. 100 mg of Fe(II) chloride tetrahydrate (99%, Honeywell Fluka) and 100 mg of ball milled □-NC were mixed in 100 mL of methanol (VWR) and the mixture was heated under reflux for 8 hours. The catalyst was washed with 1 L of deionised water twice and then leached under 0.5 M H₂SO₄ for at least 8 hours at room temperature to remove the physically adsorbed iron ions. Then, the catalyst was washed with deionised water and dried in a vacuum oven at 70 °C overnight. This sample was labelled as Fe-NC^U. The unactivated catalyst was manually ground with activating agent (see below) using a weight ratio of the catalyst to activating agent of either 2:1 or 1:1. The table of activating agents used is shown in Table 4.1. Finally, the second pyrolysis was performed at 907 °C under 5% H₂/N₂ for 1 hour and the ramping rate is 3 °C min⁻¹.

Table 4.1 The table of activating agents used

Chemicals	Brand	Purity
Dicyandiamide (DCDA)	Sigma-Aldrich	99 %
Thiourea	Sigma-Aldrich	≥ 99 %
Ammonium chloride	BDH	99 %
Ammonium phosphate dibasic	Sigma-Aldrich	≥ 98 %
Phenanthroline	Sigma-Aldrich	≥ 99 %
Triphenylphosphine	Sigma-Aldrich	99 %
Cyanamide (CA)	Sigma-Aldrich	99 %

4.2.2 Physical Characterisations

Transmission electron microscopy (TEM, Talos F200X, FEI, performed at National Institute of Chemistry in Slovenia) and scanning transmission electron microscopy (STEM, performed at National Institute of Chemistry in Slovenia) were used to analyse the morphology of the catalyst at different synthetic stages. For analysing the iron sites at atomic resolution, a probe Cs-corrected scanning transmission electron microscope Jeol ARM 200 CF, equipped with a cold field emission electron source, was used (performed at National Institute of Chemistry in Slovenia). To minimise the beam damage, 80 keV and low beam current were used. High-angle annular dark-field (HAADF) images were obtained using 68 - 180 mrad collection half-angles at 24 mrad probe convergence semi-angle. Gatan Quantum ER dual Electron Energy-loss Spectroscopy system was used for detection of carbon, nitrogen, oxygen and iron while elemental mappings were collected using Jeol Centurio EDXS system with 100 mm² SDD detector. Powder samples were directly transferred to lacey carbon-coated copper TEM grids.

Brunauer-Emmett-Teller (BET) surface area, microporous surface area and pore volume were measured in the same method as mentioned in Section 2.2.1 (Chapter 2). Inductively coupled plasma mass spectrometry (ICP-MS) was taken using an Agilent ICP-MS 7900 to determine the metal contents in the catalyst. The catalyst was digested in aqua regia overnight at 80 °C and diluted with 2 wt% of nitric acid (Sigma Aldrich, 70%) to get the sample for analysis. X-ray photoelectron spectroscopy (XPS) measurements were taken by the collaborator in

HarwellXPS using a Thermo Scientific K-Alpha X-ray Photoelectron Spectrometer system (Al K α , 1486.6 eV). Data were analysed by CasaXPS and calibrated with C 1s peak at 284.8 eV. Raman spectra were obtained using a Bruker Confocal Raman Microscope SENTERRA II. The wavelength used was 532 nm and the substrate was a glass slide.

X-ray absorption spectroscopy (XAS) was obtained at Synchrotron SOLEIL in France. Zn K-edge was measured in transmission mode and Fe K-edge was determined using fluorescence mode. The detailed measurement and analysis method were discussed in the paper.⁶ The transmission mode of ^{57}Fe Mössbauer spectrometer (Wissel, Germany) was used and the catalysts were mounted in a 2 cm² holder. The measurements were operated at 5 K in a helium flow cryostat (SHI-850 Series from Janis, USA) and all measurements was obtained at CNRS in France.⁶

4.2.3 Electrochemical Measurements

There are two main electrochemical measurements performed in this chapter: oxygen reduction reaction and nitrite stripping. Ink for deposition of catalyst on the RDE electrode is prepared in the same way as in Section 2.1.4 (Chapter 2). The measurement setup is the same as shown in Section 2.1.1 (Chapter 2).

For oxygen reduction reaction, a self-made reversible hydrogen electrode (RHE) was used as reference electrode; glassy carbon was used as counter electrode and the working electrode was a rotating ring disk electrode (RRDE) with a glassy carbon disk and a gold ring. The electrolyte was 0.5 M sulfuric acid (95%, VWR). The ink was drop casted on the glassy carbon disk and the loading of catalyst is varied between 0.1 - 0.8 mg cm⁻². The catalyst was first activated by measuring cyclic voltammetry (CV) between 0.00 V_{vs. RHE} and 1.00 V_{vs. RHE} at a scan rate of 10 mV s⁻¹ with 1,600 rpm rotation. This activation step is normally helpful for the Pt based catalyst to remove the oxide on surface; however, for non-precious metal catalysts, this activation is to

make sure catalyst is properly wetted by electrolyte and normally the ORR performance will not change during the CVs. Linear sweep voltammetry (LSV) was measured from 1.00 V_{vs. RHE} to 0.00 V_{vs. RHE} at a scan rate of 5 mV s⁻¹ with rotating rate of either 1,600 or 900 rpm. The potential of the gold ring is held at 1.5 V_{vs. RHE} to calculate the hydrogen peroxide yield. A LSV under N₂ was recorded for background correction and electrochemical impedance spectroscopy (EIS) was used to determine the Ohmic resistance to correct the solution iR loss.

For nitrite stripping, the measurement conditions are the same as mentioned in Section 3.2.3 (Chapter 3).

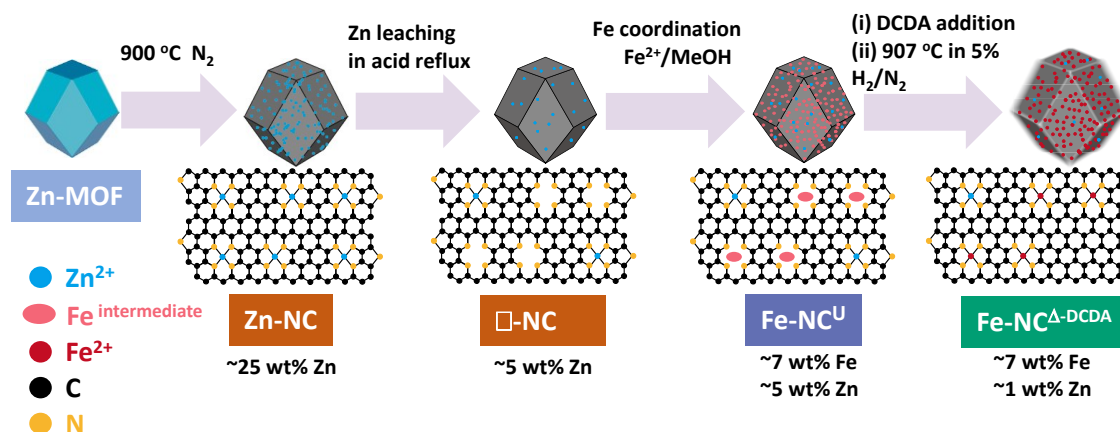
4.2.4 Fuel Cell Measurements

For single cell proton exchanged membrane fuel cell (PEMFC) measurements, the membrane electrode assemblies (MEAs) were prepared in the same method in Section 2.1.6 (Chapter 2). The bipolar plates with serpentine type flow field were used. The compression of MEA was controlled by the glass-reinforced PTFE gaskets and the compression was 20 - 25%. The operating temperature of fuel cell was 80 °C and hydrogen (BIP Plus, 99.99996%) and oxygen (Ultra Pure Plus, 99.9998%) / compressed air are supplied to anode and cathode side respectively. The gases supplied are all provided at 100% relative humidity (RH) and 1 bar gauge back pressure was maintained during the measurement. For hydrogen and oxygen measurement, the flow rate for each side was 200 standard cubic centimetre per minute (sccm). However, for hydrogen and air condition, the flow rate of hydrogen was 300 sccm and that of air was 1,000 sccm. The polarisation curves were measured by 850e Fuel Cell Test System (Scribner Associates).

4.3 Result and Discussion

4.3.1 Optimisation of the Synthesis of Fe-N/C

Several optimisations were made during the synthesis of catalyst compared to the method used in Section 3.2.1 (Chapter 3) and the optimised schematic diagram is shown Scheme 4.1. Firstly, the pyrolysed Zn-NC was leached with 2 M sulfuric acid under reflux instead of 80 °C in order to remove the zinc more efficiently. According to the ICP-MS data, refluxing in acid would decrease the Zn content from 25 wt% to around 5 wt%; however, if the leaching was performed at only 80°C, there were still around 10 wt% of Zn left in □-NC. Generating more empty vacancy sites would be beneficial for achieving high Fe loading in the catalyst as there are more places that Fe could metalate. Furthermore, the extra Zn leached out should come from the more stable Zn-N_x sites. If iron could metalate to those more stable sites, it potentially benefits the ORR activity.



Scheme 4.1 Schematic diagram of preparing optimised Fe-NC^{A-DCDA}. [Printed with permission from ref⁶]

Secondly, four different solvents were tested during the (trans)metalation step, including water, isopropanol, methanol and ethanol. ORR performances of the catalysts prepared with different solvents are shown in Figure 4.1 (a). Water was the worst solvent as the half-wave potential is the smallest; however, for isopropanol, ethanol and methanol, there was not a significant difference. One of possible reasons why water is not as good as other is that the catalyst is very

hydrophobic, and this could trigger the wetting issues. Moreover, the iron oxides or oxyhydroxides, which might be formed during reflux, are not soluble in water. (Trans)metalation under methanol had slightly better performance than others and this probably is due to high polarity compared with the other two solvents. Therefore, methanol was used in the following synthesis.

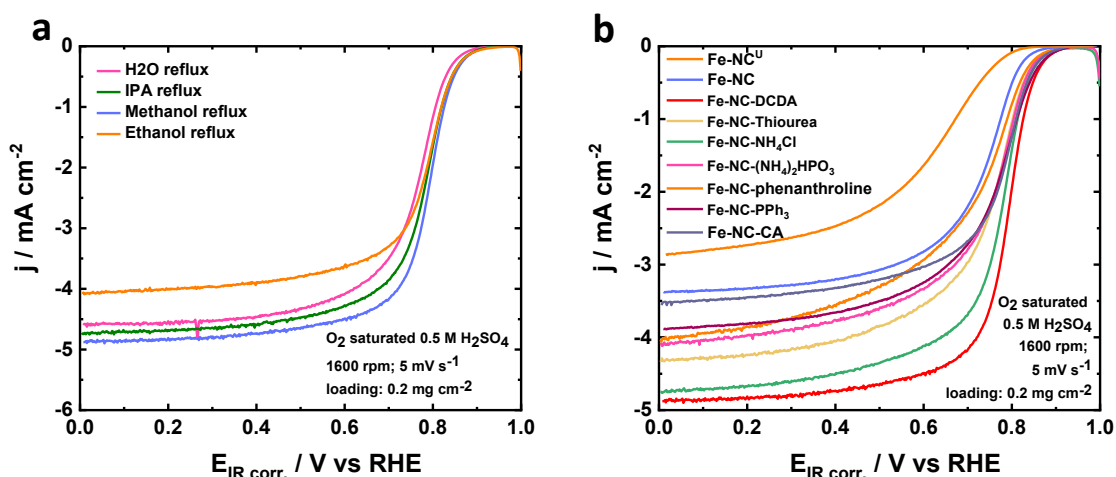


Figure 4.1 (a) ORR measurements of catalysts prepared by different solvents during (trans)metalation; (b) ORR measurements of catalysts pyrolysed with different activating agents. [BM: ball milling, IPA: isopropanol, DCDA: dicyandiamide, CA: cyanamide]

Moreover, seven different activating agents were tried during second pyrolysis and the ORR performances were compared to Fe-NC^U and second pyrolysed Fe-NC as shown in Figure 4.1 (b). Compared the performance of Fe-NC^U to that of Fe-NC, the second pyrolysis could improve the ORR activity significantly and this will be explained in later section. All of the activating agents could improve the ORR activity slightly, especially at the high potential region ($0.8 - 1.0 \text{ V}_{\text{vs. RHE}}$). Ammonium chloride and dicyandiamide are the two species which exhibited a significant improvement; and those two reagents potentially activate the catalyst in a similar way. Dicyandiamide is a commonly used as blowing agent and will decompose to ammonia at $300 - 350 \text{ }^\circ\text{C}$.⁷ Ammonium chloride is also easily decomposed around $350 \text{ }^\circ\text{C}$ and generates ammonia and hydrochloric acid as products.⁸ Therefore, the activating agent would release ammonia at $350 \text{ }^\circ\text{C}$, which potentially improves the performance of these catalysts through its ability to help the formation of pyridinic-N on the graphene layer.^{9,10} Therefore,

dicyandiamide and ammonium chloride improve the ORR activity more compared with other activating agents. In this chapter, dicyandiamide would be used during second pyrolysis.

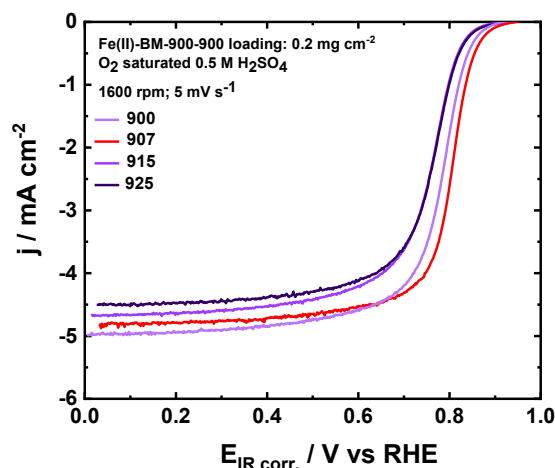


Figure 4.2 ORR measurements of catalysts pyrolysed at different temperature with DCDA.

Finally, the temperature of pyrolysis had been investigated as well. High temperature pyrolysis would be helpful to generate a more graphitic carbon, which would increase the conductivity of catalyst. Furthermore, increasing the pyrolysis temperature could help remove some residual Zn from the catalysts. However, a high temperature treatment also increased the risk of demetallation and loss of nitrogen, which would decrease the number of active sites and also ORR activity. Therefore, the temperature of pyrolysis is a trade-off and an optimised temperature should be considered.

Table 4.2 Nitrite stripping data and ORR performances of catalysts which are pyrolysed at different temperatures.

Temperature of 2 nd pyrolysis	Site Density / 10 ¹⁹ sites g ⁻¹	TOF / e site ⁻¹ s ⁻¹			J _{kin} in 0.5 M H ₂ SO ₄ / mA cm ⁻²		
		0.80 V	0.85 V	0.90 V	0.80 V	0.85 V	0.9 V
900	3.93	0.58	0.07	0.01	3.72	0.23	0.03
907	4.67	0.96	0.12	0.01	5.44	0.65	0.08
915	2.22	1.03	0.12	0.02	1.12	0.17	0.02
925	2.20	0.81	0.10	0.01	1.17	0.19	0.03

Four different temperatures were tested, and the ORR performances are shown in Figure 4.2. As the limiting current of all measurements were slightly different, the kinetic current was used to compare the ORR activity and the calculated value is shown in Table 4.2. Nitrite stripping of all these catalysts was also exhibited and the calculated site density and turnover frequency (TOF) are shown in Table 4.2. 900 °C is a commonly used temperature for preparation of SACs to give a good performance and the catalyst prepared at 900 °C was the reference material to compare. If the pyrolysis temperature increases to 915 °C or 925 °C, the ORR performance and site density of catalyst decrease significantly. Also, a significant mass loss was observed when 915 °C or 925 °C was set. The mass loss could be triggered by removing Zn from the catalyst or losing nitrogen sites. The catalyst pyrolysed at 907 °C showed an improvement in both site density and ORR activity and this might be because 907 °C is the temperature where Zn boils and holding at 907 °C for one hour will help to remove the residual Zn. Removal of the residual Zn could improve the conductivity of materials and also generate more free N/C sites. Therefore, 907 °C was used for the second pyrolysis to activate the catalyst.

4.3.2 Physical Characterisations

The TEM and STEM images are shown in Figure 4.3 to analyse the structural characterisations of catalysts. The morphology of unactivated Fe-NC^U is still polyhedron, which is exactly same as the ZIF-8 precursor as shown in Figure 4.3 (a); and the particle size of catalyst is mainly around 350 nm. In comparison to Fe-NC^{A-DCDA}, there was not any regular polyhedron shape shown in the catalyst anymore, because ammonia could etch the carbon and change the structure of carbon, as depicted in Figure 4.3 (b).¹¹ The HAADF-STEM with energy dispersive X-ray spectroscopy (EDXS) Fe mapping is shown in Figure 4.3 (c); it showed that the iron is evenly distributed on the catalysts.

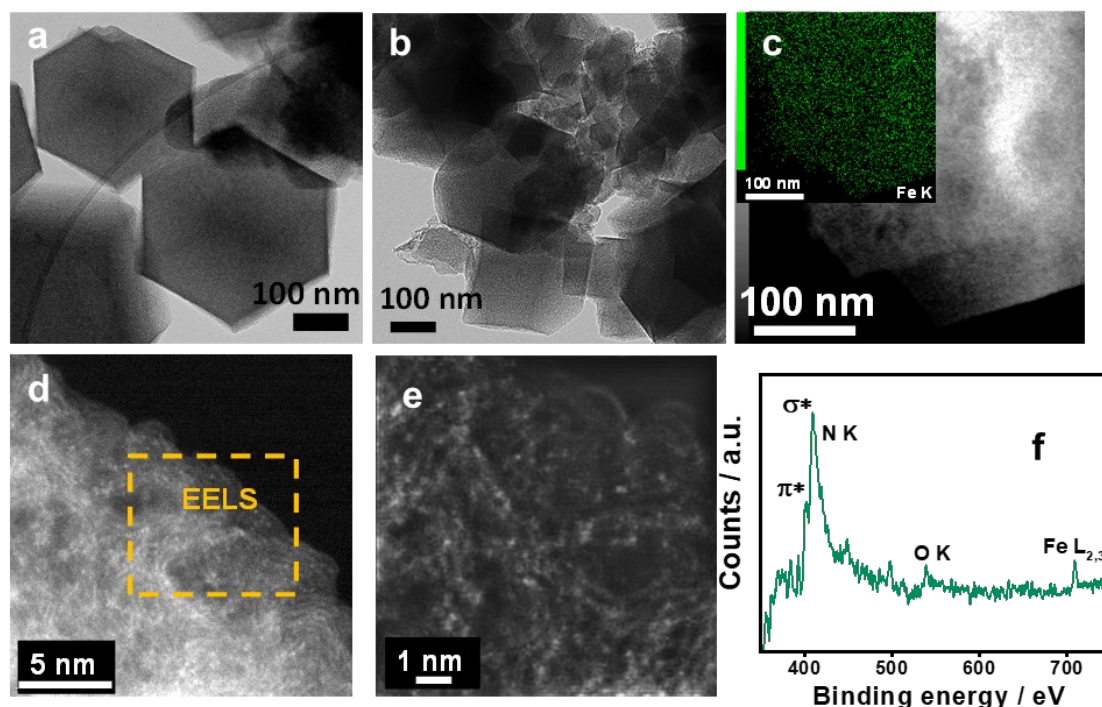


Figure 4.3 (a) TEM image of Fe-NC^U and (b) TEM image of Fe-NC^{A-DCDA}; (c) HAADF-STEM of Fe-NC^{A-DCDA} with inset EDXS Fe mapping; (d) & (e) aberration corrected atomic resolution HAADF-STEM; (f) EELS spectrum of region shown in (d). [Printed with permission from ref⁶]

Furthermore, the strong Fe signal intensity also proved the loading of Fe in the catalyst is high. According to the ICP-MS, there are around 7 wt% of Fe and only less than 1 wt% of Zn left in the Fe-NC^{A-DCDA}. Figure 4.3 (d) and (e) are the aberration-corrected HAADF-STEM of Fe-NC^{A-DCDA} and the bright white spots stand for the atomic Fe sites in the catalysts. All bright dots are distributed singly instead of clustering, which indicates there is no metal nanoparticle formed. The electron energy loss spectroscopy (EELS) of the rectangular region in Figure 4.3 (d) is displayed in Figure 4.3 (f) and there is a clear Fe L_{2,3} peak, which is rarely shown in Fe-SACs as the loading of other literatures is limited to around 1 - 2 wt%. Also, the carbon peaks in EELS suggest the catalyst is mainly amorphous carbon, instead of graphitic or glassy carbon.¹²

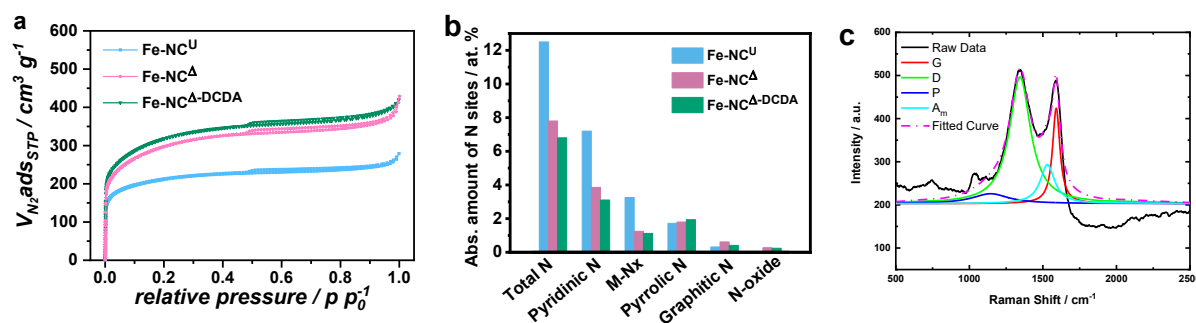


Figure 4.4 (a) BET nitrogen isotherm of Fe-NC^{U} , Fe-NC^{A} , $\text{Fe-NC}^{\text{A-DCDA}}$; (b) absolute amount of nitrogen sites in Fe-NC^{U} , Fe-NC^{A} , $\text{Fe-NC}^{\text{A-DCDA}}$; (c) Raman Spectroscopy of $\text{Fe-NC}^{\text{A-DCDA}}$ [Printed with permission from ref⁶]

BET surface area, pore size and pore volume are determined as shown in Table 4.3 and the nitrogen isotherm of three Fe-NCs at different synthetic stages is shown in Figure 4.4 (a). All catalysts had a type I / H4 isotherm, suggesting the catalysts were dominated by micropores. $\text{Fe-NC}^{\text{A-DCDA}}$ had the largest surface area ($1,155 \text{ m}^2 \text{ g}^{-1}$) and the largest micropore volume ($0.432 \text{ cm}^3 \text{ g}^{-1}$). There is a huge increase in both surface area and also microporous volume after the second pyrolysis and this is potentially caused by removing Zn.

Table 4.3 BET specific surface area, micropore area and micropore volume of Fe-NC^{U} , Fe-NC^{A} , $\text{Fe-NC}^{\text{A-DCDA}}$. [Printed with permission from ref⁶]

Catalyst	Surface area and porosity		
	BET SSA ($\text{m}^2 \text{ g}^{-1}$)	t-plot micropore area ($\text{m}^2 \text{ g}^{-1}$)	Micropore volume ($\text{cm}^3 \text{ g}^{-1}$)
Fe-NC^{U}	775	614	0.277
Fe-NC^{A}	1070	752	0.398
$\text{Fe-NC}^{\text{A-DCDA}}$	1155	836	0.432

Nitrogen functionalities were analysed by XPS and the data fitting was done using the similar value used in Section 3.3.1 (Chapter 3). The summarised absolute amount of nitrogen sites graph is shown in Figure 4.4 (b). Before the second pyrolysis (Fe-NC^{U}), there are around 12.5 at% of nitrogen left but trace amount of Fe (less than 0.1 at%) had been detected by XPS. If only a small amount of nitrogen is left in the catalyst post pyrolysis, nitrogen might not be enough to stabilise Fe ions and form Fe-N_4 . The total nitrogen content decreased to 6.8 at% for

Fe-NC^{Δ-DCDA}, which shows that high temperature treatment will lose some of nitrogen on the catalyst. The majority of nitrogen in the Fe-NC catalysts are pyridinic nitrogen, M-N_x and pyrrolic nitrogen; only a very small amount of graphitic nitrogen and nitrogen-oxide present. Raman spectroscopy is used to analyse the carbon structure of Fe-NC^{Δ-DCDA} and the spectrum is shown in Figure 4.4 (c). There are four peaks normally observed in this type of material, including a graphitic peak (G), disorder peak (D), amorphous carbon (A_m) and pentacene (P) peak.¹³ Graphitic peak and disorder peak should be at 1573 - 1600 cm⁻¹ and 1340 - 1356 cm⁻¹, and these peaks are corresponding to E_{2g} and A_{1g} type of vibrations in graphene.¹⁴ Cancado *et al.* claimed that the intensity of the disorder peak and graphitic peak could be used to determine the plane size of carbon (L_a) by Equation (4.1)¹⁵

$$L_a = \frac{560}{E_l^4} \times \left(\frac{A_D}{A_G}\right)^{-1} \quad (4.1)$$

where E_l stands for the excitation laser energy in eV and the A_D and A_G are the integrated intensity of D and G peaks respectively. All peaks were fitted to a Lorentzian shape and the integrated intensity of D and G peaks are determined. The wavelength of Raman spectroscopy was 532 nm and the average graphene domine size for Fe-NC^{Δ-DCDA} is calculated as 7.3 nm.

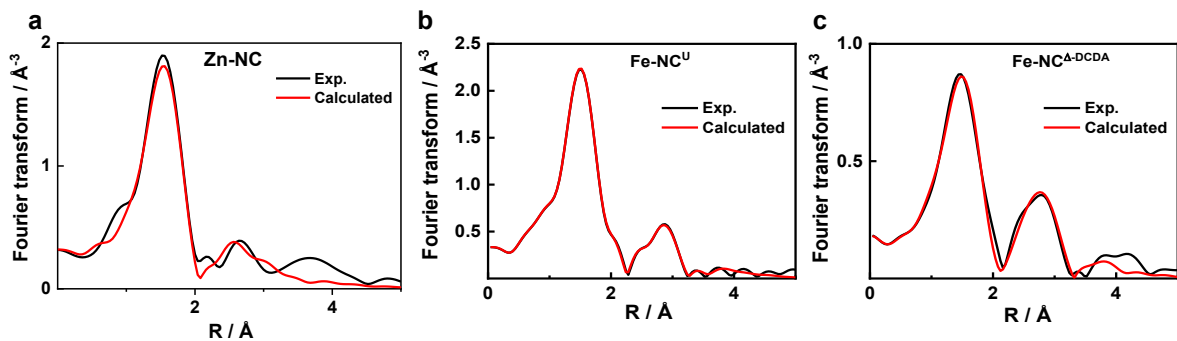


Figure 4.5 (a) Zn K-edge EXAFS analysis of Zn-NC; (b) Fe K-edge EXAFS analysis of Fe-NC^U; (c) Fe K-edge EXAFS analysis of Fe-NC^{Δ-DCDA}. [Printed with permission from ref⁶]

XAS measurements were used to determine the Fe coordination number and also to confirm the formation of single atom sites in the catalyst. The Fourier Transform EXAFS of Zn-NC, Fe-NC^U and Fe-NC^{Δ-DCDA} are shown in Figure 4.5 and the best fit parameters are shown in

Table 4.4. The pyrolysed ZIF-8 (Zn-NC) showed a single atomic zinc site feature as there is a peak at 1.5 Å in the Fourier Transform EXAFS (Figure 4.5 (a)), which corresponding to M-N/O peak.¹⁶ The first coordination shell is Zn-N₄ with bond length of 2.02 Å and the second coordination shell is consist of Zn-C with average bond length of 3.19 Å. Hence, it is in an agreement that the pyrolysed ZIF-8 would give Zn-N₄ moieties and removing Zn would leave empty □-N₄ sites. The high content of □-N₄ sites would be able to stabilise Fe-N₄ preventing formation of Fe cluster during the second pyrolysis. For the Fe-NC^U, the first coordination shell contains around four nitrogen and two oxygen, which is believed interact axially with Fe. Therefore, at this stage Fe-NC^U coexists both Fe-N₄ and iron oxide. There are Fe-C and Fe-Fe interactions in the second coordination shell. The EXAFS of activated Fe-NC^{Δ-DCDA} could be fitted well with FeN_xC_y moiety and the first coordination shell with four nitrogen atoms at 2.02 Å and two Fe-C interactions in higher coordination shells. A similar coordination was observed with other pyrolysed materials.¹⁷

Table 4.4 Best-fit parameters obtained from the EXAFS analysis of Zn-NC, Fe-NC^U, and Fe-NC^{Δ-DCDA}. R is the interatomic distance, σ² represents the Debye-Waller factor, and CN is the coordination number. [Printed with permission from ref⁶]

Catalyst		R(Å)	σ ² (10 ⁻³ Å ²)	CN
Zn-NC	Zn-N	2.02±0.01	6.3±0.05	4.0±0.02
	Zn-C	3.19±0.02	35±0.10	6.2±1.00
Fe-NC ^U	Fe-N	2.09±0.01	6.3±0.02	3.8±0.02
	Fe-O	1.95±0.01	3.7±1.00	1.8±0.02
	Fe-C	3.50±0.02	11±0.03	7±0.02
	Fe-Fe	3.20±0.02	19±0.03	2.2±0.03
Fe-NC ^{Δ-DCDA}	Fe-N	2.02±0.02	9±0.02	3.9±0.01
	Fe-C ₁	3.10±0.02	12±0.02	5±0.02
	Fe-C ₂	3.47±0.02	11±0.02	3±0.01

Furthermore, the averaged bond length of Fe-N and Fe-C decreases after second pyrolysis compared to the result of Fe-NC^U and Fe-NC^{Δ-DCDA}. This indicates iron was reorganised during the pyrolysis and the interaction between Fe and N/C was stronger. Also, the absence of Fe-O in Fe-NC^{Δ-DCDA} suggested the iron oxides was converted to Fe-N interaction.

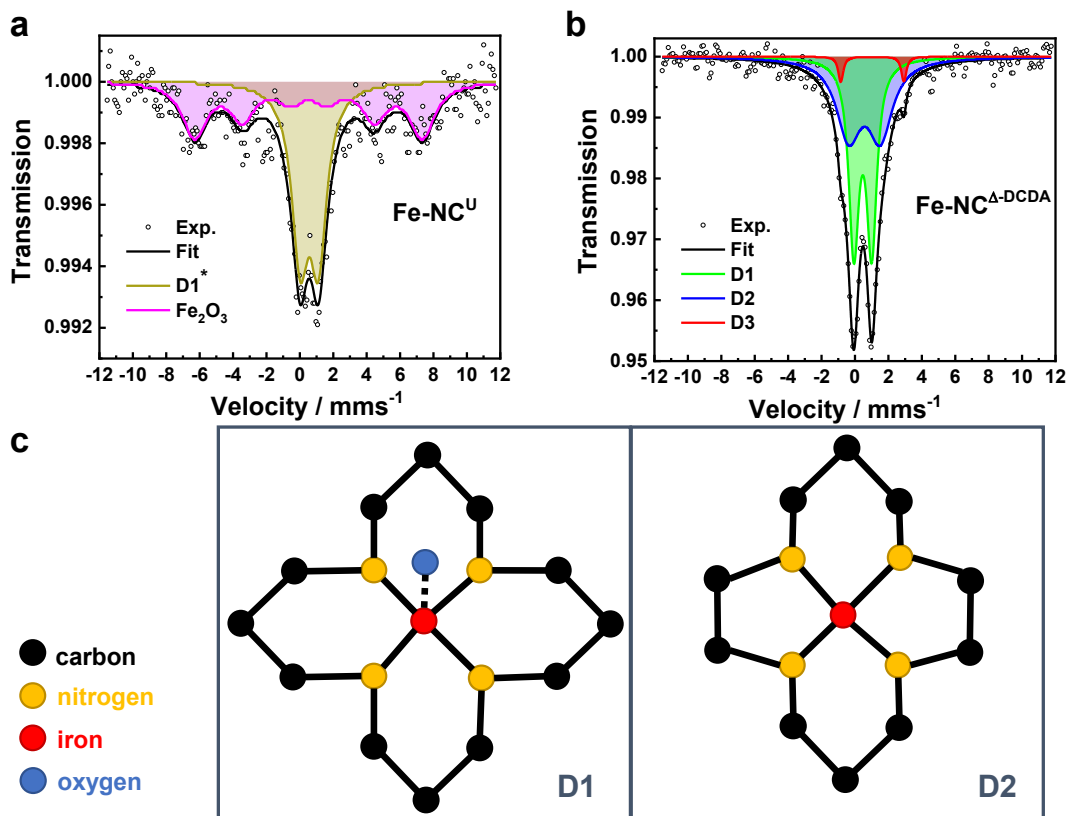


Figure 4.6 (a) ^{57}Fe cryo Mössbauer spectrum of Fe-NC^{U} ; (b) ^{57}Fe cryo Mössbauer spectrum of $\text{Fe-NC}^{\Delta\text{-DCDA}}$; (c) schematic diagram of D1 and D2 sites. [Printed with permission from ref⁶]

The ^{57}Fe Mössbauer spectroscopy of Fe-NC before and after activation were also measured at 5 K as shown in Figure 4.6 (a) and (b) to understand the Fe speciation and the function of second pyrolysis. The spectrum of unactivated Fe-NC^{U} is very noisy compared with that of $\text{Fe-NC}^{\Delta\text{-DCDA}}$, which potentially caused by weak interaction between Fe and NC framework. The unactivated Fe-NC^{U} was fitted with two components, including a sextet Fe_2O_3 and a doublet D1^* with quadrupole splitting (QS) of 1.1 mm s^{-1} . D1^* peak could be the Fe-N_x sites according to the literature.^{18, 19} However, it is clear that Fe_2O_3 makes a major contribution to the unactivated Fe-NC^{U} even though there was not any visible iron oxide nanoparticles shown in the HAADF-STEM, which means Fe_2O_3 is present at a sub-nanometre size.

Table 4.5 Fitted parameter of the ^{57}Fe Mössbauer spectra obtained at 5 K for Fe-NC^{U} and $\text{Fe-NC}^{\Delta\text{-DCDA}}$. Δ is the isomer shift and ΔE_{Q} stands for the quadrupole splitting. [Printed with permission from ref⁶]

Catalyst	Component	Rel. Area / %	δ / mm s^{-1}	ΔE_{Q} / mm s^{-1}
Fe-NC^{U}	D1 *	50.25	0.565	1.104
	D2	0	-	-
	Fe_2O_3	49.75	0.520	0
$\text{Fe-NC}^{\Delta\text{-DCDA}}$	D1	49.03	0.468	1.072
	D2	47.87	0.572	1.895
	D3	3.1	1.04	3.776

For the activated catalyst, the sextet Fe_2O_3 peak disappeared and three doublets, which are labelled as D1, D2 and D3, were used to fit the spectrum. D1 was identified by combination of an *ex-situ* experiment and also DFT calculation. D1 site corresponds to the high spin state O-Fe(III) N_4C_{12} moiety with a small quadrupole splitting (QS) value ($\sim 1.0 \text{ mm s}^{-1}$) and D2 site could be assigned to a low- or medium-spin Fe(II) N_4C_{10} with slightly higher quadrupole splitting value (between 1.8 and 2.8 mm s^{-1}) as shown in Figure 4.6 (c) and (d).^{20, 21} The minor D3 peak represents the high-spin ferrous centres due to the high isomer shift (IS), which potentially could be either the third type of Fe- N_x sites²² or FeCl_2 hydrate or graphitic intercalated FeCl_2 ^{23, 24} due to similar in isomer shift. Comparing the Mössbauer spectra of Fe-NC^{U} and $\text{Fe-NC}^{\Delta\text{-DCDA}}$, it seems that second pyrolysis converts the inactive Fe_2O_3 sites into activate Fe- N_x sites. This also explained why the catalysts with second pyrolysis improved the ORR activities significantly compared to the Fe-NC^{U} as shown in Figure 4.1 (b).

4.3.3 Oxygen Reduction Reaction Performances and Site Densities

Although there are 7 wt% iron content in both Fe-NC^{U} and $\text{Fe-NC}^{\Delta\text{-DCDA}}$ according to ICP-MS data, not all of the iron is present as the active sites for ORR as some of irons might be buried in the catalysts and not accessible to the reactants, or in other, inactive sites. Therefore, it is crucial to quantify the electrochemical accessible and active sites, which were determined by *in situ* nitrite stripping and the CV scans of unpoisoned, poisoned and recovered stages for Fe-NC^{U} , Fe-NC^{Δ} and $\text{Fe-NC}^{\Delta\text{-DCDA}}$ catalysts with results shown in Figure 4.7. The reduction of

adsorbed nitrite takes place between 0.29 V_{vs. RHE} and -0.3 V_{vs. RHE}; for both Fe-NC^Δ and Fe-NC^{Δ-DCDA}, the reduction peaks were well-defined and visible. However, for the unactivated Fe-NC^U, the reduction peak was imperceptible in a similar scale.

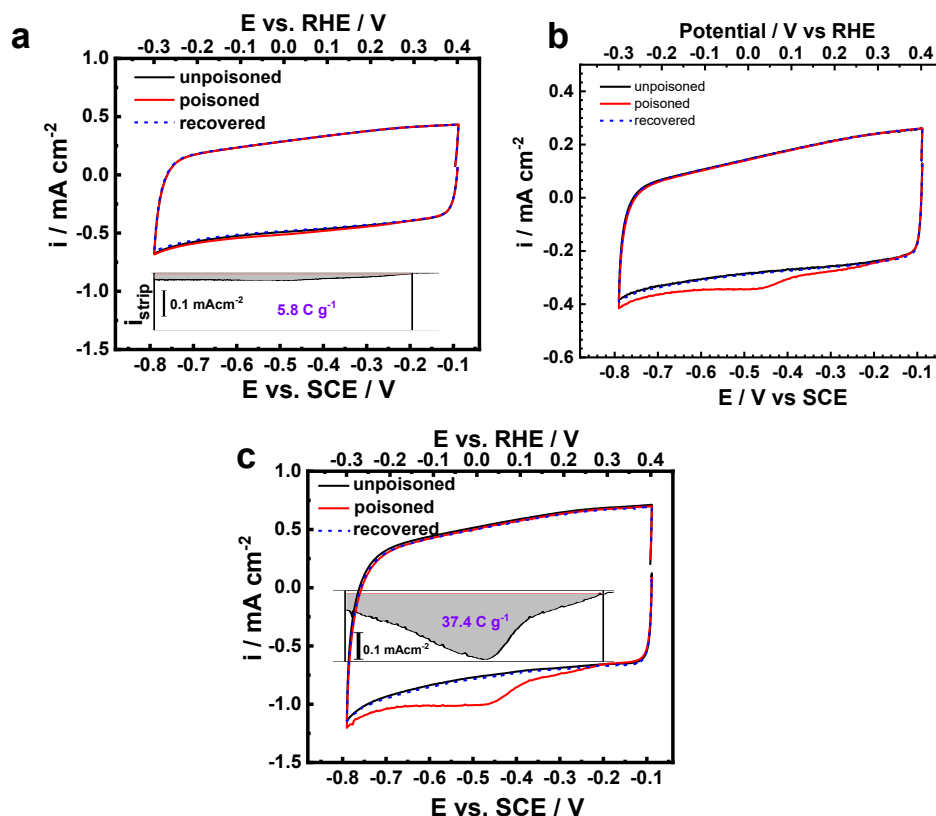


Figure 4.7 (a) nitrite stripping of Fe-NC^U, (b) nitrite stripping of Fe-NC^Δ and (c) nitrite stripping of Fe-NC^{Δ-DCDA} with unpoisoned, poisoned and recovered CV scans and the inset is the charge of nitrite reduction. [Printed with permission from ref⁶]

The total amount of charge involved in reduction of nitrite for Fe-NC^U was only around 5.8 C g⁻¹, however, for Fe-NC^Δ and Fe-NC^{Δ-DCDA}, the total charge are 9.0 C g⁻¹ and 37.4 C g⁻¹ respectively. According to the total charge and also ORR performance at pH 5.2 electrolyte, the site density of catalyst and also TOF under different potential were calculated and shown in Table 4.6.

The active sites of Fe-NC^U catalyst were only 0.72 x 10¹⁹ sites g⁻¹; however, the thermal activated Fe-NC^{Δ-DCDA} had 4.67 x 10¹⁹ sites g⁻¹ active sites, which is six times higher. These differences also support the Mössbauer result that the second pyrolysis could convert inactive

Fe₂O₃ nanoparticles to Fe-N_x active sites, including D1 and D2 sites. Compared the site densities of Fe-NC^Δ and Fe-NC^{Δ-DCDA}, the DCDA treatment actually increased the active site density during second pyrolysis. In Chapter 3, it was demonstrated that the TOF is independent of the site density, indicating that achieving high TOF is equally crucial as reaching high site density. Comparing all TOFs at 0.8 V_{vs. RHE} for Fe-NC^U, Fe-NC^Δ and Fe-NC^{Δ-DCDA}, the TOF increases; especially the Fe-NC^{Δ-DCDA} had 22 times higher TOF than the Fe-NC^U and 1.5 times higher than Fe-NC^Δ. Hence, activating with DCDA not only increases the site density but also improves the TOF of electrochemical accessible sites.

Table 4.6 The summary of the site density and TOF at pH 5.2 electrolyte. [Printed with permission from ref⁶]

Catalyst	SD / 10 ¹⁹ sites g ⁻¹	TOF _{5.2} / electrons site ⁻¹ s ⁻¹		
		@0.80 V _{RHE}	@0.85 V _{RHE}	@0.90 V _{RHE}
Fe-NC ^U	0.72	0.05	0	0
Fe-NC ^Δ	1.12	0.72	0.09	0
Fe-NC ^{Δ-DCDA}	4.67	1.12	0.13	0.02

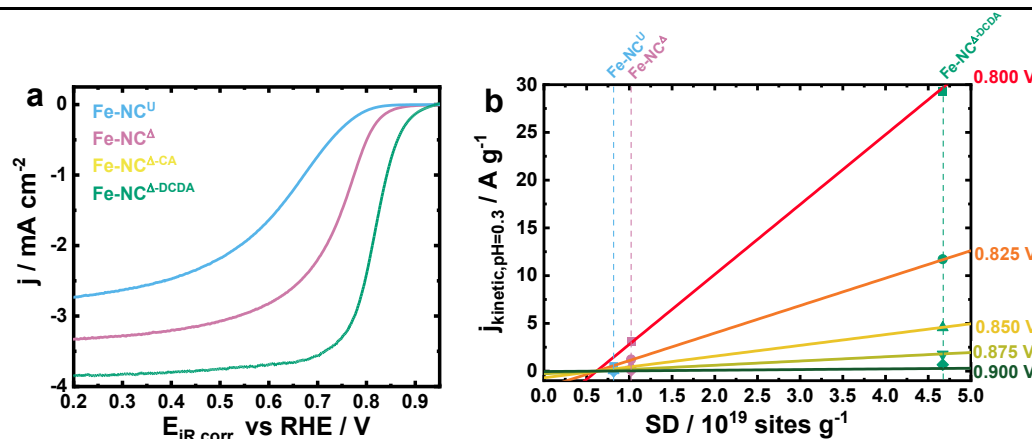


Figure 4.8 (a) The ORR measurement of Fe-NC^U, Fe-NC^Δ, Fe-NC^{Δ-DCDA} in 0.5 M H₂SO₄ with a rotation rate of 900 rpm; (b) correlation of kinetic ORR activity in 0.5 M H₂SO₄ at different potentials with the site density determined by nitrite stripping. Line stands for the best fit. [Printed with permission from ref⁶]

The ORR performances of Fe-NC^U, Fe-NC^Δ, Fe-NC^{Δ-DCDA} in 0.5 M H₂SO₄ electrolyte at 900 rpm were measured and are shown in Figure 4.8 (a). The half-wave potential ($E_{1/2}$) of Fe-NC^{Δ-DCDA} is around 0.815 V_{vs. RHE} and the kinetic mass activity at 0.80 V_{vs. RHE} is 31.9 Ag⁻¹, which

is much higher than the benchmark Fe-NCs ($\sim 2.5 \text{ Ag}^{-1}$)^{17, 25, 26}. It is very important to correlate the ORR performance measured at pH 0.3 with the site density determined at pH 5.2 together; therefore, the graph of kinetic mass activity at pH 0.3 under different potential against the site density was plotted in Figure 4.8 (b). It showed a very good linear relationship between the kinetic mass activity and the site density and the line was fitted by equation (4.2)

$$j(\eta, SD) = (SD - SD_0) e j_{0,site} \exp\left(\frac{-\alpha\eta F}{RT}\right) \quad (4.2)$$

where j stands for the kinetic mass activity (A g^{-1}), η is the overpotential (V), SD is the site density (sites g^{-1}), e is the charge of an electron, $j_{0,site}$ is the exchange current density associated for a single site ($\text{electrons site}^{-1} \text{ s}^{-1}$), α is the symmetry factor, F stands for the Faraday constant (C mol^{-1}), R is the ideal gas constant and T stands for the temperature (K). SD_0 is the minimum site required to have any ORR activity as the fitted line did not go through the origin, which means there is a threshold requirement to get the ORR activity. In Chapter 3, a hypothesis about having more than one active site had been discussed because there is a similar site density and ORR activity shown across a wide range of different metal based M-N/C catalysts. This indicates there are two different types of sites; one is metal based M-N_x site and the other one is called ‘framework’ site. Based on the fitting on Figure 4.8 (b), the SD_0 in this graph is $6.2 \times 10^{18} \text{ sites g}^{-1}$, which potentially to be framework site. Therefore, it means there are 6.2×10^{18} framework sites presented in the catalyst, which had no contribution to the ORR activity. The other fitted parameters are $j_{0,site} = 5.0 \times 10^{-7} \text{ electron site}^{-1} \text{ s}^{-1}$ and $\alpha = 0.96$. The exchange current density of Pt site is $0.012 \text{ electron site}_{\text{Pt}}^{-1} \text{ s}^{-1}$, which is around 20,000 times higher than the Fe-NC.²⁷ Therefore, the activity of Fe-NC site is much smaller than that of Pt site.

4.3.4 Fuel Cell Performances

Single cell PEMFC measurements were tested in both 5 cm^2 and 50 cm^2 cell active area. The loading of Fe-NC^{Δ-DCDA} in 5 cm^2 cell is around 3.9 mg cm^{-2} . The hydrogen-oxygen and

hydrogen-air polarisation curves are shown in Figure 4.9. For hydrogen-oxygen condition, the current density at 0.9 V_{iR-free} was around 41.3 mA cm⁻², which is almost the highest reported value for the non-precious metal catalysts.^{3, 17, 28-33} The comparison of catalytic activities under hydrogen-oxygen condition was shown in Figure 4.10 (a). Although some of catalysts also had very high current density at 0.9 V_{iR-free} (around 20 - 35 mA cm⁻²), the mass activity of those catalysts is not as high as that of Fe-NC^{Δ-DCDA}. As the loading of Fe-NC^{Δ-DCDA} used is only 3.9 mg cm⁻², the mass activity at 0.9 V_{iR-free} is 10.6 A g⁻¹. At high current density region, the measured performance is still quite good, and the peak power density is close to 1.2 Wcm⁻².

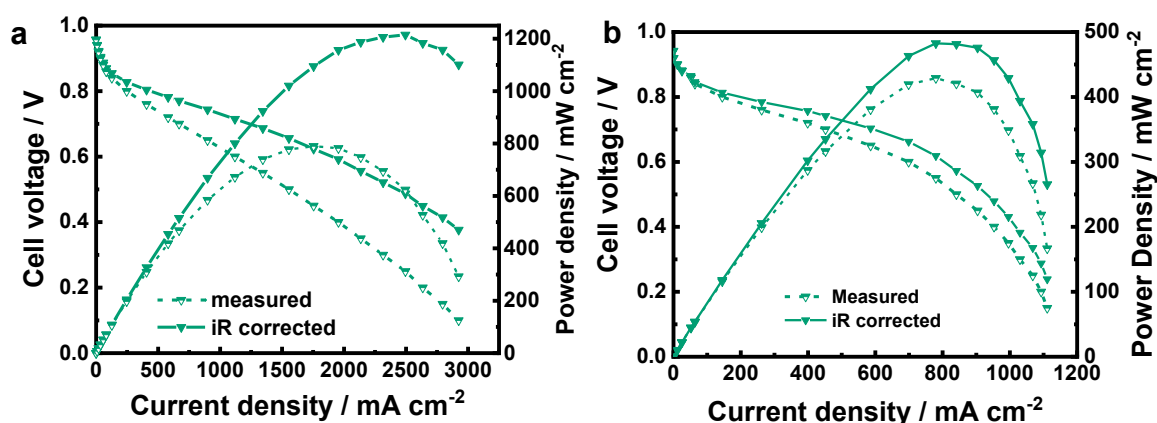


Figure 4.9 (a) H₂-O₂ polarisation curve with measured and iR corrected; (b) H₂-Air polarisation curves with measured and iR corrected. Commercial Pt/C anode with 0.4 mg_{Pt} cm⁻²; Nafion[®] 211 membrane and the operating temperature is 80 °C; 100% RH and 1 bar gauge on both sides. The flow rate of H₂-O₂ measurement is 200 sccm on both sides; for H₂-Air test, the flow rate of hydrogen and air is 300 and 1,000 sccm respectively. [Printed with permission from ref ⁶]

Under hydrogen-air operating conditions (Figure 4.9 (b)), the measured current density at 0.8 V is 145 mA cm⁻², which is much higher than other reported values.^{3, 28-32, 34, 35} The peak power density of Fe-NC^{Δ-DCDA} is around 450 mW cm⁻² without iR correction. With iR correction, the peak power density is around 500 mW cm⁻². The reason why the performance changed a lot with iR correction is that the high resistance in the material, which could potentially be improved by using a better coating method, which would give a better layer structure. Moreover, a further reduction of particle size might also be helpful to improve the structure of catalytic layer, which could potentially lead to even higher performance.

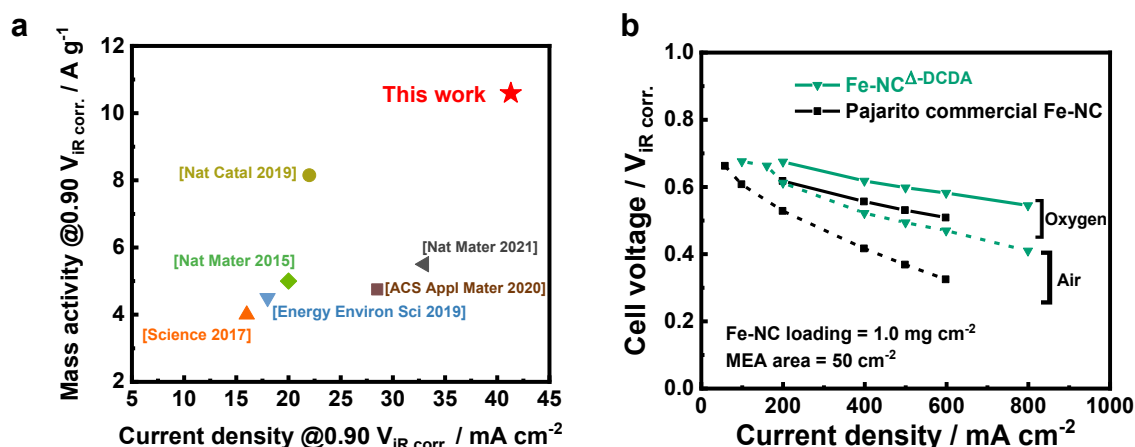


Figure 4.10 (a) The comparison of catalytic activities under hydrogen-oxygen condition at 0.9 V_{IR-free}. (b) fuel cell polarisation curve of Fe-NC^{Δ-DCDA} and commercial Pajarito powder in a 50 cm² single cell. This measurement was performed by Johnson Matthey; cell temperature is 80 °C and 1.7 bar gauge pressure on both sides. [Printed with permission from ref⁶]

A comparison of Fe-NC^{Δ-DCDA} with the commercial Pajarito powder in a relatively large fuel cell was done by Johnson Matthey in order to evaluate the performance in an industrial fuel cell. The MEA was prepared by decal transfer method instead of drop casting. The anode is a commercial 0.1 mg_{Pt} cm⁻² electrode and the cathode is 1.0 mg cm⁻² of Fe-NC catalyst, which would give a thin catalyst layer and comparable to Pt/C layer used on the cathode side. The membrane used is PFSA reinforced Gore Back Up power membrane with 15 μm thickness. The hydrogen-oxygen and hydrogen-air measurements were operated as shown in Figure 4.10 (b). Clearly, the current density of Fe-NC^{Δ-DCDA} is higher than that of commercial Fe-NC catalyst at the same potential, which suggests Fe-NC^{Δ-DCDA} has higher ORR activity. However, the high frequency resistance (HFR) of Fe-NC^{Δ-DCDA} is higher than Pajarito powder, which could be improved by adding conductive carbon Vulcan XC72R into the ink.

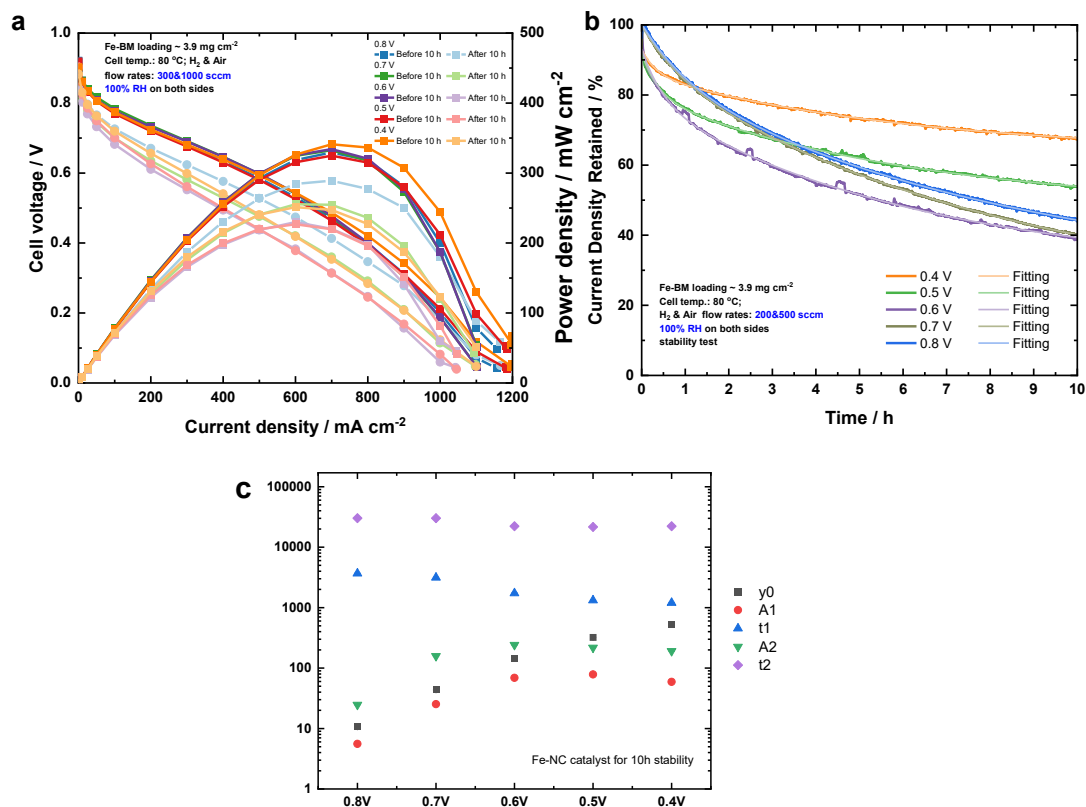


Figure 4.11 (a) hydrogen-air polarisation curve before and after 10 h stability test hold at different potential; (b) the current density retained versus time at a fixed potential for 10 h and the fitted curves are plotted in pale colour; (c) the fitted parameters at different potentials.

The short stability tests (10 hours) of Fe-NC^{Δ-DCDA} were done at 0.40, 0.50, 0.60, 0.70 and 0.80 V, as shown in Figure 4.11 (a) and (b). The initial performances overlapped with each other very well, especially at high potential region, indicating the performances of the catalyst under hydrogen and air conditions were reproducible. However, Fe-NC^{Δ-DCDA} catalyst showed a relatively poor stability, which needs to be improved in the future. At 0.40 V, around 70% of initial current density retained after 10 h stability test; however, around 60 - 65% of initial current density lost when the potential was hold at higher voltage (0.70 V and 0.80 V).

There are four commonly known reasons for the degradation of non-precious metal catalysts in fuel cells, including carbon oxidation by the hydroxyl and/ or hydroperoxyl radicals, demetallation of iron, carbon corrosion and water flooding.³⁶ However, the degradation rate at low potential (0.4 V) was smaller than that at high potentials, which suggested water flooding

should not be the major reason for the degradation in this catalyst. Although more water will be generated at low potential, a lower degradation rate was observed, indicating the water flooding did not influence the durability significantly. The Fe-N/C catalyst was hydrophobic, which potentially prevents micropore flooding. This hypothesis could be tested through DVS measurements in the future. The other three degradation factors were interrelated and they all result from the formation of hydrogen peroxide. The formation of peroxide would generate hydroxyl and hydroperoxyl radicals by Fenton reactions as mentioned before.³⁷ The reactive oxygen species (ROS) could cause the carbon oxidation and also corrosion.³⁷ Furthermore, the demetallation of iron from the active sites is also potentially triggered by hydrogen peroxide.

The degradation process was more vigorously at high potentials, which suggests that the loss of performance might be trigger by the demetallation of Fe-N₄ sites and the hydrogen peroxide-induced carbon oxidation.^{36, 37} It seems like there are two degradation process happened for this catalyst. One of degradations take place within a short time period and contribute to the significant decreases in the beginning. The other one is a slow process which contribute to the decreases in long period of times. Therefore, the current density *versus* time graph is fitted by Equation (4.3)

$$y = y_0 - A_1 e^{-x/t_1} - A_2 e^{-x/t_2} \quad (4.3)$$

where A_1 and A_2 are the pre-exponential factors; and this is the magnitude of the two degradation processes. y_0 is the initial performance and t_1 and t_2 are the corresponding time constants for degradation process 1 and 2. The fitted parameters are plotted in Figure 4.11 (c). The values of t_2 are almost identical for all different potential, which suggests that this long term degradation process is actually potential independent. However, for the short term degradation, the time for total degradation actually decreases with the potentials. A further

study on this degradation is required to understand the mechanism of degradation, which would be helpful to improve the stability of this Fe-NC catalyst.

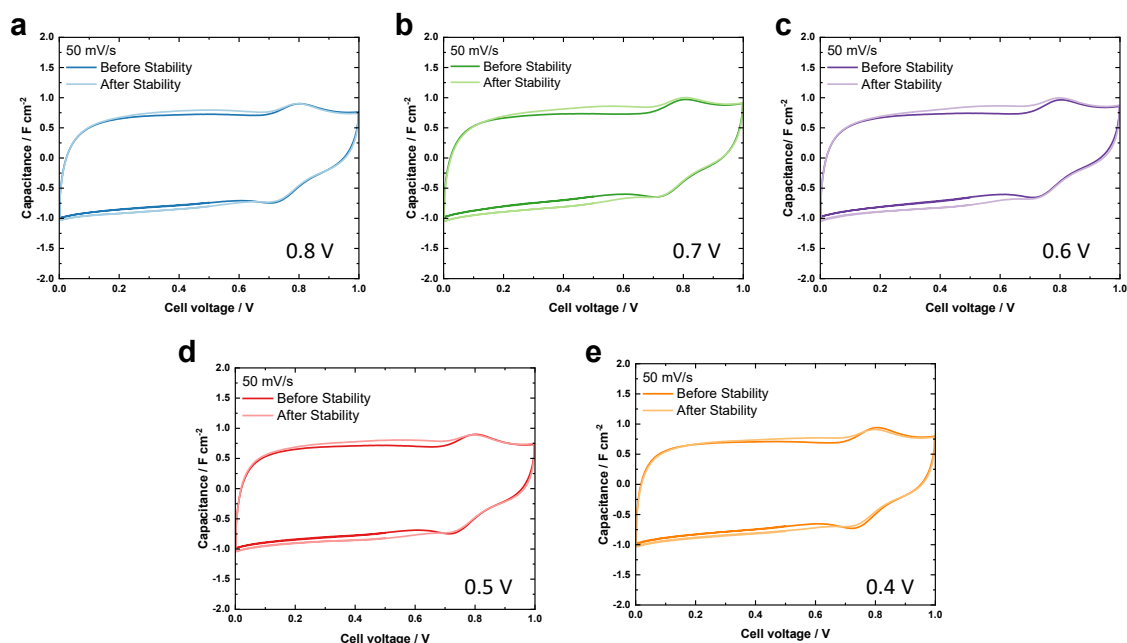


Figure 4.12 Cyclic Voltammetry under nitrogen of fuel cell before and after stability test. (a) 0.80 V; (b) 0.70 V; (c) 0.60 V; (d) 0.50 V and (e) 0.40 V.

Except the fitting of the current density loss with time, cyclic voltammetry under nitrogen before and after the stability tests were taken and the comparisons were shown in Figure 4.12. The redox peak at 0.75 V should be the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox potential, which was not observed in the RDE system as the loading in fuel cell (3.9 mg cm^{-2}) is much higher than that of in RDE (0.2 mg cm^{-2}). There are small increases in the capacitance after the stability test, which suggests some corrosion and oxidation of carbon might take place.³⁸

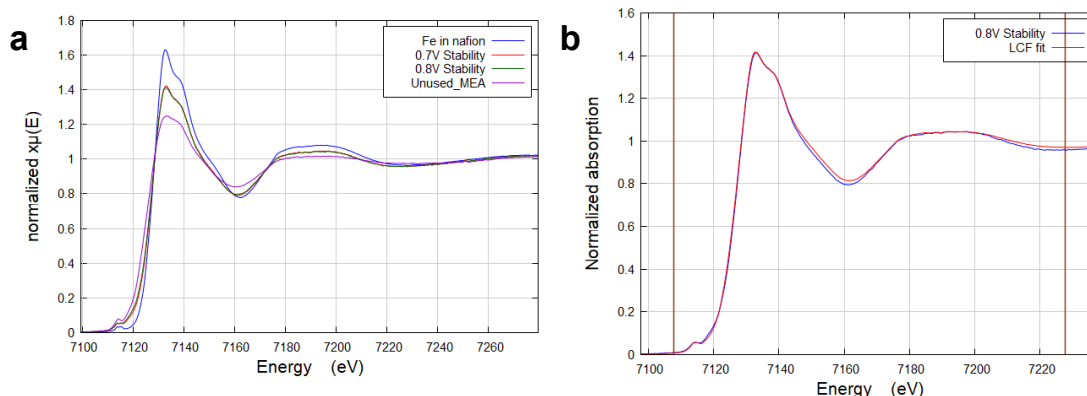


Figure 4.13 (a) Fe K-edge XANES spectrum of unused MEA, Fe in Nafion[®] and MEAs after 0.70 V and 0.80 V stability test; (b) Linear combination fit (LCF) of MEA after 0.80 V stability test using unused MEA and Fe in Nafion[®]. [Printed with permission from ref⁶]

The XANES was also used to understand the degradation of Fe-NC^{Δ-DCDA} as shown in Figure 4.13; the cross-section XANES measurements and data fitting were done by the collaborators. There are three samples studied, including an unused MEA, two MEAs after 0.70 and 0.80 V stability tests. Fe in Nafion[®] was prepared by soaking the Nafion[®] membrane in an acidic solution, which contained iron acetate. As shown in Figure 4.13 (a), the unused MEA had the lowest peak intensity; whereas the peak intensity of Fe in Nafion[®] is the highest. The used MEAs is somewhere between the unused MEA and Fe in Nafion[®], which suggests that iron is demetallated from the catalysts to the Nafion[®] membrane. Therefore, the linear combination fitting (LCF) would be helpful to estimate the percentage of iron in Nafion[®] membrane and in Fe-N₄ sites. Based on the LCF, around 45% of Fe converted from Fe-N₄ into Fe in Nafion. Therefore, it seems likely the two major reasons why the stability of Fe-NC^{Δ-DCDA} is quite poor are demetallation of Fe and the corrosion of carbon.

4.4 Conclusion

A highly active Fe-NC catalyst was prepared using pyrolysed ZIF-8 as the precursor and several optimisations were performed to enhance the activity of Fe-NC. Firstly, a reflux with 2 M H₂SO₄ was utilised to remove more residual Zn in the catalyst precursor, creating

additional vacant sites for iron to coordinate. Secondly, different activating agents were tested to improve the catalyst's performance and active site density. Dicyandiamide (DCDA) and ammonium chloride showed the most significant improvement in RDE measurements, and this could be due to the *in-situ* generation of ammonia gas at around 330 °C. Finally, various pyrolysis temperatures were explored. Increasing the temperature of pyrolysis could remove the residual Zn in the catalyst efficiently and improve the conductivity of catalyst, but high temperature might lead to the formation of iron clusters and also loss of active sites. After testing different pyrolysis temperatures, 907 °C was identified as the optimum temperature for the activation process, resulting in the highest site density and ORR performance in the RDE.

The physical characterisations of the catalysts at different stages were tested, including ^{57}Fe Mössbauer spectroscopy, XAS, ICP-MS, BET, XPS and also STEM. According to the STEM, ICP-MS and also XAS, it was confirmed that $\text{Fe-NC}^{\Delta\text{-DCDA}}$ contained 7 wt% of Fe as Fe-N_4 sites and the catalyst with DCDA activation did not have a regular shape as ammonia generated by thermal decomposition could etch the carbon and alter the morphology. The second pyrolysis played a crucial role in the formation of Fe-N_4 sites and the conversion of inactive iron nanoparticles to D1 and D2 active sites. This observation was supported by analysing the ^{57}Fe Mössbauer spectra and EXAFS of Fe-NC^{U} and $\text{Fe-NC}^{\Delta\text{-DCDA}}$.

Furthermore, the electrochemical site density was determined by the nitrite stripping method. The total active sites of $\text{Fe-NC}^{\Delta\text{-DCDA}}$ are 4.67×10^{19} site g^{-1} , which is around 3 -18 times higher than other reported Fe-NCs. Furthermore, the site densities of catalysts were directly proportional to the ORR activity at pH 0.3. To gain a deeper understanding of the catalyst's performance, a fitting analysis was conducted. It is interesting to notice that the x- intercept was not zero, which suggested there were 6.2×10^{18} site g^{-1} did not exhibit any ORR activity,

and this potentially be the framework sites. The results suggest that increasing the number of Fe-N4 sites in the catalyst can lead to a substantial improvement in ORR performance.

Finally, the PEMFC tests with the Fe-NC^{Δ-DCDA} were done under both hydrogen-oxygen and hydrogen-air conditions. The current density at 0.90 V_{iR-free} was measured to be 41.3 mA cm⁻² under hydrogen-oxygen conditions, which is higher than other reported values. Under hydrogen-air conditions, the current density at 0.80 V was 145 mAcm⁻² and peak power density reached around 430 mWcm⁻². Furthermore, the comparison of Fe-NC^{Δ-DCDA} with the commercial Pajarito powder in a relatively large PEMFC was done. Clearly, Fe-NC^{Δ-DCDA} exhibited better performance even at large scale measurements, but the conductivity of Fe-NC^{Δ-DCDA} is poorer than the Pajarito powder. Although Fe-NC^{Δ-DCDA} had a very high initial performance in PEMFC, which is comparable with Pt, the stability of Fe-NC^{Δ-DCDA} was not as good as Pt catalyst. The catalyst degraded rapidly at high potential and two possible reasons for the degradations are oxidation of carbon and demetallation, which are proved by *ex-situ* XANES and *in-situ* CV respectively.

4.5 Possible future work

For future works, the mechanism of degradation should be investigated and understood to improve the durability of the catalysts. Based on the current conclusion about the degradation, there are several strategies could be explored, such as doping the catalysts with a small amount of Pt or Ag nanoparticles. Pt and Ag nanoparticles have the ability to decompose the hydrogen peroxide generated quickly, which potentially protect the carbon from oxidation and demetallation.³⁹ Furthermore, the ICP-MS or ion chromatography could be used to investigate the amount of Fe leached out after stability test.

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Chapter 5 Using molecular oxygen and Fe-N/C heterogeneous catalysts to achieve Mukaiyama epoxidations and Baeyer-Villiger Oxidation via *in situ* produced organic peroxy acids and acylperoxy radicals*

The usage of Fe-N/C catalysts was extended in this chapter. Fe-N/C could activate the molecular oxygen with an aldehyde to generate strong oxidising agents, peroxy acids and acylperoxy radicals in situ. Different aldehydes and concentrations of reactants were tested for the Mukaiyama epoxidation. The focus of the study was on the kinetics and mechanism to understand the Mukaiyama epoxidation. Furthermore, electrochemical measurements, including open circuit potential and cyclic voltammetry, were done with the reaction. Open circuit potentials were used to assess the suitability of the aldehyde for the Mukaiyama epoxidation. Finally, a similar condition was used for Baeyer-Villiger oxidation. A rate equation and possible mechanism were proposed.

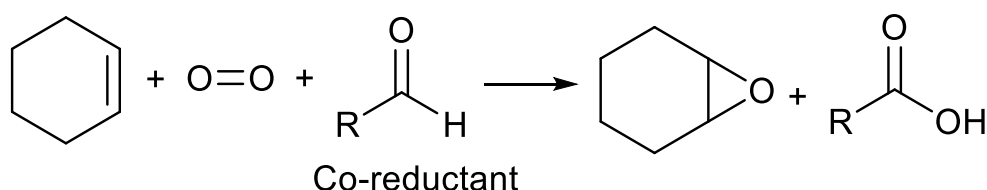
5.1 Introduction

Oxidation is a crucial reaction for not only the electrochemical process but also the organic synthesis and there are several oxidants present and used in different industries, such as hydrogen peroxide, peroxy acid *etc.* However, due to the safety and high cost of producing these oxidants, oxygen is a promising alternative oxidant, which is safer, more abundant and sustainable. However, oxidation with molecular oxygen is kinetically sluggish due to its triplet ground state; therefore, either harsh reaction conditions or a catalyst is required to activate oxygen. Non-precious metal single atom catalysts could activate the molecular oxygen for the

* Parts of this chapter have been published in the paper: “Using molecular oxygen and Fe-N/C heterogeneous catalysts to achieve Mukaiyama epoxidations via *in situ* produced organic peroxy acids and acylperoxy radicals” of which I am the first author.

oxygen reduction reaction in electrochemical process efficiently and these kinds of catalysts had a very similar structure with the metal porphyrins. Furthermore, metal porphyrins are known to catalyse the Mukaiyama epoxidation.¹⁻⁵ Investigating the organic oxidation with M-N/Cs not only can expand the usage of these kind of catalysts, but also could potentially provide more information about the active sites of the catalysts in a different aspect. According to the previous work in the Kucernak group, which investigate the epoxidation reaction with Fe-N/C(ODAN)⁶, M-N/Cs have great potential to apply heterogeneous organic catalysis as well. Epoxide (ethylene oxide: 34.5 million tons in 2006⁷) and lactone (caprolactone: \$ 245.1 million in 2020⁸) are highly demanded for both pharmaceutical and cosmetic industries, since they are the common intermediates in organic synthesis. Hence, the Mukaiyama epoxidation and Baeyer-Villiger oxidation (BV Oxidation) were studied with the M-N/Cs in this chapter.

5.1.1 Mukaiyama Epoxidation Reaction



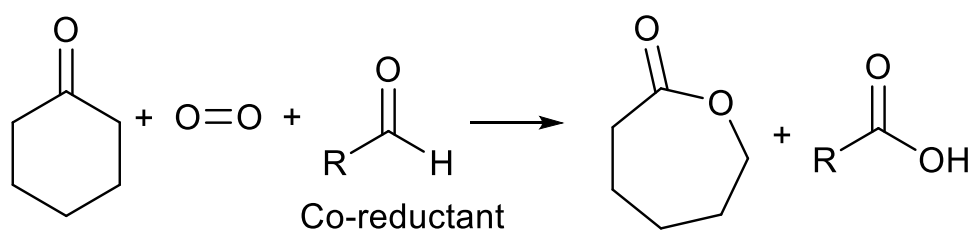
Scheme 5.1 Reaction scheme of Mukaiyama epoxidation.

In 1983, Groves *et al.* found that 5,10,15,20-tetraphenyl-21H,23H-porphyrin iron(III) chloride (FeTPPCL) was an efficient catalyst for the epoxidation of cyclohexadiene with molecular oxygen with the yield of 93%.⁹ Mukaiyama and co-workers have studied the epoxidation with molecular oxygen using an aldehyde as a co-reductant, which is shown in Scheme 5.1. Moreover, they showed that not only the Fe(III)-based catalyst¹⁰ but also Ni(II)^{3, 11} and Mn(III) complexes⁵ are efficient catalysts for this kind of epoxidation, leading to the epoxidation reaction with oxygen and aldehyde being known as the Mukaiyama epoxidation. Furthermore, Nam *et al.* proved that metal cyclams are also suitable catalysts for Mukaiyama epoxidation.¹² However, none of those works was done with a heterogeneous catalyst, which make this

process undesirable for industry, since separating and recycling the catalyst will be very difficult. Although the efficiency of homogeneous catalyst usually is better than that of heterogeneous catalyst since the contact of reactants is more efficient, M-N/Cs could solve this problem by providing a high surface area. Hence, an interesting possibility would be to try Mukaiyama epoxidation with M-N/Cs.

One of the most important things to study for organic synthesis is to understand the mechanism as it could improve the selectivity and avoid forming the undesirable side products. Several possible mechanisms of Mukaiyama epoxidation are proposed. Although the mechanisms proposed are different, they all agreed that peroxy acids, acylperoxy radicals or M-oxo species are produced *in-situ* as the oxidising agent for olefins.^{13, 14} Hence, a detailed mechanism of Mukaiyama epoxidation with Fe-ODAN was investigated not only to understand the active sites of Fe-N/C catalysts, but also to improve the yield of epoxidation and maximise the selectivity of catalytic oxidation.

5.1.2 Baeyer-Villiger Oxidation



Scheme 5.2 Reaction scheme of Baeyer-Villiger oxidation

In 1899, A. Baeyer and V. Villiger reported a new method of synthesising esters and lactones by oxidising the ketone with peroxy acid, which is named as Baeyer-Villiger oxidation.¹⁵ *m*-chloroperbenzoic acid (*m*-CPBA) is one of the most well-known peroxy acids that could give a high yield of BV oxidation. However, the oxidation with peroxy acids could not be applied into industries due to their highly explosive properties. An alternative oxidising reagent for BV oxidation which is not explosive is thus highly required. Since the peroxy acid is the oxidising

agent used in both epoxidation and BV oxidation and aldehyde with molecular oxygen might produce peroxy acid *in-situ*, the similar reaction conditions were tested for BV oxidation, as shown in Scheme 5.2. There is only limited research on the heterogenous catalytic BV oxidation with molecular oxygen.^{16, 17}

5.2 Experimental

5.2.1 Preparation of catalysts

The Fe-N/C(ODAN) catalyst was synthesised similarly as reported by Malko and it was prepared by Jack Dawson.¹⁸ 9.00 g (56.9 mmol) of 1,5-diaminonaphthalene (97%, Sigma-Aldrich) and 320 mg of FeCl₂·4H₂O (≥99.0%, Honeywell) were mixed in 2 L of ethanol (absolute, VWR). 100 mL of 0.394 mol dm⁻³ ammonium persulfate (≥98%, Sigma-Aldrich) solution in DI water (MilliQ 18.2 MΩ) was added and stirred at room temperature for 24 hours. The solvent was removed under reduced pressure and dried in an oven overnight. The dried powder was pyrolysed in the tube (quartz) furnace (Carbolite) at 950 °C for 8 hours with a heating rate of 7 °C/min, under a constant flow of N₂ (BOC, 99.9995%). After pyrolysis, some iron formed nanoparticles or clusters instead of Fe-N/C(ODAN) and the excess iron nanoparticles or clusters were removed from the catalyst by leaching in 0.5 M H₂SO₄ (95%, VWR) for 16 hours under reflux. The sample was filtered and washed with DI water. The dried sample was further pyrolysed at 900 °C for 5 hours with the same condition as the last pyrolysis. Around 6 g of Fe-N/C catalyst was collected after this pyrolysis. For the NO-poisoned catalyst, the catalyst was ground manually and immersed into 0.125 M sodium nitrite solution for 15 min. Then the catalyst was washed with DI water for three times to remove the residual solute. Finally, the poisoned catalyst was dried in the oven at 80 °C under vacuum overnight. This catalyst was used to investigate the epoxidation.

Another Fe-N/C(ZIF-8) catalyst was prepared in the same method as discussed in Chapter 4. The Baeyer-Villiger reaction was mainly investigated with this catalyst.

5.2.2 Epoxidation and Baeyer-Villiger Oxidation

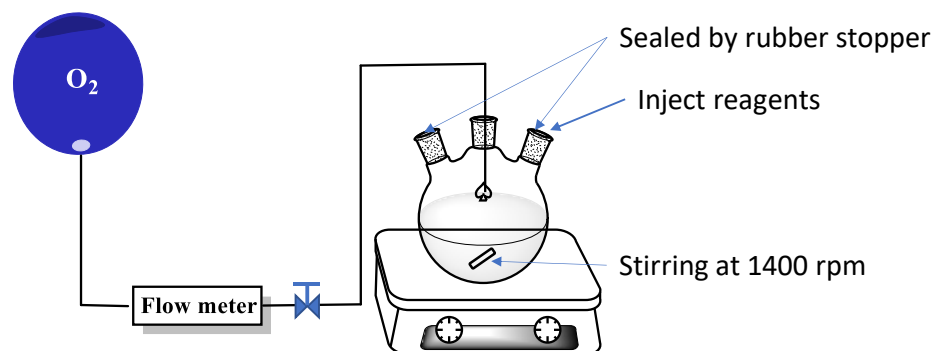


Figure 5.1 The schematic diagram of experimental setup. [Printed with permission from ref¹⁹.]

The glassware was cleaned in the base bath for at least 4 hours, rinsed with deionised water (MilliQ 18.2 MΩ cm) and dried in the oven at 110 °C before use. All the epoxidation, BV oxidation and oxidation of aldehyde reactions were done under room temperature (25 ± 2 °C) and the mixture were stirred at 1,400 rpm unless stated. The catalyst (6 mg for epoxidation, and 4 mg for BV oxidation) and anhydrous acetonitrile (25 mL, 99.9% VWR) were mixed and sonicated for 10 minutes to obtain a homogeneous dispersion. A balloon of oxygen (approx. 2 L, UltraPure Plus, 99.9998%) was attached as shown in Figure 5.1. The system was degassed by flushing oxygen for around 5 min and the pressure was balanced before injecting any reagents. Oxygen flow was monitored by a mass flow meter (15 mL/min O₂ full-scale range, Bronkhorst Flow Meter). Once the oxygen flow decreased to zero, cyclohexene (cyclohexanone for BV oxidation) and aldehyde were added respectively. The reaction was run until the oxygen flow reached zero. All epoxidation and BV oxidation followed this procedure, apart from the specific cases noted. For reduced partial pressure measurement, the solution and system are saturated with air instead of pure oxygen. The balloon is still filled with pure oxygen; so when the oxygen in the reactor is used up, the pure oxygen will flow into the reactor and the partial pressure of oxygen maintain at 20 vol%. Aliquots were taken from the reaction mixture

by using a syringe filter to remove the heterogeneous catalyst and the solution was analysed by gas chromatography (GC) or 400MHz ^1H nuclear magnetic resonance (NMR) spectrums in CDCl_3 .

5.2.3 Electrochemical Measurement

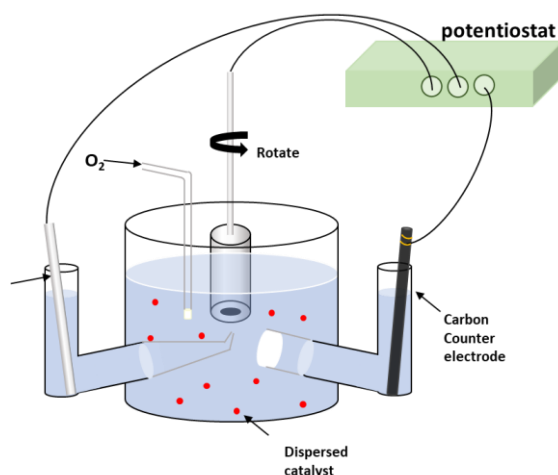
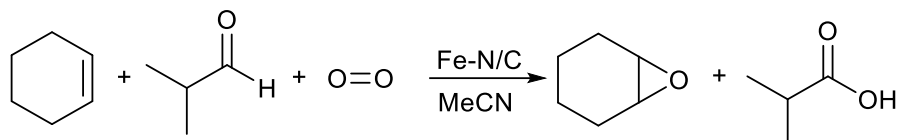


Figure 5.2 The setup of a three-electrode electrochemical cell with dispersed catalyst and deposited catalyst on rotating disk electrode. [Printed with permission from ref¹⁹.]

A 0.1 mol dm^{-3} solution of tetrabutylammonium tetrafluoroborate in dried acetonitrile was used as electrolyte in order to increase the conductivity of the reaction mixture. All other conditions were the same as for the epoxidation reaction. For open circuit potential (OCP) measurements, Ag/AgCl is used as reference electrode and glassy carbon as counter electrode; the OCP was taken by Gamry (Ref 600 Potentiostat/Galvanostat). For cyclic voltammetry, a rotating ring disk electrode (Pine Instruments, model AFE6R1AU having a mirror polished glassy carbon as disk and rotator model AFMSRCE) was used and the catalyst was deposited on the glassy carbon disk unless stated. A three-compartment electrochemical glass cell was used as shown in Figure 5.2; glassy carbon was used as counter electrode. A potentiostat (Autolab, model PGSTAT20) was used for current and potential control during the electrochemical measurements and all the potentials were reported against the Fc/Fc^+ couple.

5.3 Result and Discussion

5.3.1 Kinetic Studies of Mukaiyama Epoxidation Reaction



Scheme 5.3 Balanced epoxidation of cyclohexene with molecular oxygen and isobutyraldehyde. [Printed with permission from ref¹⁹.]

Understanding the kinetics of reaction is useful to study the mechanism of reaction, since rate equation will give information about the rate determining step (rds). To investigate the reaction order for the epoxidation reaction of cyclohexene using isobutyraldehyde as a co-reductant (Scheme 5.3), the reaction was carried out in the apparatus as displayed in Figure 5.1 at a temperature of 25 °C under pure oxygen (except where noted) at atmospheric pressure. Once the oxygen is used up in reactor, which will trigger an uneven pressure between the reactor and the balloon, the oxygen in balloon will flow into the flask via flowmeter to balance the pressure. This design allows monitoring of the rate of reaction by measuring the rate of oxygen flow into the reaction system as oxygen is the reactant in this process.

A typical oxygen flow graph of epoxidation is shown in Figure 5.3 (a), in which the oxygen flowrate can be treated as oxygen consumption rate. The oxygen flow remained at 0 mLs⁻¹ if only the catalyst and cyclohexene was added into the flask with acetonitrile as solvent. However, there is a noticeable increase in the flow of oxygen as shown in Figure 5.3 (a), when isobutyraldehyde is added in. This flow (i.e. the rate of oxygen consumption) increases and reaches a peak around 500 s after the injection of isobutyraldehyde, and then decays away with $t_{1/2} \sim 2,500$ s, reaching close to zero after 15,000 s. When only isobutyraldehyde is added in absence of cyclohexene, the total oxygen consumption (area under the curve) equals half the moles of isobutyraldehyde in the reaction mixture as shown in Figure 5.7, which indicates the aldehyde reacts with oxygen swiftly. The initial rate of reaction was estimated as associated

with the peak of oxygen flow as it is reasonable to assume that the initial rate of reaction should be the maximum rate.

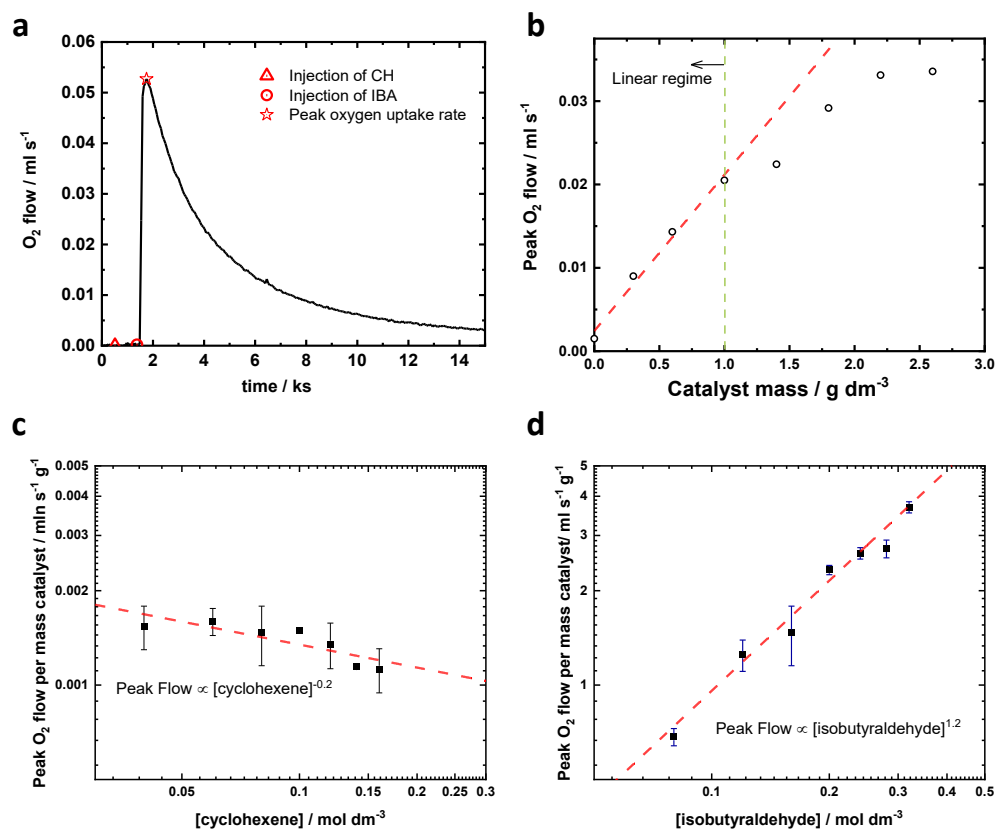


Figure 5.3 Analysis of kinetics (as measured by peak O_2 consumption rate) of the epoxidation of cyclohexene using Fe-N/C catalyst in the presence of isobutyraldehyde (a) Oxygen uptake profile during the epoxidation reaction showing the cyclohexene and isobutyraldehyde additions along with the peak oxygen consumption rate; (b) Catalyst dosing plot showing the peak oxygen consumption rate versus the amount of catalyst in the reaction mixture; red trendline linear region of catalyst undersaturation; (c) kinetic reaction order plot for cyclohexene with 4 mmol of isobutyraldehyde; (d) kinetic reaction order plot for isobutyraldehyde with 2 mmol of inhibitor-free cyclohexene. All reactions were carried out at $25 \pm 2\ ^\circ C$ under pure oxygen and 6 mg of Fe-N/C catalyst in 25 cm^3 of anhydrous acetonitrile ($0.24\ g_{Fe-N/C\ catalyst}\ dm^{-3}\ acetonitrile$) were used for (a), (c) and (d). [Printed with permission from ref¹⁹.]

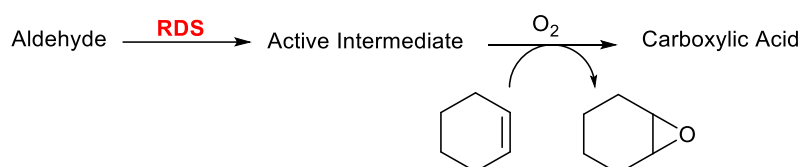
The influence of catalyst and reactant concentration on the reaction rate was studied where all other variables were kept constant. As shown in Figure 5.3 (b), when the amount of catalyst was higher than 1 $g_{Fe-N/C\ catalyst}\ dm^{-3}\ acetonitrile$, the catalyst was no longer saturated, i.e. the linear relationship between the rate of reaction and amount of catalyst only showed up below 1 $g_{Fe-N/C\ catalyst}\ dm^{-3}\ acetonitrile$. At higher amounts of catalyst, the peak oxygen consumption levelled off, which suggests the diffusion of reactant (probably oxygen) to the catalyst determines the maximum rate of reaction, in other words, the catalyst is not saturated. All subsequent

experiments were performed with the catalyst amount within the linear region (less than 1 g_{Fe-N/C catalyst} dm⁻³ acetonitrile) so that the catalyst was saturated with initial reactant, and thus the rate of reaction is not limited by diffusion of reactants to the catalyst.

$$-\left(\frac{d(O_2)}{dt}\right)_{max} = k_{obs}[isobutyraldehyde]^{1.2}[catalyst][oxygen]^0[cyclohexene]^{-0.2} \quad (5.1)$$

The rate equation of this epoxidation with molecular oxygen and isobutyraldehyde was shown in Equation (5.1). The rate of reaction is 1st order with respect of the catalyst, -0.2th order with cyclohexene, 0th order with the concentration of oxygen and 1.2th with isobutyraldehyde. There are some studies on metal porphyrin catalysed epoxidation which claimed that the concentration of cyclohexene had no effect on the rate of reaction and a first order with catalyst was observed. For example, research on the olefin epoxidation with hydrogen peroxide and ferric chloride²⁰ or iron(III) tetrakis(pentafluorophenyl) porphyrin catalysts²¹ reported that the reaction rate was independent of the concentration of the olefin. However, the reaction order of catalysts, such as Mn(III) tetraphenylporphyrin chloride (Mn(TPP)Cl)²² or phthalocyanine iron(III) chloride²³, in the epoxidation of olefins with molecular oxygen was reported to be close to one. However, there are some discussions on the reaction order of aldehyde in the epoxidation. Some papers reported the order of aldehydes was one.^{13, 24} However, the other studies, published by Takeuchi *et al.*²⁵, Zhou *et al.*²² and Nam *et al.*¹³, pointed out that the reaction order for isobutyraldehyde was approximately 3/2. Although there is not a clear conclusion for this, there is no doubt that the presence of isobutyraldehyde is crucial for the epoxidation. For the heterogenous epoxidation with Fe-ODAN, the reaction order of isobutyraldehyde was 1.2. Finally, epoxidations under reduced partial pressure of oxygen have also been carried out and the initial rate is the same as the rate under pure oxygen as shown in Figure 5.8, which indicate the concentration of oxygen will not change the rate of reaction. Only the concentrations of catalyst and isobutyraldehyde are able to change the rate of reaction,

therefore, the activation of aldehyde by catalyst should be the rds of this epoxidation. The active intermediate epoxidises the alkene in the following step as shown in Scheme 5.4.



Scheme 5.4 Possible reaction steps in cyclohexene epoxidation [Printed with permission from ref¹⁹.]

Within the literature the active intermediate is still under debated. There are three possible species, including peroxy acid, acylperoxy radical ($\text{RCOOO}\cdot$) and a metal-oxo complex. For the catalytic epoxidation with biomimetic catalysts and haem Cytochrome P-450, they claimed the formation of metal-oxo species.^{20, 23} Due to the similarity in structure, M-N/Cs may also produce metal-oxo species during the epoxidation reaction. However, Takeuchi *et al* claimed that the non-catalytic oxidation of isobutyraldehyde could form peroxy acid as product, which is a strong oxidising agent and commonly used in organic synthesis.²⁵ The epoxidation with peroxy acid is stereospecific, which means cis-alkene will only produce cis-epoxide as product; however, the catalytic epoxidation of cis-stilbene produced trans-epoxides as a major product, based on the previous study in the Kucernak Group.⁶ Therefore, another active oxidising intermediate should be produced in this epoxidation reaction to give a mixture of two geometrical isomers as products. Nam *et al.*¹³ and Wentzel *et al.*^{14, 26} stated that, the acylperoxy radical ($\text{RCOOO}\cdot$), which is formed through the oxidation of aldehyde, is another possible oxidising agent for epoxidation especially when transition metal based catalyst are used. Rodrigues *et al.* stated that the addition of the radical scavenger butylated hydroxytoluene (BHT) could efficiently react and remove the acylperoxy radicals.²⁷ Hence, epoxidation with the addition of BHT could be able to prove whether the epoxidation with Fe-N/C(ODAN) involved the formation of radicals or not. As shown in Figure 5.4, there is a clear induction time of oxygen flow ($\sim 2\text{h}$) when 0.01 mmol of BHT (around 0.02 vol%) is added into the

reaction flask before the addition of isobutyraldehyde. Therefore, this strongly suggests that the epoxidation with molecular oxygen and aldehyde on the Fe-NC catalysts involves the formation of radicals.

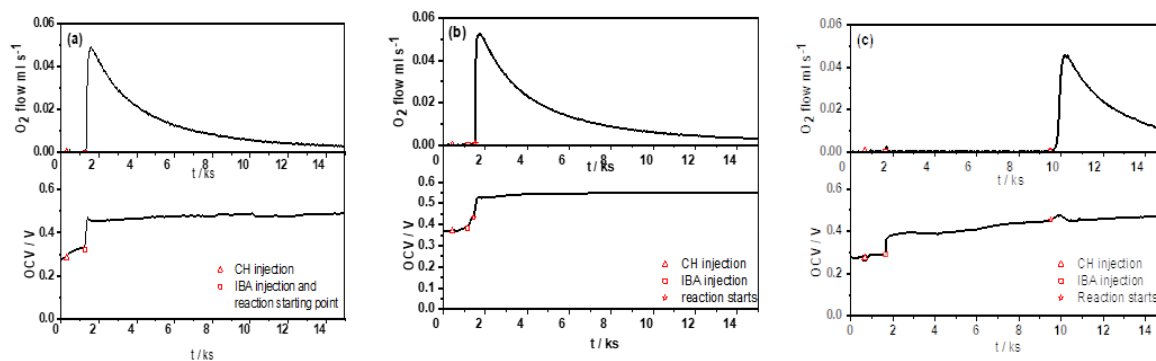


Figure 5.4 Effect of inhibitor at the early reaction stage (a) Inhibitor free cyclohexene epoxidation (b) inhibitor containing cyclohexene epoxidation (c) 0.01 mmol BHT injected at the beginning of inhibitor-free cyclohexene epoxidation. [Printed with permission from ref¹⁹.]

5.3.2 Mechanistic Studies of Epoxidation Reaction

As mentioned above, there are three possible intermediates involved in the oxidation of cyclohexene. Firstly, in order to confirm the potential involvement of Fe-oxo species in this epoxidation reaction, the NO poisoned Fe-N/C(ODAN) catalysts were used in the epoxidation as the Fe-oxo species would not be generated on the surface of catalyst if the catalyst is NO poisoned. In these experiments, we poisoned the catalyst with the exposure to nitrite (NO_2^-) solution whereupon the nitrite ions will strongly interact with the iron metal centre in this Fe-N/C(ODAN) catalyst. The NO poison will not destroy the active sites irretrievably. As mentioned previously in Chapter 3, the NO would interact with the metal ions and some intrinsic N/C sites for oxygen reduction reaction; nevertheless, the NO could be removed by electrochemical reduction and the activity could be fully recovered. Hence, this method could be used to calculate the site density of M-N/Cs.^{18,28} Epoxidation with the poisoned catalyst and different types of aldehydes is shown in Figure 5.5, where the error bar is the standard deviation of three repeats. Although the yield of epoxidation slightly decreased with the poisoned catalyst,

the trend of oxygen flow and the amount of aldehyde consumed did not change significantly. This result illustrates that the main active intermediate is not Fe-oxo as the Fe sites are blocked by NO already. However, the presence of Fe centre could help to improve the selectivity of cycloalkene to epoxide and avoid forming other side products. The active oxidising intermediates should be generated by the oxidation of aldehyde and the main role of Fe-N/C(ODAN) catalyst is to initiate the formation of radicals.

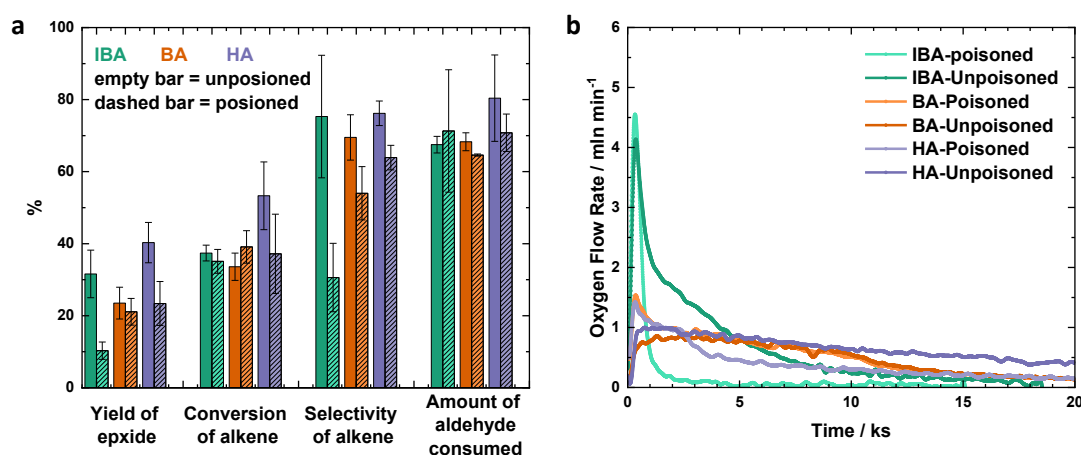


Figure 5.5 Epoxidation of cyclohexene with different aldehyde and NO-poisoned Fe-N/C catalyst. (a) the yield of epoxide, conversion and selectivity of cyclohexene and the amount of aldehyde consumed with poisoned and unpoisoned catalyst. (b) the oxygen flow diagram of epoxidation with different aldehydes and catalyst. For all reaction, 2 mmol of cyclohexene and 4 mmol of aldehyde were used. 6 mg of catalysts was mixed in 25 mL of dried acetonitrile. IBA: isobutyraldehyde; BA: butanal; HA: n-hexanal. [Printed with permission from ref¹⁹.]

It is very challenging to prove and detect the formation of peroxy acids and acylperoxy radicals by using NMR as they are highly active and will convert to carboxylic acid with a very fast kinetics. The colour of ABTS (2,2'-Azino-bis(3-ethylbenzthiazoline-6-sulfonic acid) diammonium salt) will turn green in the presence of peroxy acid.^{29, 30} Moreover, the coloured products is able to not only prove the formation of peroxy acid, but also quantify the amount of peroxy acid generated *in-situ*; since the oxidation of colourless ABTS to green ABTS⁺ absorbs several wavelengths, including 415 nm, 650 nm, 732 nm and 820 nm.²⁹ This could be monitored by UV-Vis spectroscopy as shown in Figure 5.6 a and the peak heights should be directly proportional to the concentration of the peroxy acid. In these experiments the

spectrophotometric response was calibrated by using *m*-CPBA as a test peroxy acid. With increasing reaction time of epoxidation, the absorbances' peak of $\text{ABTS}^{\cdot+}$ height also increases, which indicate the concentration of peroxy acid increases. Moreover, this experiment could also prove the formation of acylperoxy radicals because the radical is the intermediate, which will generate the peroxy acid as product. As the peroxy acid is one of the most well-known oxidising agents for epoxidation, the subsequent epoxidation reaction of cyclohexene with peroxy acid is inevitable.³¹

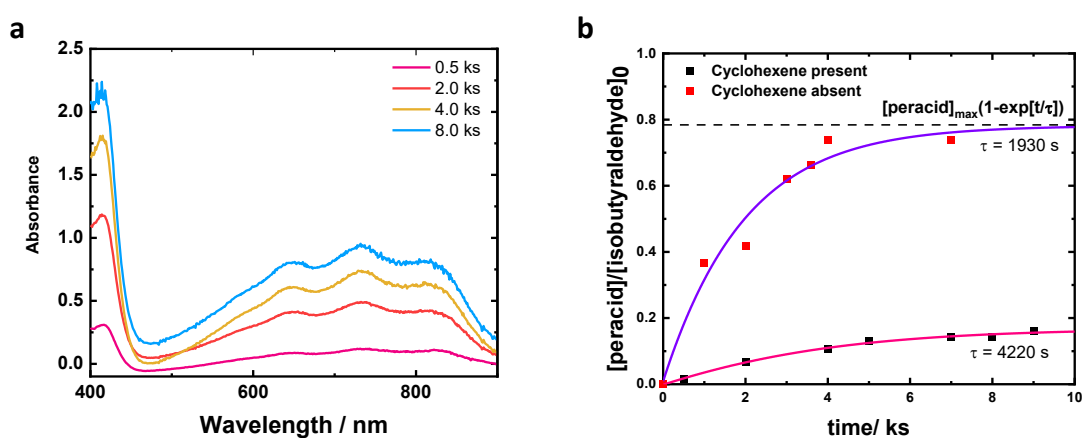


Figure 5.6 Analysis of the reaction intermediate using UV-Vis spectra of ABTS doped reaction aliquots. (a) UV-Vis spectra of 25-fold diluted samples which contain ABTS, KI and an aliquot taken from the epoxidation of cyclohexene with isobutyraldehyde in acetonitrile at different reaction times; (b) the amount of peroxide generated at different reaction times with and without the addition of cyclohexene according to the peak at 415 nm. All reactions were carried out with 3 mg of Fe-N/C catalyst in 10 mL of anhydrous acetonitrile ($0.3 \text{ g Fe-N/C catalyst dm}^{-3} \text{ acetonitrile}$), 1 mmol of inhibitor-free cyclohexene and 2 mmol of isobutyraldehyde under pure oxygen at $25 \pm 2^\circ\text{C}$. [Printed with permission from ref⁹.]

Figure 5.6 (b) is the plot of the concentration of peroxy acid versus time according to the calibration with *m*-CPBA. In order to study the effect of cyclohexene, experiments with cyclohexene (black dots and red trend line) and without cyclohexene (red dots and purple trend line) are tested. It is interesting to notice that around 75% of initial concentration of isobutyraldehyde is converted to peroxy acid without addition of cyclohexene, which suggests Fe-N/C(ODAN) is a good catalyst to oxidise the aldehyde with gaseous oxygen. However, when alkene is introduced to the reaction mixture, the amount of peroxy acid present is only around one fourth of the initial concentration of aldehyde, which is much smaller than the

reaction without alkene. There are three potential reasons which triggers this decrease. One is that the amount of peroxy acid produced by oxidising the aldehyde remain unchanged, but it is consumed by the cyclohexene. The other is that the amount of peroxy acid generated decreases and the addition of cyclohexene inhibits the oxidation of aldehyde. Also, the decreases in concentration could be triggered by the combination of the previous two reasons. In order to investigate the reason for this variation in peroxyacid production, the total oxygen consumption with and without cyclohexene were compared as shown in Figure 5.7. Oxygen is the reactant for the activation of aldehyde to produce peroxy acid; therefore, the total oxygen consumption is able to indicate the amount of peroxy acid generated. The total oxygen consumption decreases from 4 mmol to 3 mmol when cyclohexene is added; also, the peak of oxygen flow (initial rate) decreases. Therefore, this reveals the amount of peroxy acid produced with cyclohexene is less than that of peroxy acid produced without cyclohexene. In previous papers it was suggested that some selective allylic oxidations of cyclohexene with oxygen was catalysed by metal-free nitrogen-doped carbon catalyst (N/Cs); and the authors advocated the double bond in cyclohexene would interact with the N/Cs by π -interaction.³²⁻³⁴ Therefore, the addition of cyclohexene blocked active sites for oxidation of aldehyde, which reduced the rate of acylperoxy radical formation and hence, the concentration of peroxy acid decreases. Additionally, as shown previously the reaction order with respect to the concentration of cyclohexene is -0.2^{th} , which also supports the idea of blocking of the active sites for oxidation of aldehyde. However, the amount of peroxy present in the mixture with cyclohexene is much smaller than the amount of peroxy formed without adding cyclohexene. Therefore, the decreases in concentration of peroxy acid is caused by the combination of two reasons, including using up the peroxy acid by cyclohexene and inhibiting the oxidation of aldehyde.

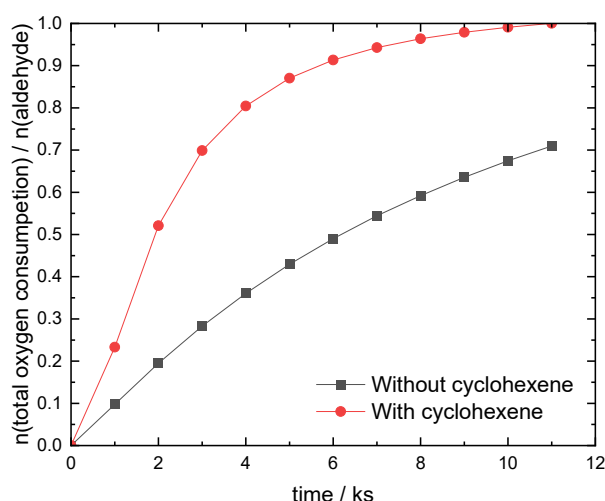
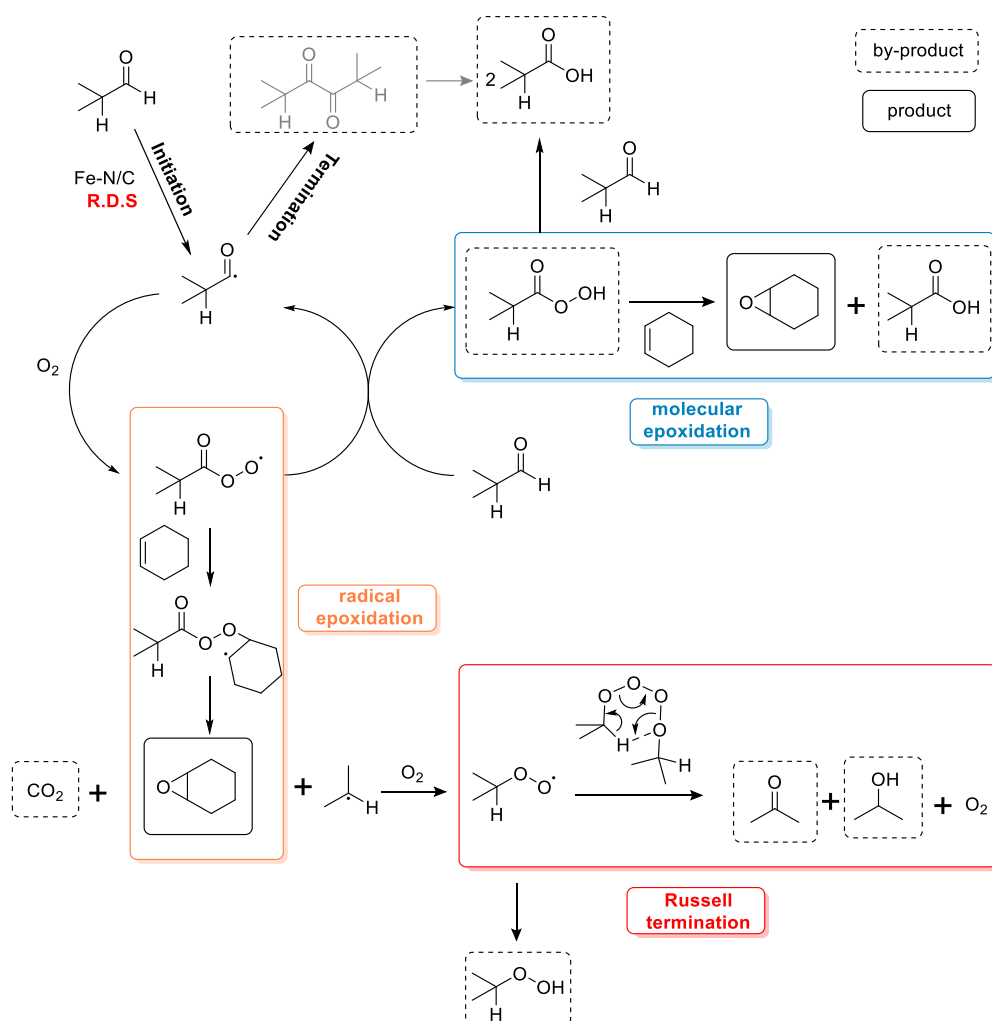


Figure 5.7 Total oxygen consumption with and without the addition of cyclohexene at different time. [Printed with permission from ref¹⁹.]

Considering all facts observed in this reaction, a possible mechanism is proposed and displayed in Scheme 5.5. The first step, which is also the rds, initiates acyl radical ($\text{RO}\cdot$) formation from aldehyde by Fe-N/C(ODAN) . In the following step, the radical produced would interact with the triplet state oxygen rapidly to produce acylperoxy radical as they all contain unpaired electrons. If the cyclohexene is not added in, the acylperoxy radical would propagate with aldehyde and produce carboxylic acid and another acyl radical. Finally, the termination of two radical would produce an α -diketone by dimerization of acyl radicals. However, it is unlikely to produce α -diketone as final product and it is not detected by GC because of its instability. α -diketone is highly reactive and could be oxidised to two carboxylic acids by oxygen.³⁵ When cyclohexene is involved in the reaction, the initiation process will not be influenced. In the propagation step, the acylperoxy radical could directly oxidise the cyclohexene by a radical epoxidation as labelled in orange bracket. The radical epoxidation will produce an alkyl radical as intermediate, which could be determined by Russell termination labelled in red. When isobutyraldehyde was used as co-reductant, the Russell termination would produce isopropanol and acetone and these indeed are detected by GC.²⁶ Another possible epoxidation is the

molecular based process (labelled in blue), where the peroxy acid produced by oxidation of aldehyde is able to oxidise the cyclohexene.



Scheme 5.5 Possible mechanism for epoxidation of cyclohexene with isobutyraldehyde as a co-reductant. (Grey colour shows the prospective termination product.) [Printed with permission from ref¹⁹.]

Two possible epoxidation pathways are shown previously; however, the true process could be very complicated, and it is hard to determine which pathway has greater chance to take place. Noticeably, the rate of radical reaction should be higher than that of molecular reaction because the radical has higher energy and is more reactive; a kinetic study would be useful to determine the dominating reaction pathway. Two aldehydes were chosen for the kinetic study, including a hindered isobutyraldehyde and a linear n-hexanal. One of the reasons why those two

aldehydes were chosen is that their oxygen flow plot (shown in Figure 5.8 (a)) are different and this potentially indicates two different types of mechanism. For isobutyraldehyde, there is a clear peak in the beginning and the oxygen flow drops quickly, no matter the concentration of oxygen is 100 vol% or 20 vol%. Nonetheless, there was a smaller increase in the oxygen flow when n-hexanal was added to the system and the oxygen uptake did not decline quickly once it reaches the maximum flow. The concentrations of epoxide generated at different reaction times are shown in Figure 5.8 (b). Clearly, the rate of epoxide formation is much quicker when isobutyraldehyde is used. Only 3,800 s were taken to form 20% of theoretical epoxide with isobutyraldehyde; however, 12,000 s were needed to produce the same amount of epoxide if n-hexanal is used as co-reductant. Therefore, the linear aldehyde is more favourable towards the molecular epoxidation reaction and radical epoxidation plays a more important role in epoxidation with hindered aldehydes. However, it is still impossible to confirm whether these two pathways are competitive or happen simultaneously. Future work could use EPR to trap, measure and determine the radical concentration for the different reactions.

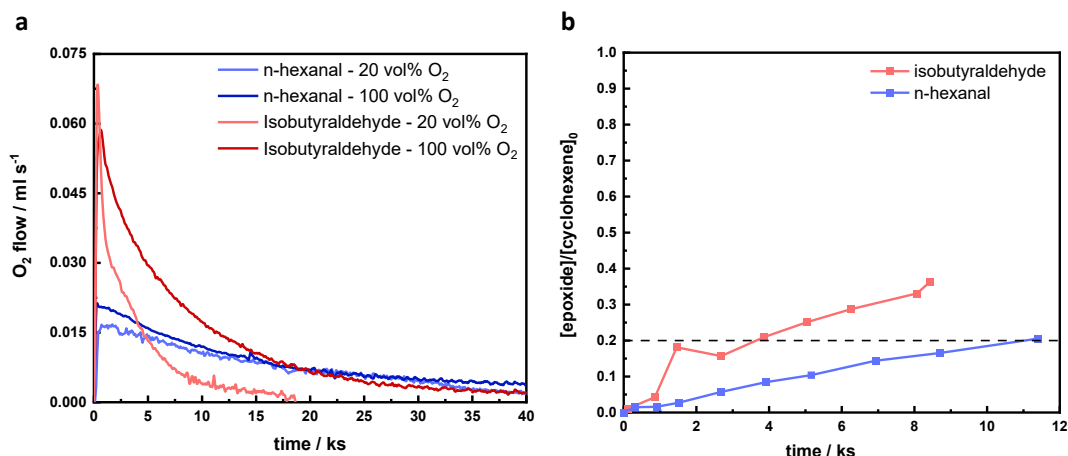


Figure 5.8 Analysis the epoxidation reaction with different aldehydes (a) oxygen uptake profile during the epoxidation reaction with isobutyraldehyde and n-hexanal under different concentration of oxygen (the molar ratio of cyclohexene to aldehyde is 1:2); (b) the conversion of cyclohexene to cyclohexene epoxide with time under 20 vol% of oxygen (the molar ratio of cyclohexene to aldehyde is 1:2). All reactions were taken at 25 ± 2 °C under pure oxygen, 6 mg of Fe-N/C catalyst and 25 cm³ of anhydrous acetonitrile (0.24 gFe-N/C catalyst dm⁻³ acetonitrile). [Printed with permission from ref¹⁹.]

5.3.3 Electrochemical Analysis of Epoxidation Reaction

Although Mukaiyama epoxidation is a purely organic synthesis and there is not any analysis of organic process by electrochemistry measurement, it is still worth to analyse the organic synthesis in a different aspect. In this section, electrochemical measurements, including open circuit potential (OCP) and cyclic voltammetry (CV), were tested with Mukaiyama epoxidation. In order to increase the conductivity, 0.1 moldm⁻³ solution of tetrabutylammonium tetrafluoroborate in acetonitrile was used as solvent for the epoxidation.

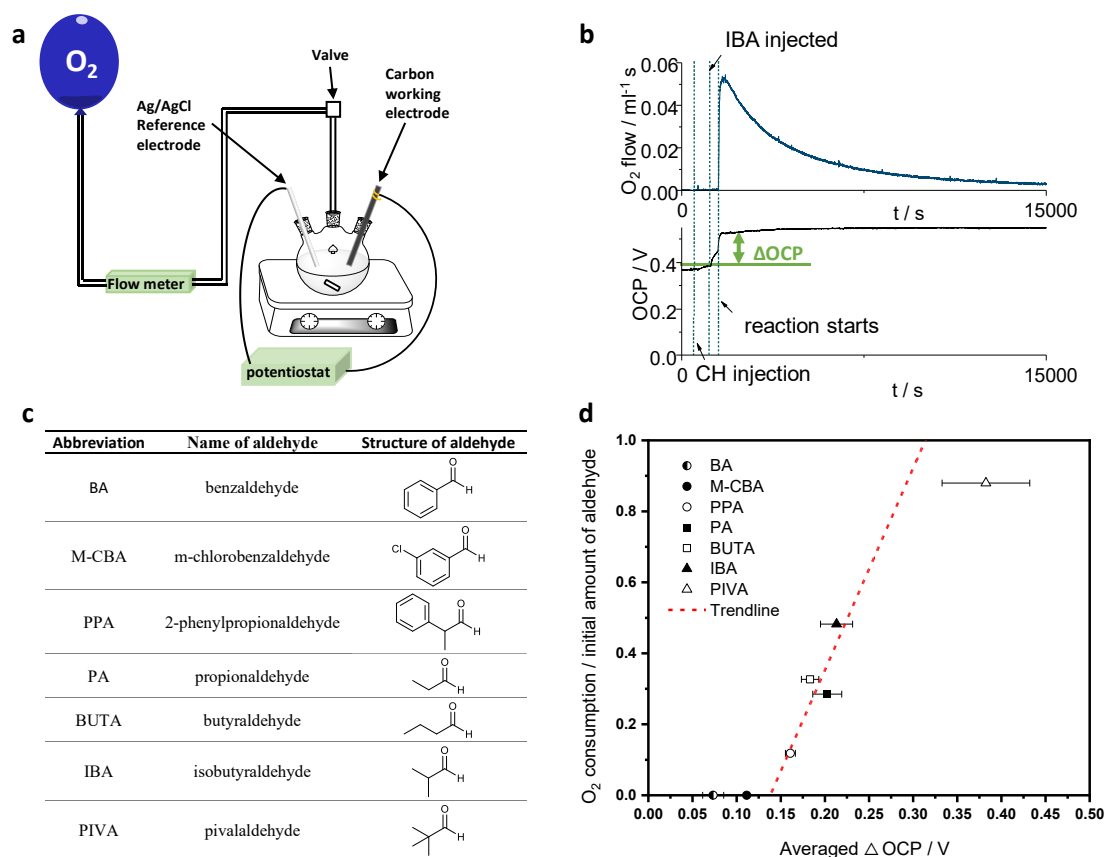


Figure 5.9 Analysis of Open Circuit Potential (OCP) of epoxidation of cyclohexene using Fe-N/C catalyst in the presence of aldehyde (a) experimental setup of the epoxidation reaction with monitoring the oxygen flow and open circuit potential simultaneously (b) oxygen uptake profile and open circuit potential (OCP) during the epoxidation reaction showing the injection of cyclohexene and isobutyraldehyde; (c) different aldehydes investigated in this section; (d) the relationship between the change in OCP of epoxidation with different aldehydes and oxygen consumption. All experiments were performed in 0.1M solution of tetrabutylammonium tetrafluoroborate in dried acetonitrile for Fe-N/C catalyst and the ratio of cyclohexene to aldehyde is 1:2; reference electrode: Ag/AgCl; working electrode: glassy carbon. [Printed with permission from ref¹⁹.]

In order to measure the OCP while the epoxidation, the experimental setup was modified slightly as shown in Figure 5.9 (a). Two-electrode system was used, including carbon working electrode and an Ag/AgCl reference electrode. A high impedance potentiostat related to those two electrodes and the OCP could be monitored with the oxygen flow uptake. An example of OCP measurement and oxygen flow versus time for the epoxidation with isobutyraldehyde is shown in Figure 5.9 (b). The oxygen uptake graph is exactly the same with Figure 5.3 (a), which suggested the addition of tetrabutylammonium tetrafluoroborate (required to perform the electrochemical measurement) will not influence the epoxidation reaction. Seven aldehydes

were tested with the OCP measurement as well as oxygen flow measurement and the structure of seven aldehydes were shown in Figure 5.9 (c).

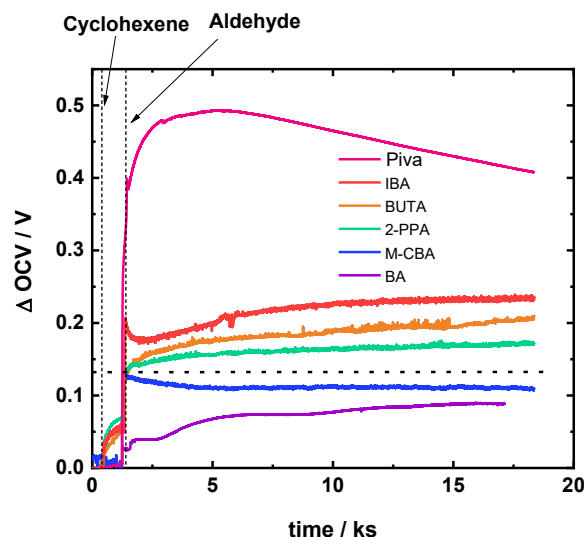


Figure 5.10 The open circuit potential measurement versus time of cyclohexene epoxidation with different aldehyde. [Printed with permission from ref¹⁹.]

The change in OCP measurements with seven different aldehydes were shown in Figure 5.10; when cyclohexene was added into the system, there was not any changes on the OCP. With the injection of aldehyde, the OCP increased dramatically, which suggests the formation of a strong oxidising agent. However, not all of aldehyde tested are able to epoxide the cyclohexene. *m*-CBA and BA did not uptake any oxygen from the balloon and their OCP changes were much smaller than the one that react with oxygen. Hence, change in OCP could be an indicator to determine whether the epoxidation is able to happen or not. A higher OCP value shows the formation of stronger oxidising environment. Hence, the relationship between change in OCP and total oxygen consumption was investigated as shown in Figure 5.9 (d). The molar ratio of total oxygen consumption to the initial aldehyde added should be one according to the balanced equation shown in Scheme 5.3. Therefore, the higher the ratio indicates the higher the yield of epoxide if there is not any side reaction. A linear trend between those two variables is observed and the x-intercept indicates the minimum amount of OCP changes required for the epoxidation,

which should be around 0.139 V. Therefore, the OCP measurements could potentially be applied to other organic oxidation to allow *in situ* analysis and monitoring of complex catalytic systems.

m-CBA was chosen because the oxidation of *m*-CBA would give *m*-CPBA, which is the most well-known oxidising agent for epoxidation and also BV oxidation. Also, BA is very light sensitive to produce radical under lights.³⁶ However, for the Mukaiyama epoxidation with Fe-N/C(ODAN), *m*-CBA and BA were not a good co-reductant. This potentially indicates that aromaticity in the aldehyde was not favourable for the activation of aldehyde with Fe-N/C(ODAN). As discussed before, π -interaction might be the reason why aldehydes with benzene were not active. The benzene ring could be strongly attracted to the surface of catalyst and block the active sites.³⁷ However, not all of the aldehydes with benzene rings were unactive, since PPA was still able to proceed the reaction. Therefore, only aldehydes with α -aromatic are not suitable for the Mukaiyama epoxidation with Fe-N/C(ODAN).

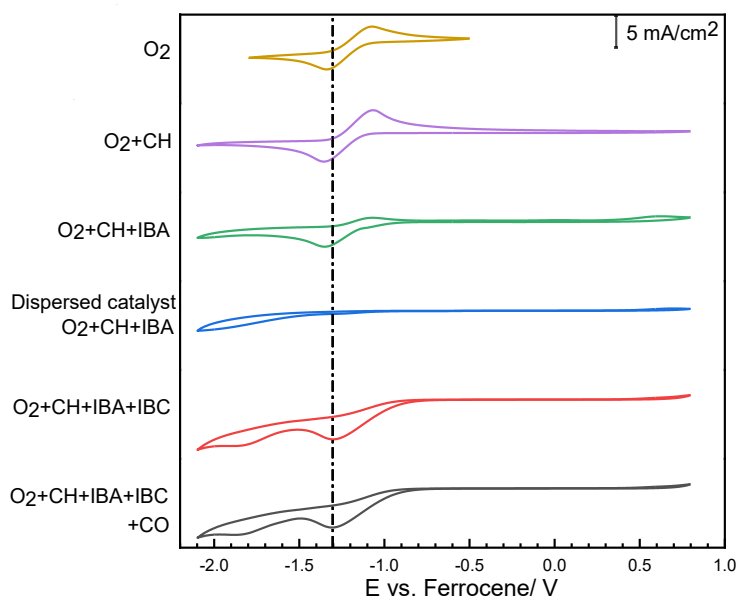


Figure 5.11 Cyclic Voltammetry of epoxidation of cyclohexene with isobutyraldehyde and Fe-N/C catalysts. the CV of systems with different compositions using either a working electrode composed of Fe-N/C catalyst or Fe-N/C catalyst dispersed in solution and a glassy carbon working electrode. (CH: cyclohexene, IBA: isobutyraldehyde, IBC: isobutyric acid, CO: cyclohexene oxide.) [Printed with permission from ref¹⁹.]

Cyclic voltammograms were performed with the setup shown in Figure 5.2 and the aim for running CV is to understand the epoxidation more. The conditions for all CV measurements mimic the real condition for Mukaiyama epoxidation. CV with different reactants is shown in Figure 5.11. It compared the change of CV with the addition of reactants and also possible products (carboxylic acid and cyclohexene oxide). With only the reactants, two different systems were tried, including depositing the catalysts on the glassy carbon and dispersed catalyst in the solution, which is more similar with the real epoxidation reaction. Without any organic reactants and products, there is one reversible peak shown at -1.3 V_{vs. Fc} when only oxygen is purging to the electrolyte, which indicates the oxygen reduction to the superoxide anion radical.³⁸ With the addition of cyclohexene into the solution, the CV curve did not change significantly, which means the reaction between superoxide anion with alkene is negligible. However, if isobutyraldehyde is added, the oxidation peak for superoxide anion to oxygen disappeared, which means the superoxide anion is used up by the isobutyraldehyde added. Moreover, superoxide anion radical is a strong oxidising agent and it should be able to oxidise

the alcohol to carboxylic acid and ketone directly.^{39, 40} Possible reactions with aldehyde are shown below:

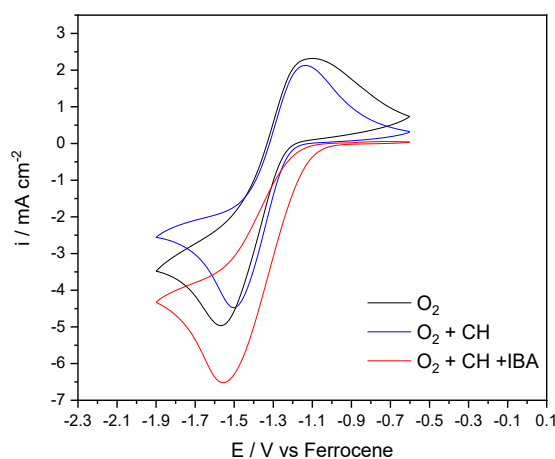
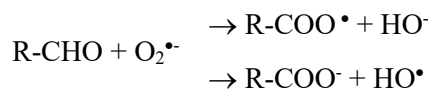


Figure 5.12 The cyclic voltammetry of epoxidation, the cyclic voltammetry without Fe-N/C(ODAN) catalyst. (CH: cyclohexene; IBA: isobutyraldehyde.) [Printed with permission from ref¹⁹.]

Also the CVs without any Fe-N/C(ODAN) were done as well to understand the role of catalyst, as shown in Figure 5.12. However, the re-oxidation of superoxide anion radical still disappeared even without any catalyst deposited; so, the reaction between superoxide anion radical and isobutyraldehyde is not catalysed by Fe-N/C(ODAN).

For the electrochemical measurement with dispersed catalyst, the shape of CV changed completely. The reversible peak of oxygen to superoxide anion radical disappeared when the catalyst is mixed in the solution. This observation might indicate the oxygen is reacted on the surface of catalyst and there isn't any oxygen reduced on the glassy carbon surface. However, the reduction peak at lower potential increased. In order to understand the reduction peak at lower potential, possible products, including isobutyric acid and cyclohexene oxide were added respectively. There are two new peaks (at 0.8 V_{VS.Fc} and -2.1 V_{VS.Fc}) were seen when isobutyric

acid was added. However, there was not obvious change when cyclohexene oxide was introduced.

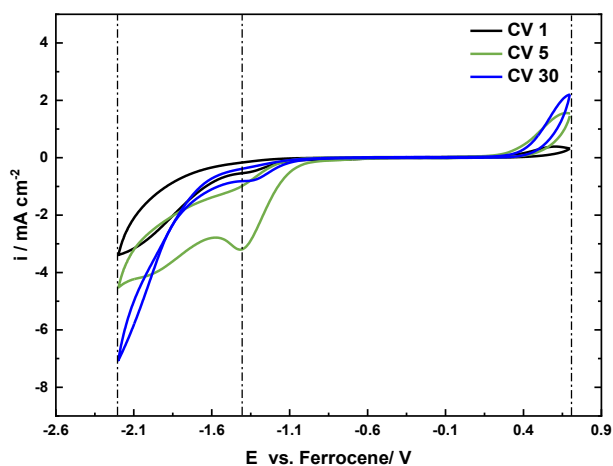
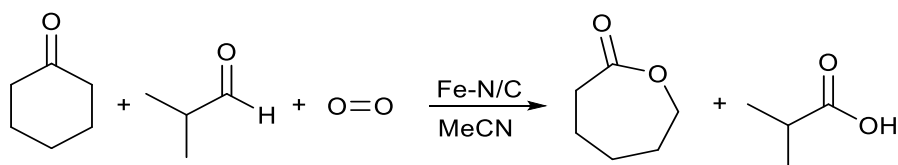


Figure 5.13 The cyclic voltammetry of epoxidation. the long-term scan of cyclic voltammetry of epoxidation with dispersed Fe-N/C(ODAN) with stirring. [Printed with permission from ref¹⁹.]

Finally, a long-term CV scans were done with the dispersed Fe-N/C(ODAN) catalyst as shown in Figure 5.13. According to our previous study (Figure 5.11), the increasing in amplitude of peaks at 0.8 V_{VS. Fc} and -2.1 V_{VS. Fc} suggests the formation of isobutyric acid shown in CV5 (labelled in green). The peak at -1.3 V_{VS. Fc} disappeared after long-time running as shown in CV 30 (labelled in blue), indicating the rate of oxidation of isobutyraldehyde is very fast and the concentration of oxygen near glassy carbon electrode is near zero.

5.3.4 Kinetic Studies of Baeyer-Villiger Oxidation



Scheme 5.6 Balanced equation of Baeyer-Villiger oxidation of cyclohexanone with isobutyraldehyde.

Since peroxy acid or acylperoxy radical could be generated by oxidation of aldehyde with Fe-N/C catalyst, this activation could be applied to other organic synthesis process such as BV oxidation as well. Fe-N/C(ZIF), which is prepared in the same way as mentioned in Chapter 4, has higher iron content, active sites, and also ORR performance comparing with Fe-

N/C(ODAN). Therefore, a more ORR active Fe-N/C(ZIF) was used for BV oxidation in a similar way as the Mukaiyama epoxidation and the reaction scheme is shown in Scheme 5.6. The reaction setup used was the same as Mukaiyama epoxidation and a typical oxygen flow diagram is shown in Figure 5.14 (a).

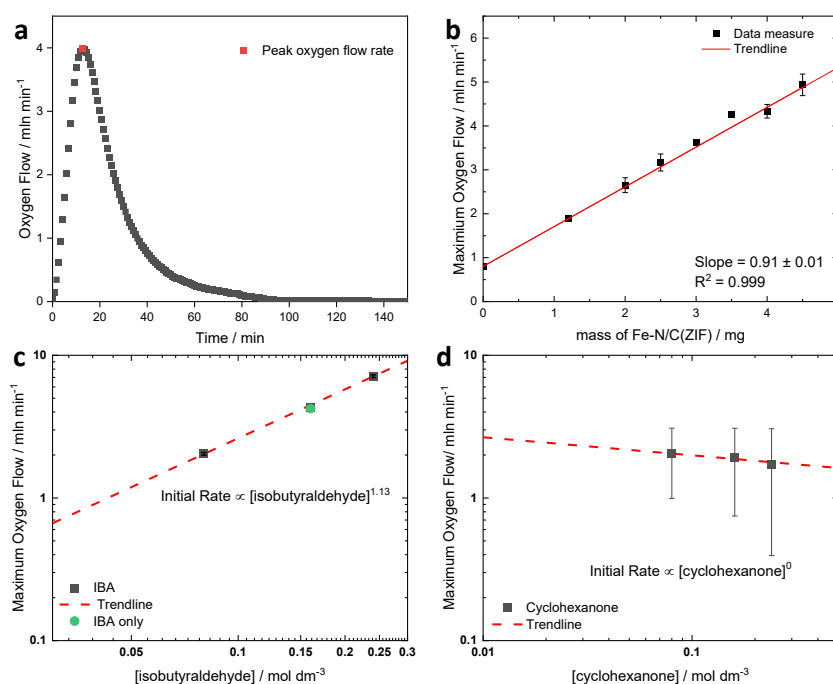


Figure 5.14 Kinetic study on the BV oxidation of cyclohexanone using Fe-N/C(ZIF) catalyst in presence of isobutyraldehyde. (a) Oxygen flow plot with addition of reactants; (b) Catalyst dosing plot showing the peak oxygen consumption rate versus the amount of catalyst in the reaction mixture; red line: trend line; kinetic reaction order plot of (c) isobutyraldehyde and (d) cyclohexanone. (4 mg of Fe-N/C(ODAN), 25 mL acetonitrile, 4 mmol isobutyraldehyde, 2 mmol cyclohexanone, ambient conditions.) Standard error bars were plotted based on 3 repeats on each reaction.

A kinetic study of BV oxidation was investigated in order to determine the rds of BV oxidation as the mechanism of BV oxidation might be different with Mukaiyama epoxidation. Firstly, different amount of catalysts were tested and the maximum oxygen flow was treated as initial rate. The relationship between the initial rate of reaction and mass of catalyst added was shown in Figure 5.14 (b). When the amount of catalyst used in the reaction doubled, the initial rate of reaction also doubled. Therefore, a first order with catalyst is observed. Different concentrations of isobutyraldehyde were investigated and similarly with the epoxidation, the reaction order of isobutyraldehyde is approximately first order, which is slightly lower than the

reaction order in epoxidation. Most of the literature also reported the rate order of aldehyde were between 0 and 2 and the rate order also depends on the types of aldehydes used.^{41, 42} The maximum oxygen flow when only isobutyraldehyde was used (green dot) is shown in the Figure 5.14 (c); and it is exactly the same as the initial rate of BV oxidation, which suggests the cyclohexanone does not inhibit the reaction and block the active sites as cyclohexene. Although C=O also contains a π bonding, this π bonding is more polar than the π bonding in C=C. Therefore, cyclohexanone did not lower the rate of reaction. Finally, the effect of concentrations of cyclohexanone on rate was studied and it seems the rate of reaction is independent with the concentration of cyclohexanone. The reason why it is not a perfectly horizontal line is probably caused by system error or the amount of catalyst added. Therefore, the rate equation of BV oxidation could be summarised as:

$$-\frac{d(O_2)}{dt} = k_{eff}[catalyst][isobutyraldehyde]^{1.13}[cyclohexanone]^0 \quad (5.2)$$

Once the rate equation is determined, the activation energy of reaction could be calculated according to the Arrhenius Equation, and it could be rearranged to the equation shown below:

$$\ln(k) = -\frac{E_a}{RT} + \ln(A) \quad (5.3)$$

where k is the rate constant; E_a stands for the activation energy; R is the ideal gas constant; T is the temperature in Kelvin and A is the pre-exponential factor.

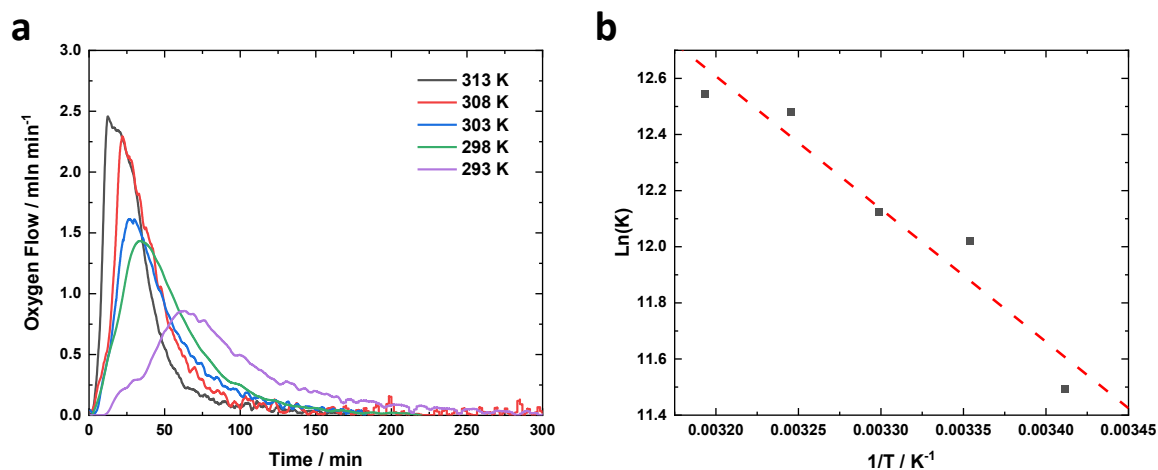


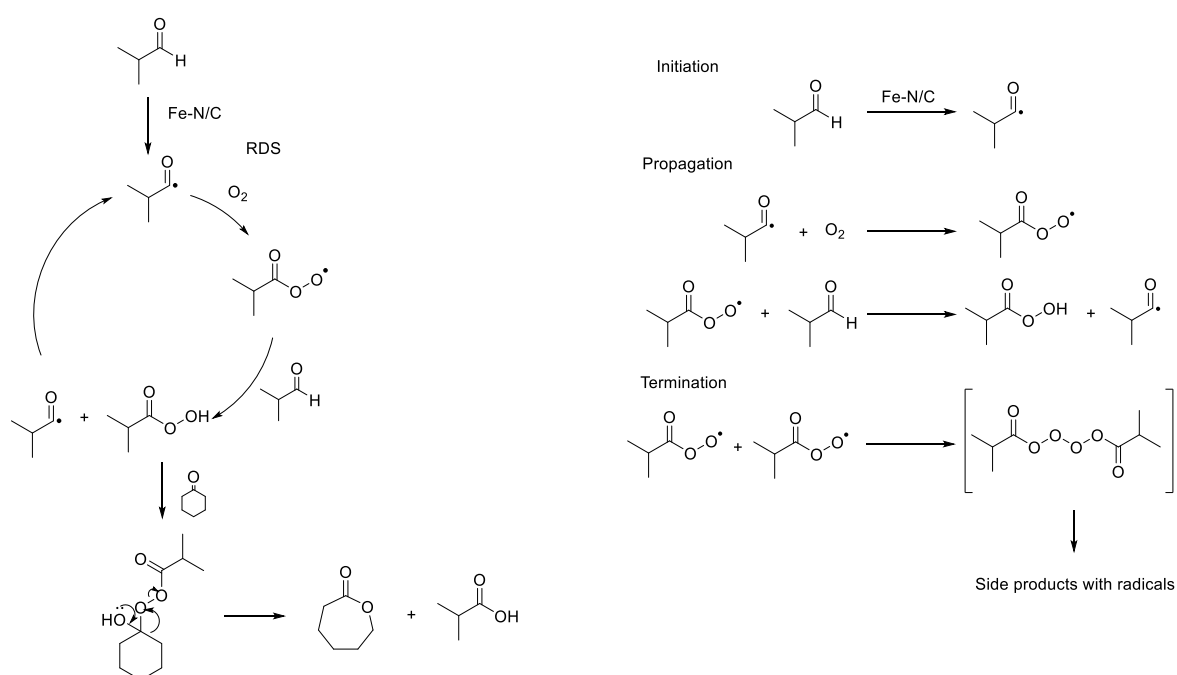
Figure 5.15 Activation Energy Analysis (a) Oxygen flow under different temperature; (b) Ln(K) versus 1/T graph, black dot is the experimental value taken and red line represent the trend line. (4 mg of Fe-N/C(ZIF) in 25 mL dried acetonitrile and 2 mmol of cyclohexanone with 4 mmol of isobutyraldehyde.)

In order to determine the activation energy of BV oxidation, five different temperatures were chosen, and the oxygen flow plot is shown in Figure 5.15 (a). As the temperature increases, the peak of oxygen uptake raises due to higher energy of reactants; but the total oxygen consumptions under various temperature are the same. The initial rate of reaction was taken from the oxygen flow plot, and the rate constant is calculated by Equation (5.2). Hence, a graph of $\ln(k)$ versus $1/T$ could be plotted and a linear trend was observed. The slope of this line should be $-E_a/R$; so the E_a could be calculated (39.3 ± 6.2 kJ/mol). Although there is not any other reported E_a value of this type of BV oxidation available, there is one study on the activation energy of BV oxidation with hydrogen peroxide. Cornard *et al.* claimed the activation energy between 318 K and 338 K was 13.9 kcal mol⁻¹ (58.2 kJ mol⁻¹) and the activation energy dropped to 5.2 kcal mol⁻¹ (21.8 kJ mol⁻¹) if temperature is higher than 338K.⁴³ Therefore, Fe-N/C(ZIF) is a very good catalyst for BV oxidation as the activation energy for BV oxidation with isobutyraldehyde is around one third of the activation energy Cornard *et al.* stated.

5.3.5 Mechanistic Studies of Baeyer-Villiger Oxidation

According to the kinetic studies of BV oxidation, the rate of reaction is only depended on the concentration of isobutyraldehyde, and amount of catalyst used. Hence, a similar activation of

aldehyde by catalyst should be the rds and an acyl radical should be generated. Following by propagation steps, the peroxy acid and acylperoxy radical are generated. The peroxy acid generated interacts with cyclohexanone to form a Criegee intermediate. A CH_2 migration takes place and give ϵ -caprolactone as the product and isobutyric acid as by-product. The possible mechanism is shown in Scheme 5.7. There are several papers also reported a similar mechanism.⁴⁴⁻⁴⁷



Scheme 5.7 Possible mechanism for Baeyer-Villiger oxidation of cyclohexanone with isobutyraldehyde as co-reductant

As stated in Scheme 5.5, acylperoxy radical could also be the oxidising agent for cyclohexanone, which will form an alkyl radical during the propagation step.¹⁹ Russell termination is the possible termination step for alkyl radical and this hypothesis is also proved by the NMR analysis and also GC analysis as propan-2-ol had been detected.

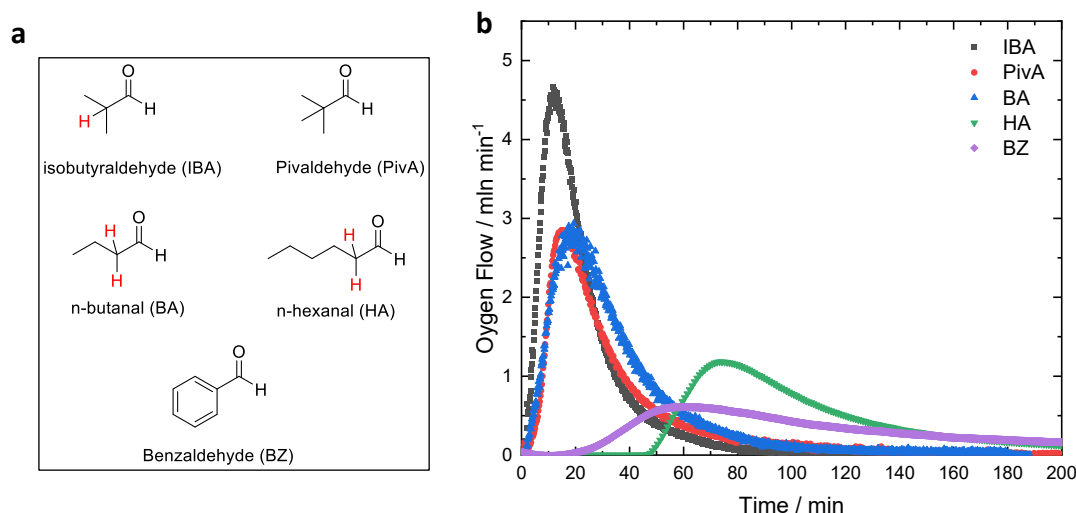


Figure 5.16 BV oxidation with different aldehydes (a) the skeletal structure of five aldehydes tested in BV oxidation and their abbreviation used; (b) the oxygen flow of BV oxidation with different aldehydes. (4 mg Fe-N/C(ZIF) in 25 mL dried acetonitrile; 2 mmol of cyclohexanone and 4 mmol of aldehyde.)

Furthermore, five different aldehydes were investigated with the BV oxidation. The structures of aldehydes tested and also the oxygen flow plots with each aldehyde were shown in Figure 5.16. All of them were tested in Mukaiyama epoxidation as well. Since the catalyst used in BV oxidation is slightly different with the catalyst used in Mukaiyama epoxidation, the selectivity of reaction pathway could be different. In Mukaiyama epoxidation, the reaction with hindered aldehyde (less α -H atom attached) gave an evident peak at the beginning and the oxygen flow dropped quickly; however, the oxygen flow in the reaction with linear aldehyde (more α -H atom attached) increased steadily and did not decrease a lot with time as shown in Figure 5.5. However, for the BV oxidation, a different trend was observed as shown in Figure 5.16 (b) and the peak oxygen flow, induction period, total reaction time and also the conversion of cyclohexanone calculated from NMR analysis were shown in Table 5.1. This differences in the trend of oxygen flow and conversion of substrates potentially suggested the structure of catalysts and also the major mechanism of reaction were different. Interestingly, the benzaldehyde worked for the BV oxidation with Fe-N/C(ZIF); but it was not working for Mukaiyama epoxidation with Fe-N/C(ODAN). As benzaldehyde is very light sensitive and it

showed an induction period (~ 20 min) in the first test as shown in Figure 5.16 (b), so four different conditions were tested with benzaldehyde shown in Figure 5.17. Reaction without any coverage of aluminium foil (red line) is the standard condition normally used for BV oxidation; however, if the reaction flask is covered by aluminium foil all the time (grey line), the induction period increased to around 850 min (40-fold higher than the reaction with light) and lower initial rate and total oxygen consumption were observed as well. Therefore, it indicated there are some side reactions happened before BV oxidation and light could accelerate the rate of side reaction. A normal reaction flask without any coverage and Fe-N/C(ZIF) catalyst (blue line) was tested and there was not any oxygen flow from the balloon to the reaction flask, which suggested Fe-N/C(ZIF) were necessary for the BV oxidation. Finally, 200 min coverage with aluminium foil in the beginning and then removal of the coverage (green line) was tried. The reaction did not have immediately after the removal of coverage, and there was induction period before oxygen uptake. Interestingly, the total oxygen consumption and conversion of cyclohexanone in this reaction is the same as the reaction without any coverage (red line). Light is only required for the side reaction and it will not change the BV oxidation. The possible side reaction might involve benzyl alcohol as it usually will be added into benzaldehyde to stabilise the aldehyde and benzyl alcohol could inhibit the autooxidation of benzaldehyde.⁴⁸ Although it is not stated in the bottle of benzaldehyde used in the reaction, it is reasonable to believe that trace amount of benzyl alcohol is present in the bottle since benzyl alcohol is the reactant to prepare benzaldehyde. Moreover, the BV oxidation with the addition of small amount of benzyl alcohol inhibited the reaction completely as shown in yellow line. There was no obvious oxygen flow. However, the side reaction is still unknown and should be investigated in the future.

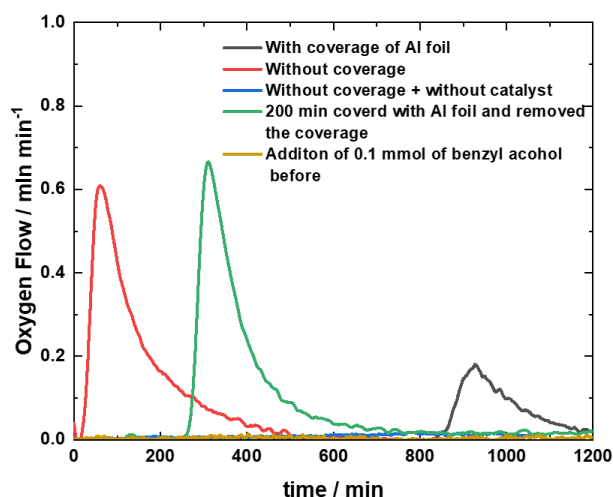


Figure 5.17 Oxygen flow plot of BV oxidation with benzaldehyde under different conditions. (4 mg Fe-N/C(ZIF) in 25 mL dried acetonitrile; 2 mmol of cyclohexanone and 4 mmol of benzaldehyde.)

Except benzaldehyde, there were also differences between BV oxidation with Fe-N/C(ZIF) and Mukaiyama epoxidation with Fe-N/C(ODAN). The pivaldehyde, which did not have any α -H atom, worked very well with Mukaiyama epoxidation. The Mukaiyama epoxidation with pivalaldehyde and Fe-N/C(ODAN) had not only the highest yield of epoxide, but also highest rate of reaction. However, for the BV oxidation, reaction with pivaldehyde did not give the highest initial rate and had the lowest conversion of cyclohexanone as shown in Table 5.1. The reaction with isobutyraldehyde had higher initial rate compared with the reaction with n-butanal and this observation were the same as the Mukaiyama epoxidation. N-hexanal had longer reaction time than all others and it also showed an induction time before the BV oxidation, which was not noticed in the Mukaiyama epoxidation. However, the reason why the induction period occurs was still unknown and more research is required to establish the cause. The BV oxidation with benzaldehyde had the highest conversion of cyclohexanone, and also longest reaction time. Comparing all data shown in Table 5.1, it seems as if a higher conversion of cyclohexanone is correlated with a longer the reaction time and lower the initial rate of reaction. This could be explained by the competition of reactions in the mechanism. If the rate of forming peroxy acid is too fast, side reactions or autooxidation of aldehyde could happen. However, forming the peroxy acid in a relatively low rate, all peroxy acids formed could be

used for BV oxidation directly and avoid further oxidation of aldehyde to carboxylic acid. This is one of possible explanations and it still requires experiments to support this idea; so, a similar UV-Vis study with BV oxidation with different aldehydes could be done to find out the relationship between the concentration of peracid and the conversion of cyclohexanone.

Table 5.1 The peak oxygen flow, induction period, total reaction time and conversion of cyclohexanone with different aldehydes.

Aldehyde	Peak oxygen flow rate / mln min⁻¹	Induction period / min	Total reaction time / min	Conversion of cyclohexanone / %
IBA	4.33 ± 0.18	0	100	46 ± 8
PivA	3.23 ± 0.39	0	130	28
BA	3.39 ± 0.19	0	130	47 ± 9
HA	1.46 ± 0.28	30	360	54 ± 9
BZ	0.47 ± 0.03	10	500	98 ± 1

5.4 Conclusion

For the Mukaiyama epoxidation reaction with heterogenous Fe-N/C(ODAN) catalyst, a complete rate equation was proposed, and the rate is directly proportional to the amount of catalyst added and it is independent of the concentration of oxygen. A 1.2th order respect to the concentration of isobutyraldehyde and a -0.2th order respect to the concentration of cyclohexene (subtract) were observed. These kinetic studies provided the information about the rds of the Mukaiyama epoxidation; only aldehyde and catalyst were involved in the rds. Also, the cyclohexene seems block the active sites of reaction and that is probably triggered by the π interaction with the surface of catalyst. Using NO-poisoned Fe-N/C(ODAN) proved that the Fe-oxo was not the major activation sites for Mukaiyama epoxidation as the yield of epoxide was not affected by poisoning the Fe-site. UV-Vis spectrometer was used to estimate the concentration of peroxy acid and it suggested peroxy acid could be generated by oxidising

the isobutyraldehyde with molecular oxygen and Fe-N/C(ODAN). Hence, two possible oxidising agents: (1) peroxy acid and (2) acylperoxy radicals were present in the reaction. Based on this finding and previous kinetic studies, a detailed mechanism of heterogeneous Mukaiyama epoxidation was suggested and the GC analysis could also support this mechanism as propan-2-ol, a by-product formed by Russell termination, had been measured. Several different aldehydes were tried, and the oxygen flow diagrams had different shapes with different aldehydes. Hindered aldehydes (fewer α -H atoms) had higher initial rate and also yield, suggesting that the radical epoxidation mechanism might dominate. For the epoxidation with linear aldehydes (more α -H atoms), the initial rate was lower and the reaction time was longer, and molecular epoxidation by peroxy acid should dominate. Finally, there was the introduction of utilising electrochemical approaches to understand the organic synthesis. Mukaiyama epoxidation were carried out with monitoring the OCP. The higher the OCP changes, the higher initial rate of epoxidation showed. This suggested that the change in OCP could be an indicator to determine whether aldehyde is a suitable co-reductant for the Mukaiyama epoxidation or not. Also, CV measurement which mimicked the Mukaiyama epoxidation suggested isobutyraldehyde could react with superoxide anion radical as the re-oxidation peak disappeared after introducing isobutyraldehyde into the electrolyte.

The Mukaiyama epoxidations with different types of catalyst proved the presence of different active sites. The metal-free ODAN did not work for the Mukaiyama epoxidation; however, Fe-N/C(ODAN) showed a great activity on Mukaiyama epoxidation with isobutyraldehyde. This suggested the Fe doping is crucial for Mukaiyama epoxidation. However, NO-poisoned Fe-N/C(ODAN) worked as well as the non-poisoned catalysts, which indicates Fe-oxo are not the potential active sites for expedition. Iron could activate the nitrogen doped carbon, which might be the active sites for initiating the aldehyde and produce acyl radicals.

Since the great success had achieved in heterogenous Mukaiyama epoxidation, the usage of Fe-N/C was also extended to Baeyer-Villiger oxidation. BV oxidation was carried out with the high metal content Fe-N/C(ZIF) to see whether the increasing Fe content would be helpful with organic synthesis or not. The kinetic studies were tested first, and a similar rate equation was observed as the Mukaiyama epoxidation with Fe-N/C(ODAN). Both concentration of isobutyraldehyde and catalyst were directly proportional to the rate of reaction. Moreover, different temperatures were tested, and an activation energy was calculated according to Arrhenius equation. The activation energy of this BV oxidation was 39.3 ± 6.2 kJ/mol. A possible mechanism of this type of BV oxidation was also proposed. Finally, different aldehydes were tried with the BV oxidation. However, totally different trends were observed in this BV oxidation compared with Mukaiyama epoxidation. Pivaldehyde, which worked well with Mukaiyama epoxidation, did not show a good activity with BV oxidation. Benzaldehyde, which didn't work with Mukaiyama epoxidation, gave the highest conversion of cyclohexanone but the longest reaction time. However, there are still lots of observations which had not be understood yet and more investigation with BV oxidation is required.

5.5 Possible future work

As the current work done in BV oxidation is very limited and there are still lots of experiments could be carried out to provide more information about the BV oxidation and catalyst. Therefore, in this section, several possible future work will be discussed.

Firstly, it might be worth to synthesis Fe-N/C(ZIF) with different metal loading and try them with the BV oxidation to investigate whether the metal loading will influence the rate of BV oxidation. As the metal content could be controlled during the synthesising of Fe-N/C(ZIF), the catalysts with the same nitrogen doped carbon framework allow to investigate the effect of

metal loading. Furthermore, the BV oxidation with NO-poisoned catalysts should be also investigated to confirm whether the Fe-oxo is the potential oxidising species or not.

Secondly, as mentioned in the Chapter 3, M-N/C(ZIF)s with different transition metals could be prepared and tried with this BV oxidation and this would allow to not only deconvolute the two possible active sites (intrinsic N/C + M-N_x) and relate this BV oxidation with ORR to see whether there is any relationship between two reactions.

Finally, it might be worth to try the electrochemical analysis with BV oxidation as well to confirm whether change in OCP could also be an indicator for choosing suitable co-reductant or not.

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Chapter 6 Conclusions

This chapter included all the important findings and achievements in this thesis, questions raised by the research, and the potential improvements that could be done in the future.

6.1 Final Conclusions

PEMFC is one of the best energy generation systems as it will not produce any greenhouse gases or other toxic gases to the environment. However, the cost of PEMFCs is the major barrier that obstructs the commercialisation of PEMFCs, and around 40% of the total cost of PEMFCs stack comes from the platinum group catalysts. The sluggish ORR required a high loading of Pt on the cathode side, so substituting the Pt catalyst on the cathode side with low-cost non-precious metal single atom catalyst is vital. Nevertheless, there are still several problems that need to be addressed:

- 1) Although M-N/C catalysts are quite active due to the high surface area, the preparation of M-N/C would be challenging as the energy of single atom is very high, which tends to form other unreactive species.
- 2) Pyrolysis is an inevitable method to activate the M-N/C catalysts, but this process increases the complexity of the structure of catalysts. The exact structure of M-N/C and its active site for ORR still remains a topic of discussion and investigation. Therefore, understanding and quantifying the active sites of M-N/C catalysts would be useful for optimising the catalysts.
- 3) The metal loading of M-N/C catalysts limits the activity of M-N/Cs. However, increasing the loading content would lead to the formation of metal clusters, including metal nanoparticles, metal carbides, metal oxides, *etc*, which do not give a high ORR performance.

- 4) As the M-N/C catalysts could activate the molecular oxygen, which is a green oxidising agent, heterogeneous catalytic oxidation with molecular oxygen could be one of the potential applications. A completely different reaction with M-N/C could prove more understanding of the active sites in M-N/Cs from a different aspect.

By conducting extensive investigations on a diverse array of M-N/C catalysts within a unified framework, this research successfully addresses the aforementioned issues. Additionally, delving into the mechanisms underlying an organic oxidation reaction enhances the comprehensive understanding of the active sites.

6.1.1 Chapter 3 - Oxygen Reduction Reaction Activity in non-precious metal catalysts- contribution of metal and carbon-based sites

This chapter focused on the first two questions, including the preparation of catalysts with single atom sites and the study of the active sites in M-N/C.

- Seven different metals based single atom catalysts were prepared through (trans)metalation with pyrolysed ZIF-8 as starting material. Pyrolysed ZIF-8 provided a template for Zn-N_x sites, and these sites could be (trans)metalated with other metal ions. In this chapter, Fe, Co, Ni, Mn, Sn, Sb and Bi were tried, and all of them successfully formed M-N_x sites according to the EXAFS. All the prepared M-N/Cs should have a nearly identical framework with the only difference being the metal centre.
- The ORR performances of all M-N/Cs were tested under three electrolytes with different pH values: 0.3, 5.2 and 13.0. Several findings were based on the ORR performances:
 - M-N/Cs, except Fe and Co, exhibited very similar ORR performances in the same electrolyte, indicating that the ORR activity should be contributed by the

framework sites and the metals (Ni, Mn, Sn, Sb and Bi) did not enhance the activity.

- Under acidic and near-neutral conditions, the framework sites did not show high ORR performance, but the performance significantly increased when Fe and Co were doped into the catalyst.
- Under the alkaline condition, all the catalysts displayed high activity for ORR, with further improvements observed when Fe and Co were (trans)metalated.
- Nitrite stripping at pH 5.2 was used to quantify the site density of M-N/Cs and all of them exhibited a nitrite reduction peak. However, only Fe and Co-based catalysts had significantly different site densities compared to others. Since all M-N/Cs had the same framework, this allows for the deconvolution of the contribution of different active sites, including framework sites and metal-based active sites.
- The relationship between the ORR activity and site density of Fe-N/C and Co-N/C was investigated, revealing that increasing the metal-based active site could significantly improve the ORR activity, especially in acidic conditions.

Based on the results in Chapter 3, only Fe-N/C emerges as the most promising candidate to substitute the Pt catalyst in PEMFC, because the Fe-N_x sites are the most active. However, the current activity of Fe-N/C still needs improvement, which could be accomplished by increasing the metal loading, a key aspect to be discussed in the next chapter.

6.1.2 Chapter 4 - Platinum-free catalyst for air-breathing electrochemical device- increasing the surface density of single atom coordinated Fe sites to improve performance

The third question, which focuses on increasing the metal loading of single atom catalysts, was addressed in Chapter 4. It is a challenging yet meaningful topic, as previously only 2 - 4 wt%

of Fe could be synthesised as single atom sites and Fe based catalysts exhibited much higher ORR activity than others under acidic conditions.

- The optimisation of Fe-N/C preparation based on the (trans)metalation method discussed in Chapter 3 was carried out. The optimisation steps are outlined below, resulting in Fe-N/C^{Δ-DCDA} containing approximately 7 wt% Fe as single atom sites, with less than 1 wt% of Zn remaining in the catalyst.
 - Refluxing the catalyst in 2 M H₂SO₄ was performed to remove the residual Zn, which potentially generates more vacant sites for Fe coordination.
 - During the second pyrolysis step, DCDA was added to activate the catalyst. The thermal decomposition of DCDA would release NH₃ at 330 °C, and the treatment with ammonia gas can convert the buried site into the accessible surface sites.
 - The temperature of 907 °C was chosen for the second pyrolysis, which corresponds to the boiling point of Zn. This temperature effectively removed the remaining Zn in the catalyst while preventing the loss of active sites at higher temperatures.
- Based on the EXAFS of catalysts at different synthetic stages, it was observed that pyrolysed ZIF-8 resulted in the formation of Zn-N₄ sites, facilitating the coordination of iron during (trans)metalation. Successful formation of M-N₄ sites (where M = Zn or Fe) was achieved at all stages. Additionally, the bond length between Fe and N was slightly shorter after second pyrolysis, indicating second pyrolysis strengthen the bond.
- The presence of a sextet in ⁵⁷Fe Mössbauer spectroscopy of Fe-NC^U suggests the formation of some Fe₂O₃, while the second pyrolysis led to formation of D1 and D2 active sites.

- According to the nitrite stripping, the site densities of Fe-NC^{Δ-DCDA} are 4.67×10^{19} site g⁻¹ (3 - 18 times higher than the other reported values).
- For PEMFC measurements (5 cm² single cell), the current density at 0.90 V_{iR-free} under hydrogen-oxygen conditions reaches 41.3 mA cm⁻², surpassing other reported values. When operating under hydrogen-air conditions, the current density at 0.80 V reaches 145 mA cm⁻², with a peak power density of approximately 430 mW cm⁻².
- Large-scale PEMFC measurements (50 cm² single cell) were conducted by Johnson Matthey, revealing that Fe-NC^{Δ-DCDA} exhibited superior activity compared to the commercially available catalyst, Pajarito powder.
- Finally, the poor durability of Fe-NC^{Δ-DCDA} can primarily be attributed to demetallation according to the EXAFS of used MEAs (only 55% of Fe as Fe-N₄ after 10 h stability test).

Fe-NC^{Δ-DCDA} demonstrated a remarkable increase in the number of active sites significantly by boosting the iron content. Furthermore, its ORR performance in both RDE and PEMFC approached the levels achieved by platinum group catalysts. However, to enable its practical application in real systems, enhancing the durability of catalysts remains a critical area for improvement.

6.1.3 Chapter 5 - Using molecular oxygen and Fe-N/C heterogeneous catalysts to achieve Mukaiyama epoxidations and Baeyer-Villiger Oxidation via *in situ* produced organic peroxy acids and acylperoxy radicals

This chapter aimed to solve the final question, which pertains to the extensive utilisation of iron-based single atom catalysts for organic oxidation. The objective was to gain a deeper understanding of the active sites from a different perspective. Fe-N/C(ODAN) was previously reported as a sustainable heterogeneous catalyst for Mukaiyama epoxidation. However, the

mechanism underlying this type of Mukaiyama epoxidation was not investigated, which is important for comprehending and enhancing both the catalyst and also yield of epoxide.

- The kinetic study of Mukaiyama epoxidation using Fe-NC(ODAN) was conducted by varying the concentration of reactants and catalyst.
 - The rate equation of epoxidation of cyclohexene with isobutyraldehyde as a co-reductant is:

$$-\left(\frac{d(O_2)}{dt}\right)_{max} = k_{obs}[isobutyraldehyde]^{1.2}[catalyst][oxygen]^0[cyclohexene]^{-0.2}$$
 - The activation of isobutyraldehyde with catalyst was identified as the rate determining step.
 - The addition of cyclohexene resulted in the obstruction of the catalyst's active sites, causing a decrease in the reaction rate.
- The activation of aldehyde led to the formation of two possible intermediates, including peroxy acid and acylperoxy radicals. The absence of iron-oxo species was confirmed by employing a NO-poisoned catalyst. This also indicated that the framework site active the aldehyde with molecular oxygen to generate oxidising intermediates.
- Based on the kinetic studies and investigation of potential intermediates, a plausible mechanism was proposed in this chapter.
- Furthermore, the reaction was examined using electrochemical approaches, such as OCP and CV.
 - The OCP of the system exhibited a significant increase upon the addition of aldehyde, with the change in OCP serving as an indicator to determine the feasibility of Mukaiyama epoxidation. When the change in OCP was less than 0.14 V, no epoxidation occurred, vice versa.
 - According to the CV results, isobutyraldehyde interacted with superoxide anion radicals, as evidenced by the disappearance of the re-oxidation peak.

- Fe-N/C(ZIF), which is similar to Fe-N/C(ODAN), was also capable of activating the aldehyde in a similar manner and was employed for Baeyer-Villiger oxidation.
- The rate equation for Mukaiyama type Baeyer- Villiger oxidation was similar to that of Mukaiyama epoxidation, with isobutyraldehyde and the catalyst being approximately 1st order.
- The activation energy of Baeyer-Villiger oxidation was determined to be 39.3 ± 6.2 kJ/mol.

Fe-N/C can serve as a catalyst not only for PEMFC but also for organic oxidation. The NO-poisoned catalyst remained capable of activating the aldehyde and facilitating the Mukaiyama epoxidation, indicating iron was not the primary active site for this reaction. These findings also support the results presented in Chapter 3, suggesting the presence of multiple types of active sites in this kind of catalyst. Moreover, the introduction of using electrochemical approaches to investigate the organic synthesis proved to be significant and novel.

6.2 Future work

Although this thesis addressed the four questions shown above, there are still several other aspects that require further investigation in order to gain a deeper understanding of the catalyst and potentially apply the non-precious metal SACs to PEMFC in industry. This section provides a summary of the future work based on Chapters 3, 4 and 5.

6.2.1 Optimising the synthetic method of M-N/Cs and extending the utilisation of M-N/Cs in other electrochemical reactions

In Chapter 3, several different metal based M-N/Cs were prepared; however, only ORR and nitrite stripping were investigated. Therefore, there are several areas to focus on in the future research.

- Increasing the metal content of M-N/Cs has the potential to improve the site density and ORR performance. Additionally, the M-N_x sites appears to be more reactive than the framework N/C sites.
- Preparation of Fe-N/Cs with different metal loadings ranging from 1 wt% to 7 wt% can be achieved through (trans)metalation. Assessing the ORR performance and site density of these Fe-N/Cs could provide a better understanding of catalysts and help establish a correlation between site density and ORR better because only one point was available currently. This would also determine whether the activity of Fe-N_x sites depends on the number of sites.
- Optimisation of Fe-N/C and Co-N/C can be pursued as they have shown promise as catalysts for ORR. Various aspects can be considered, such as increasing the metal content and reducing the particle sites.
- Finally, other electrochemical reaction processes can be explored. Ni-based SACs are well-known for their effectiveness in the carbon dioxide reduction reaction. Additional reactions, for example nitrogen reduction reaction, nitrate reduction reaction can be also investigated to identify potential candidates.

6.2.2 Catalyst development for Fe-N/C

Although the initial ORR performances of Fe-NC^{Δ-DCDA} were comparable to Pt in PEMFC, the stability of Fe-NC^{Δ-DCDA} needs improvements.

- Vigorous demetallation was observed in Fe-NC^{Δ-DCDA} catalyst after a 10-hour stability test, as indicated by EXAFS measurements. Hydrogen peroxide could be the primary reason for this demetallation, suggesting that the addition of a substance capable of rapidly decomposing hydrogen peroxide could be a possible solution. Potential candidates for this role could include Ag nanoparticles or CeO₂ *etc.*

- Co-N/C catalysts are generally known for their superior durability compared to Fe-N/C; however, their activity is lower. Therefore, exploring the preparation of catalysts with both Fe-N₄ and Co-N₄ sites could be attempted to achieve high initial performance and long-term durability.

6.2.3 Mukaiyama oxidation reaction

Fe-N/C single atom catalysts demonstrated the ability to active aldehyde and generate *in-situ* peroxy acid or acylperoxy radical. However, there are still unanswered questions, particularly regarding to the Baeyer-Villiger oxidation.

- Different metal loadings of Fe-N/C(ZIF) with the same nitrogen doped carbon framework should be prepared and tested with the Baeyer-Villiger oxidation to study the effect of metal content.
- NO-poisoned Fe-N/C(ZIF) could also be tested to confirm the formation of Fe-oxo species with Fe-N/C(ZIF) catalyst.
- Different metal based M-N/Cs could also be employed in Baeyer-Villiger oxidation to investigate the two possible active sites, including the M-N_x and framework N/C. This would help establish a relationship between organic oxidation and ORR performance.
- OCP measurements could be conducted in Baeyer-Villiger oxidation as well, in order to confirm whether the changes in OCP still serve as a suitable indicator to determine the feasibility of organic oxidation.

The End