Role of Nitrogen Defects in Nitrogen-Doped Carbon for Catalyst Support and Electric Double-Layer Capacitor

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Electrochemical applications of carbon are wide and varied. They are used as electrodes for batteries, capacitors and proton exchange membrane fuel cells (PEMFCs). This is possible due to their excellent electrical conductivity, variable nanostructure and cost-effectiveness. Besides these properties, physicochemical properties such as microstructure and surface chemistry play a significant role in the performance of carbon as electrodes in these applications. In supercapacitors or ultracapacitors, surface oxygen functionalities can increase capacitance due to non-faradaic reactions between redox couples such as quinine and hydroquinone while in PEMFCs, surface functionalities can determine catalyst size distribution and dispersion. However, surface oxygen functionalities also facilitate carbon corrosion, which can spontaneously take place at as low as 0.2 V. This affects the long term performance of these electrochemical devices. Therefore, there has been considerable effort to improve surface chemistry of carbon using heteroatoms.

Nitrogen is at the forefront of this effort because it has been shown that by doping carbon with nitrogen, the capacitance can be increased and catalyst size distribution and dispersion can be improved. However the role of nitrogen is not well understood. To investigate the role of nitrogen-groups on capacitance and support properties of N-doped carbon, we chose Nitrogen-doped ordered mesoporous carbon (NOMC) casted on a SBA-15 template from polypyrrole precursors. Templating procedure was chosen because it allows precise control of pore structure.
which greatly affects the performance of carbon in electrochemical devices. SBA-15 was chosen because the carbon casted on it is an exact inverse replica. Polypyrrole precursor was chosen because of its high N/C ratio and forms graphitic carbon after pyrolysis.

In Chapter 1, background to physicochemical properties of carbon is given. In addition, a survey of current literature on N-doped carbon for supercapacitor and PEMFCs are provided. In PEMFCs, a detailed review of advanced carbon materials for Pt support for oxygen reduction reaction (ORR) is given. In Chapter 2, effect of N-doping on physical properties of carbon is discussed. The chapter discusses what kind of microstructural and surface modifications are expected and how they can effect its properties as a metal support and an electrode for supercapacitors. In Chapter 3, experimental methods to characterize physicochemical properties of carbon and investigate its electrochemical properties are described. In Chapter 4, the physical properties of NOMC are presented. The chapter gives experimental evidences of good ORR activity, very high capacitance and excellent stability of NOMC. In Chapter 5, the role of nitrogen and graphiticity were studied for capacitive effect. The pore structure of the NOMCs was kept constant while N-content and graphiticity was varied by the heat treatment. It is argued that the fundamental increase in capacitance of N-doped carbon is likely due to increase in electron density at the carbon surface. Chapter 6 and 7 deals with the role of NOMC as a Pt support for ORR. In Chapter 6, it was shown that the N-doped mesoporous carbon should have proper nanostructure to have better interaction with Pt that results in enhancement of Pt ORR activity. The proper nanostructure for NOMC in this work was disordered pore structure. In Chapter 7, effect of temperature-controlled N-content and graphiticity on Pt desorption and its
ORR activity was studied. It was established that high N-content and small Pt size (~ 2 nm) are required to achieve an enhancement in Pt-carbon interaction and ORR activity.

In summary, this work shows that both microstructure (graphiticity) and N-content have to be optimized for electrochemical applications of N-doped carbon. For supercapacitors, the role of nitrogen is to adjust edge plane/ basal plane ratio and electronic properties of carbon. As a catalyst support, nitrogen controls the Pt size and dispersion. Moreover, if the N-content is large and nanostructure amorphous, enhanced catalyst-support interaction could be achieved with small Pt nanoparticles which will increase Pt ORR activity.
Role of Nitrogen Defects in Nitrogen-Doped Carbon for Catalyst Support and Electric Double-Layer Capacitor

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LIST OF ABBREVIATIONS AND SYMBOLS

ε – Dielectric constant,
ε₀ – Permittivity
ω – Rotation rate
ν – Kinematic Viscosity
η_{ORR} – Oxygen reduction reaction kinetic loss
η_{tx} – Mass-transfer overpotential
ADT – Accelerated Degradation Test
at – Atomic
AFM – Atomic Force Microscopy
ATR-FTIR - Attenuated Total Reflectance-Fourier Transform Infrared
BET - Brunauer-Emmett-Teller
BE – Binding Energy
BJH - Barrett-Joyner-Halenda
C_{O}^{\circ} – Bulk O\textsubscript{2} concentration
C\textsubscript{A} – Area-specific capacitance
C\textsubscript{D} – Diffuse double-layer capacitance
C\textsubscript{H} – Helmholtz-capacitance
C\textsubscript{M} – Mass-specific capacitance
C_{SC} – Space-charge capacitance
CCG – Catalyst coated Gas Diffusion layer
CE – Counter Electrode
CNF – Carbon Nanofiber
f-CNF – Fishbone Carbon Nanofiber
p-CNF – Platelet Carbon Nanofiber
t-CNF – Tubular Carbon Nanofiber
CNT – Carbon Nanotubes
CPPy – Carbonized Polypyrrole
CV – Cyclic Voltammograms
CVD – Chemical Vapor Deposition
D<sub>O</sub> - O<sub>2</sub> Diffusivity
DOE – Department of Energy
DI – Deionized Water
DL – Double Layer
DMFC – Direct Methanol Fuel Cell
e – electron charge
E – Potential
EC – Electrochemical Capacitors
ECSA – Electrochemically Active Surface Area
EDA – Ethylene Diamine
ED-CNT – Bamboo like Carbon Nanotube
EELS – Electron Energy Loss Microscope
EDLCs – Electrochemical double layer capacitors
EG – Ethylene Glycol
F - Faraday
FWHM – Full-width at half-maximum
GDL – Gas diffusion layer

GNF – Graphitic Nanofiber

HCMS – Hollow Core Mesoporous Shell

HOPG – Highly Ordered Pyrolytic Graphite

i – Current

I_m – Mass-specific Activity

I_s – Specific Activity

j – Current Density

j_k – Kinetic Current Density

j_m – Mass-transfer Current Density

L_a – Carbon crystallite size

L_c – Carbon crystallite height

L_Pt – Pt Loading

MEA – Membrane Electrode Assembly

n – Number of Electrons

N-5 – Pyrrolic Nitrogen

N-6 – Pyridinic Nitrogen

N-Q – Quaternary Nitrogen/Graphitic Nitrogen

NC – Nitrogen-doped Carbon

NMC – Nitrogen-doped Mesoporous Carbon

NMCC – Nitrogen Modified Carbon Composite

NOMC – Nitrogen-doped Ordered Mesoporous Carbon

NP - Nanoparticles
OAL – Ordered Active Layer

OHMC – Ordered Hierarchical Mesoporous Carbon

OHNC - Ordered hierarchical nanostructured carbon

OMC – Ordered Mesoporous Carbon

ORR – Oxygen Reduction Reaction

P – Pressure

Pa – Pascal

$P_o$ – Saturation Pressure

PEMFC - Proton Exchange Membrane Fuel Cells

PPy – Polypyrrole

PSD – Pore Size Distribution

Pt – Platinum

PTFE - Polytetrafluoroethylene

Py – Pyrrole

PZC – Potential of Zero Charge

$Q_H$ – Charge under the Pt-H oxidation/formation peaks

R – Resistance

RDE – Rotating Disk Electrode

RPM – Revolutions Per Minute

RE – Reference Electrode

RHE – Reference Hydrogen Electrode

$S_{BET}$ – BET Specific Surface Area

SEM – Scanning Electron Microscope
STEM – Scanning Transmission Electron Microscope
TEOS – Tetraethyl orthosilicate
TEM – Transmission Electron Microscope
TGA – Thermogravimetric Analysis
UHP – Ultra High Purity
V – Voltage
VC – Vulcan Carbon XC-72R
V_{tot} – Total Pore Volume
WE – Working Electrode
W_{Pt} – Pt Weight Percentage
wt – Weight
XPS – X-ray Photoelectron Spectroscopy
XRD – X-ray Diffraction
CHAPTER 1

INTRODUCTION

Carbon has several unique properties including high electrical and thermal conductivity, and good chemical stability in both acidic and basic media [1]. It is cheap and readily accessible. Its structure can be modified at both micro and nano scales and different forms of carbon have been developed such as powders, fibers, thin solids, porous sheets, and large blocks [1]. Nanostructuring has led to various morphologies of carbon at the atomic scale such as carbon nanotubes, fullerenes, carbon onions, nanodiamonds, and graphene sheets [2, 3]. Because of these properties, it is the most widely used material in electrochemical devices such as batteries, capacitors, and low temperature fuel cells [4-8]. In commercial Li-ion batteries (LIB), graphitic carbon is used as the anode due to its high Li-ion storage capacity, good cycleability, and suppression of dendrite formation [3, 4]. Electrochemical double layer capacitors (EDLCs) employ porous carbonaceous materials because of their high specific surface area and conductivity [5-7]. Carbon doped with electroactive transition metal oxides, for example RuO$_2$, has high pseudocapacitance making them attractive for redox-based supercapacitors [6]. In low temperature fuel cells and stacks, carbon is used as the structural components in the form of bipolar plates and gas diffusion layer (GDL), as well as the catalyst support in the electrodes [8].

1.1 Physicochemical Properties of Carbon

One of the most important properties of these carbon materials is pore structure, which dictates surface area and mass-transfer of both chemical and ionic species. Pores have been
categorized into three groups: micropores (< 2 nm diameter), mesopores (2-50 nm diameter), and macropores (> 50 nm diameter) [9]. In conventional carbon materials, micropores provide the greatest contribution to the surface area due to its high surface area to volume ratio, while macropores contribute the least. On the other hand, macropores allow for more efficient mass-transfer than micropores. Thus, mesopores supposedly balance these two effects, providing high surface area and allowing efficient mass-transfer. However, most materials have a distribution of pores. Hence interconnection of the pores and their distribution become important in determining their performance.

The microstructure of carbon consists of crystallites of varying sizes which are arranged in a random fashion. Each crystallite is composed of polyaromatic layers of carbons in hexagonal rings with sp² hybridization called graphene. The half filled π-orbitals provide the conductivity through mobile π-electrons. The most interesting regions of the carbons are the edge and defect sites where the carbon has unfilled valence orbitals or dangling bonds. So these edge and defect sites are highly active. The basal planes, sections of hexagonal rings of carbon, are less active than the edge or defect sites; the edge plane of a graphene sheet has a heterogeneous electron transfer rate constant of 0.01 cm/s while the basal plane has a rate constant of 10⁻⁹ cm/s [10]. These edge/defect sites along with steps are believed to be active sites on carbon [11]. Furthermore, heteroatoms such as H, N and O can form bonds with carbon atom at these sites. The chemical nature of the carbon is significantly influenced by these heteroatoms.

Oxygen is the most studied heteroatom. Oxidation of carbon is often carried out to increase hydrophilicity or wettability via formation of surface oxides of a graphitic carbon which is usually hydrophobic. Three types of surface oxides have been identified: acidic, basic and neutral (Figure 1.1). Acidic surface oxides are formed by oxidizing agents at room temperature.
Figure 1.1 Oxygen functionalities of carbon: (a) carboxyl, (b) lactone, (c) hydroxyl, (d) carbonyl, (e) quinine, (f) ether, (g) pyrone, (h) carboxylic anhydride, (i) chromene, (j) lactol and (k) π-electron density [12].
or when carbon is treated with oxygen up to 400 °C. Carboxyl, lactones, anhydrides, hydroxyls, and lactols groups make up the acidic surface oxides. Especially, carboxylic groups are strongly acidic. These acidic oxides are thermally unstable and decompose at 300 to 800 °C under vacuum or inert atmosphere. Basic surface oxides are formed when oxidized carbon is freed from the surface oxides at high temperature in vacuum or inert atmosphere and exposed to air after cooling down to low temperature. Pyrone, chromene, and quinine structure are considered to be basic surface oxides. The neutral surface oxides are formed at the unsaturated sites (\(>\mathrm{C}=\mathrm{C}<\)) by irreversible adsorption of oxygen molecules. The concentration and nature of the surface oxides depend on the carbon, oxidizing reagent and the oxidizing procedure. Furthermore, the oxidation of carbon can change porosity, surface area, crystallite size, resistivity, and wettability. A mild oxidation might increase the surface area by opening of pores. However, if the carbon is highly graphitic or if the fine pores are in close proximity, the oxidation might have negligible or reverse effect.

Like oxygen, nitrogen also increases hydrophilicity or wettability of the carbon. Four types of nitrogen functionalities based on XPS studies have been identified (Figure 1.2): pyridinic (N-6), pyrrolic (N-5), quaternary (NQ), and an unknown (N-X). N-X is assigned mainly to pyridine-N-Oxides but can also be NO\(_x\) or shake-up satellite peak [13]. N-6 donates one \(\pi\)-electron while N-5 donates two \(\pi\)-electrons to the aromatic ring. This is explained more clearly in Chapter 2. NQ is also called graphitic nitrogen because of its in-plane position [13]. So, NQ is an in-plane structure while N-6 and N-5 are edge structures. However, NQ also could be protonated N-6 and N-5 could also be pyridone, a hydroxylated pyridine. Besides, interstitial, and sp\(^3\)-bonded N could also be present. This already intricate picture is further complicated by tendency of these defects to group together [14].
Figure 1.2 Nitrogen functionalities of carbon: (a) pyrrole like N, (b) nitrile, (c) secondary amine, (d) nitro group, (e) nitroso group, (f) tertiary amine, (g) primary amine, (h) pyridine like N, (i) imine, (j) amide, (k) lactam, (l) pyridone and (m) quaternary amine [12].
Experimental and theoretical studies have shown that N-doping induces electronic and structural changes in carbon. This is discussed in detail in Chapter 2. Doping with nitrogen could increase the metallic properties of carbon nanotubes (CNTs) [15]. The type of nitrogen defects, its concentration and distribution can have significant effects on electronic and transport properties of CNTs which is a subject of intense research. Incorporation of nitrogen during growth of CNTs can bring about significant structural changes. Ma et al. reported formation of bamboo-like CNTs when mixture of CH$_4$ and N$_2$ were used as precursors over mesoporous silica plates containing Fe and Ni nanoparticles in a microwave plasma-assisted chemical vapor deposition [16]. Likewise, Kurt et al. reported vermicular CNT decorated graphene sheets perpendicular to the surface with bias-enhanced hot-filament chemical vapor deposition (CVD) using CH$_4$ and N$_2$ precursors [17]. The role of nitrogen in formation of these irregular structures was unequivocal. Other groups have reported graphene basal plane distortions in carbon nanostructures doped with nitrogen during synthesis [18, 19]. This is probably caused by buckling around pentagonal defects which is stabilized by presence of N atoms [19, 20]. Hence carbon nanostructures with N-doped during synthesis clearly have more structural deformations, distortions or dislocations compared to similar non-doped carbon nanostructure.

Nitrogen can be incorporated directly into carbon by ammonia treatment or ion implantation [21]. It can also be incorporated indirectly through a nitrogen rich precursor during pyrolysis or CVD. Pyrolysis of polymers such as polyacrylonitrile, polypyrrole, polyaniline, furan resin, etc is a popular way of producing N-doped carbon. During pyrolysis, the non-aromatic linear polymers undergo thermal depolymerization and gasification, resulting in a low carbon yield [22]. On the other hand, heavy aromatic polymers such as furfuryl alcohol do not undergo thermal depolymerization, resulting in a high carbon yield [22]. If heteroatoms such as
chlorine, nitrogen or oxygen are present, the carbon yield is even lower as these elements form volatiles. The heteroatoms remain in the final product due to incomplete carbonization. Hence, the amount of nitrogen in the carbon depends on the precursor and the processing conditions.

1.2 Novel Carbon Materials for Pt Support

Proton exchange membrane fuel cells (PEMFCs) convert chemical energy of H₂ and O₂ directly into electrical energy through complementary redox processes that are not limited by Carnot or Rankine heat cycles. Hence, PEMFCs are widely considered to be one of the most promising candidates for a high efficiency and environmentally friendly energy source for the 21st century, and have been explored widely for both stationary and vehicular applications. The rate limiting reaction in PEMFCs is the oxygen reduction reaction (ORR) at the cathode [23].

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$ \hspace{1cm} 1.1

Pt and Pt-alloys supported on carbon black are the most popular catalyst for the ORR in PEMFCs. However, Pt is expensive and still suffers from large activation overpotential. The DOE target is to reduce platinum group metal loading to 0.125 mg Pt/cm² by 2017 [24]. To achieve this target, not only must the activity of the catalyst be enhanced, but also the particle size distribution and dispersion have to be improved. To date, the activity of Pt has been improved mostly through alloying and developing novel nanostructures. Recent work by several groups has shown that both the catalyst activity and dispersion can be enhanced through the implementation of novel supports [25].

The most widely accepted descriptor for ORR activity has been the binding energy of O atoms to the catalyst surface, which is a linear function of the d-band center [26-28]. Strong Pt-O binding energy eases the breaking of the O=O bond and enhances electron transfer, but results in
surface oxidation and high coverage with intermediate species. On the other hand, weak Pt-O bonding leads to an inability to break the O=O bond and poor electron transfer. The d-band center of a catalyst can be modified by the electronic and structural effect imparted by electron transfer or physical distortion of the support. Generally, raw and alloys of noble and non-noble metals in various forms have been widely investigated as supports to adjust d-band center of Pt NPs following the d-band center model [25]. However, metal “supports” are expensive. Hence, there is interest to replace metal supports with advanced carbon supports. However the traditional carbon support, carbon black, is thermodynamically unstable and bonds to catalyst particles via weak van der Waals forces. As a result, there have been considerable studies to replace carbon black or enhance its surface and structural properties. For the latter case, carbon nanotubes (CNTs), carbon nanofibers, graphene, ordered mesoporous carbon (OMC), and hierarchical/macroporous carbons have been explored.

1.2.1 Carbon Nanotubes
Carbon nanotubes (CNTs) are the most popular advanced carbon support for Pt nanoparticles (NPs). CNTs can be classified as single-walled carbon nanotubes (SWCNTs) or multi-walled carbon nanotubes (MWCNTs) depending on the number of graphene walls. They are also characterized by their geometry as arm-chair, zigzag and chiral depending on the arrangement of carbon bonds on the curved graphene surface. The surface area of CNTs depends on the number of graphene sheets that comprise the walls: 1315 m²/g for single wall, 680-580 m²/g for two walls, 295-430 m²/g for five walls and so on [29]. CNTs act as both metal and semiconductor depending on the arrangement of carbon atoms. The electronic conductivity is very high (10⁸ /ohm-m) in metallic CNTs as scattering does not occur [30, 31].
Since pristine CNTs are very difficult to disperse in solution because of their high graphiticity, surface functionalization is often carried out to prepare the surface for metallization. There are various methods of surface functionalization, one of the simplest being chemical oxidation [32-34]. Besides chemical oxidation, other methods such as sonochemical treatment and microwave irradiation can also introduce oxygen groups on CNTs. By avoiding high heat and using proper reducing agents such as ethylene glycol (EG), sintering during the reduction step can be avoided. Surprisingly, reduction of metal precursor can also take place on SWCNT in the absence of a reducing reagent. Choi et al. reported spontaneous reduction of PtCl$_4^{2-}$ and AuCl$_4^{-1}$ on SWCNTs, which they attributed to the formation of redox pairs where the Fermi level of the SWCNT was greater than the reduction potential of PtCl$_4^{2-}$ and AuCl$_4^{-1}$ [35]. In another interesting study, Sheng et al. showed that on amine functionalized MWCNTs, even after heat treatment from 200°C to 600 °C, the particle size of Pt NPs remained constant at 2 nm [36]. Hence, like in carbon blacks, surface functionalization and catalyst deposition method influence both metal dispersion and metal-support interaction.

There have been some promising studies showing that CNT-supported Pt shows enhanced ORR specific activity than that of conventional Pt/C. Against 40 wt % Pt/Vulcan (E-TEK), Kongkanand et al. demonstrated that the onset potential of Pt/SWCNT shifted 10 mV positive to Pt/C despite the electrochemically active surface area (ECSA) of the Pt/SWCNT being lower (17.8 m$^2$/g$_{PT}$ vs. 33.5 m$^2$/g$_{PT}$) than Pt/C. Recently, Kim et al. deposited Pt on amine functionalized MWCNT treated with HCl and heated at 220 °C in air, both for 2 h [37]. The intrinsic activity of such Pt/MWCNT was 0.95 mA/cm$^2_{PT}$ higher than that of as-prepared Pt/MWCNT (0.40 mA/cm$^2_{PT}$), acid treated Pt/MWCNT (0.75 mA/cm$^2_{PT}$) and 46 wt % Pt/ TKK (0.36 mA/cm$^2_{PT}$). On a similar catalyst, Sheng et al. reported comparable specific activity
compared to Pt/C [36]. However, from these studies it is not clear if the enhanced specific activity was achieved through strong interaction with the support. For the study by Kongkanand et al., the enhancement was very small, while for Kim et al. the enhancement could be due to their resulting Pt nanostructure where Pt particles blanketed the CNTs.

Numerous studies have shown that CNT-supported Pt catalysts exhibit higher electrochemical stability under accelerated degradation test than that of carbon black supported Pt. A major source of this stability is likely enhanced stability of the support itself caused by its highly graphitic nature compared to carbon black. In addition, authors have given credit to the strong interaction between Pt NPs and CNTs, though the nature of this interaction is ambiguous and has not been studied with sufficient detail. Furthermore, Pt/MWCNTs have been reported to be more stable than Pt/SWCNTs. Wang et al. has reasoned that the top layers of the MWCNT act as a protective sheath for inner layers, which then have fewer sites for corrosion [39].

1.2.2 Graphene

Graphene is a 2D crystal of sp$^2$ hybridized carbon atoms. In this form, carbon exhibits unusual electronic properties. For instance, the charge carriers on a single atomic graphene sheet are massless Dirac fermions with speeds 300 times smaller than the speed of light [39]. The electronic properties of graphene change drastically even with addition of one additional layer; bilayer graphene can act as tunable gap semiconductor [40]. With 10 or more layers, layered graphene acts as a thin film of graphite [41]. It also has robust mechanical features like extremely high breaking strength (~40 N/m) and Young’s modulus (~1.0 TPa) [42]. The theoretical specific surface area of single plane graphene is 2630 m$^2$/g [29]; however utilizing the full surface area is very challenging as they tend to aggregate due to van der Waals forces. Bulk-
produced graphenes by chemical or thermal exfoliation of HOPG are usually a few layers thick [43]. In addition, its properties differ considerably depending on the oxidation/reduction treatment, making reproducibility a potential issue. Thus, graphene as a carbon support is promising but research in this area is not mature enough. Pt on wrinkled graphene sheets prepared by thermal exfoliation of chemically oxidized graphite flakes was shown to have higher mass activity and stability by Kou et al. but the authors did not present any data on specific activity [44].

1.2.3 Carbon Nanofiber (CNF)

While graphene and CNTs are single to few layers of simple graphene structure, Carbon nanofiber (CNF) or graphitic nanofiber (GNF) is a multilayer complex graphene structure, which makes it a very interesting alternative support. CNF has been classified into fishbone (herringbone) with graphene layers at an acute angle to the growth axis, platelet (deck of cards) with graphene layers perpendicular to the growth axis and tubular (parallel) with graphene layers parallel to the growth axis. Although the tubular CNF has a similar arrangement to the graphite planes of MWCNT, the former has a solid core in contrast to the hollow core of the latter [45]. However, some authors do not make such distinction [46]. It can also have different structures such as bidirectional, helical, twisted and branched [47]. The diameter of the CNF (2- 100 nm) depends on the size of the catalyst that catalyzes its growth [47]. Like CNTs and graphene, surface functionalization must be carried out to achieve acceptable dispersion of metal particles. The most attractive feature of CNF is the exposed graphitic edge planes on the surface. The fishbone CNF (f-CNF) and platelet CNF (p-CBF) have very high edge to basal plane ratio while tubular CNF (t-CNF) has very high basal plane to edge ratio. Since edge planse are
thought to be the active sites, catalyst particles on f-CNF and p-CNF are expected to have better higher ORR activity than that of t-CNF. Researchers have shown that metal free f-CNF and p-CNF are more active than on t-CNF [48, 49]. Also, Zheng et al. concluded that 5 wt % Pd on f-CNF and p-CNF have higher ORR activity than 5 wt % Pd on activated carbon [50]. The unique arrangement of sp² planes in f-CNF and p-CNF also allows for a unique pathway for electron conduction that occurs by hopping along the a-axis (basal plane) and c-axis (perpendicular to the basal plane) [51, 52]. However, Yoon et al. showed that the microstructure of CNF is more complex than a planar or conical stack of graphene as previously assumed [53, 54]. They found that the basic structural unit of the CNFs to be carbon nano-rods, 2.5 nm in diameter and varying lengths, consisting of a few graphene layers with open edges at low temperature that close at high graphitization temperature (2800 °C, used by the authors) to conical or pyramidal caps. They proposed that these rods arrange in carbon nano-plates, the stacking of which give rise to fishbone or platelet or tubular structures. This finding demands a closer experimental and theoretical look into structure and properties of CNFs.

1.2.4 Carbon Aerogel

Carbon aerogel is a pyrolyzed organic aerogel usually synthesized using resorcinol-formaldehyde (RF) sol-gels. In a typical synthesis [55, 56], a mixture of resorcinol (R) and formaldehyde (F) in a certain molar ratio is base or acid catalyzed to form a colloidal sol, which is converted to gel by slow heating to promote cross-linkage. At this stage, the aqueous solvent can be exchanged with an organic solvent. Then the gel is dried subcritically in air/nitrogen to produce xerogel, supercritically in CO₂ to produce aerogel or freeze-drying to produce cryogel. The latter two drying methods prevents collapse of the structure by avoiding formation of a
liquid-vapor interface retaining high porosity. The surface area, mesoporosity/microporosity, pore size distribution, surface texture, and carbon particle size can be modified by controlling reactant ratio (R/F), gel pH, catalyst, curing and drying process and carbonization temperature. The microstructure of the carbon aerogel consists of slightly overlapping carbon nanospheres in a continuous chain giving arise to porous 3D interconnected network [57]. Aerogels are attractive for PEMFCs because of their mesoporosity; high mesoporosity can be obtained independent of micropores [58]. In addition, by molding, the aerogels can be produced in various shapes such as monoliths, beads, thin-films etc [56]. The performance of carbon aerogel supported Pt catalysts was reported in a PEMFC by Smirnova and coworkers [59]. During 60h of operation, the cell showed good ECSA retention. Unfortunately, the cell performance was hindered significantly by mass-transfer limitations, though correction for IR and mass-transfer resistances showed good catalyst activity.

1.2.5 Hierarchically Ordered Mesoporous Carbon

Hierarchically ordered mesoporous carbons (HOMC) are attractive as a support for fuel cell applications because of their interconnected bimodal pore size distribution. Both pore systems can be mesoporous or one can be mesoporous while other can be macroporous. While a mesoporous pore structure imparts high surface area and uniform distribution of catalyst particles, macropores provide efficient mass-transfer. Of course, the interconnectivity between pores has a significant role in realizing the advantages of both pore structures. Also, a novel feature about these structures is that the two pore structures can be adjusted independently, allowing for good control over their porosity [60, 61]. Like OMC, controllable pore structure, and carbon microstructure and surface chemistry makes them an attractive support for fuel cell
catalysis. Fang et al. have shown that Pt on hollow core/mesoporous shell (HCMS) and ordered hierarchical nanostructured carbon (OHNC) outperforms Pt/Vulcan in single cell fuel cell tests [62-64], which might be due to better mass-transfer; however, the authors did not discuss or present data supporting such hypothesis.

1.2.6 Ordered Mesoporous Carbon (OMC)

Ordered mesoporous carbon (OMC) was first synthesized in 1999 by Ryoo et al. by casting sucrose into a cubic ($Ia3d$) mesoporous silica template, MCM-48, and carbonizing at high temperature [65]. Though an OMC with a narrow pore size distribution was prepared, X-ray diffraction (XRD) revealed that the resulting carbonized material was comprised of a structure that was significantly different than the template. The following year, Jun et al. [66] reported the first OMC with identical hexagonal symmetry ($p6mm$) to its template using SBA-15. The ordered mesoporous structure is a result of the three-dimensional matrix of interconnecting micropores and mesopores in the walls of the template that are a result of solution phase self-assembly of solubilized surfactant with the carbon precursor during synthesis [67, 68]. Since then, several other silica templates have been explored to synthesize OMCs. In addition, soft template methods have been developed that can be completed in fewer synthesis steps by directly incorporating carbon precursors into the structure-directing surfactant [67, 69]. Soft template OMCs can be highly stable, up to 1400 °C, in contrast to OMCs made from hard template methods, which are generally stable to around 900 °C [65, 70]. One of the advantages of the OMC synthesis is that various precursors can be used to produce carbons with different surface chemistry and pore structure depending on the template or surfactant. This has been successfully exploited to make novel carbon materials for electrochemical applications.
Song et al. analyzed OMCs from a CMK-3 template and wormhole-like mesoporous carbon (WMC). Both showed a very narrow pore size distribution centered around 4.3 nm, comparable BET surface area (992 and 1076 m$^2$/g for CMK-3 and WMC, respectively), similar mesopore volume (1.21 and 1.24 cm$^3$ g$^{-1}$ for CMK-3 and WMC, respectively), and nearly identical average Pt size (3.2 and 3.1 nm for Pt/CMK-3 and Pt/WMC, respectively) [71]. The Pt/WMC catalyst showed higher electrochemically active surface area and higher activity for ORR. This shows that having a large surface area and uniform pore size alone do not yield a high performance catalyst support with improved mass-transfer; accessibility and interconnectivity of these pores also play significant roles. This was supported by Du et al. [72] who reported a 1-D, steady-state numerical model comparing ordered active layers (OAL) oriented perpendicular to the membrane against a conventional active layer with randomly distributed pores and agglomerates as that of in Pt/Vulcan. The authors showed that alignment of the OAL in the direction of the mass-transfer reduced the electrode concentration polarization due to faster O$_2$ diffusion through the thin electrolyte wrapping the OAL rather than an increase of O$_2$ concentration throughout the active layer.

Joo and coworkers [73] synthesized a 33 wt % Pt/OMC catalyst with pipe-like carbon fibers, 5.9 nm inside diameter, 4.2 nm between adjacent fibers, and 2000 m$^2$/g BET surface area prepared using a SBA-15 template and furfuryl alcohol as the carbon precursor (Figure 1.3). They reported a mass activity for Pt/OMC of 0.1 A/mg$_{Pt}$ in O$_2$ saturated 0.1 M HClO$_4$ at 10,000 RPM, which was more than 10 times greater than the mass activity of 33 wt % Pt/C under identical experimental conditions. Likewise, Hayashi et al. reported enhanced ORR for a 30 wt % Pt/OMC (7–9 nm pore diameter, 600 m$^2$/g BET surface area) synthesized through a soft-template method when compared with 50 wt % Pt/C [74]. Interestingly, they also reported a
mass-transfer limited current higher than the Levich theoretical value, which they assigned to the transport and storage of \( \text{O}_2 \) in the pores [74, 75]. Ding et al. also have demonstrated a 669 \( \text{m}^2/\text{g} \) BET surface area, 3.2 nm pore diameter Pt/OMC with greater ORR performance than commercial Pt/C when used in gas diffusion electrodes [76].

Therefore, OMCs display unique and unusual properties regarding mass-transfer enhancement or attenuation of concentration polarization during the ORR, though the mechanism for this enhancement is currently not well understood. Hence, it has proven difficult to translate the high activity observed in ex-situ, three electrode experiments into high performance PEMFCs. The PEM fuel cell performance of a 20 wt % Pt/OMC (754 \( \text{m}^2/\text{g} \) BET surface area, 3.1 nm pore diameter) could not match the performance of 20 wt % Pt/C (ETEK) in real fuel cell conditions [77-80], which suggests that the internal pores of the OMC were not entirely accessible to the ion-conducting phase during fuel cell testing. Therefore, to exploit the full potential of Pt/OMC electrocatalysts, it is imperative to optimize the pore diameter, the ionomer type and loading, and Pt size and loading [74, 81, 82]. One advantage with OMCs is the flexibility of the synthesis procedure, which allows for numerous variations. This should facilitate the synthesis of next generation OMCs with increased diameter, which will allow for the penetration of ionomer into the internal structure, leading to high activity Pt/OMC catalysts for PEMFCs.

To increase the stability of Pt nanoparticles on OMCs, Gupta et al. [83] prepared a highly graphitic OMC from mesophase pitch and compared it to an amorphous OMC made from furfuryl alcohol. After Pt deposition, the OMCs were subjected to ADT. The Pt/graphitic OMC showed little or no alteration while significant changes were observed for Pt/amorphous OMC in terms of mass activity, specific activity, and ECSA. Compared to Pt/VC, even the Pt/amorphous
OMC demonstrated enhanced stability, leading to higher activity retention and maintained high ECSA. Similarly enhanced stability was reported by Wu et al. [84] who synthesized Pt embedded graphitic OMC by impregnating Pt precursor on silica walls and CVD process to form carbon with methane as a precursor. However, they report a slight increase in mass activity after ADT, which shows that their system has mass-transfer limitations. This was also supported by Shanahan et al. [85], who fabricated graphitized OMCs using a soft template method followed by high temperature carbonization at 2600 °C. This material also showed higher stability than Pt/Vulcan. The stability enhancement was mainly assigned to interaction between the Pt d and carbon π-orbitals, though no supporting data was presented.

1.3 Carbon-Pt interaction

The bonding of metal with carbon takes place by exchanging electrons between π-sites of carbon and vacant d-orbitals of metals. Metals lacking vacant d-orbitals such as Cu, Ag, Au, and Al have negligible interaction while metals having large number of vacant d-orbitals such as Ti, V and Nb form carbides. Metals with few vacant d-orbitals such as Fe, Co, and Ni dissolve carbon. In that respect, Pt has the fewest possible vacant orbitals. Hence its interaction with carbon is expected to be very weak. Indeed, first-principle studies have shown that the binding energy between Pt and graphene surface is low [86, 87]. However, the surface of synthesized carbons is not smooth; it has defects and edges, which have dangling bonds and many theoretical studies have shown that Pt has higher adsorption energies at these sites [88-92]. In addition, surface curvature can induce stronger bonding by rehybridization of bonding orbitals like in CNTs. In CNTs, depending on their diameter, stronger metal interaction can occur relative to a flat
Figure 1.3 (a) TEM image of ordered nanoporous carbon (ONC) and its Fourier diffraction; (b) Schematic of pipe-like ONC; (c) Mass activities (A/g) of ONC compared to carbon black at different Pt loading; (d) Polarization curves in 0.1 M HClO4 at 10,000 RPM with a scan rate of 50 mV/s of carbons with 33 wt % Pt [73].
graphene layer. Also, microstructural spatial constraints can cause geometric strain, which may positively affect activity.

The magnitude of the metal-support interaction also depends on the catalyst particle size. In a first-principles study by Okazaki-Maeda et al., the shape of Pt clusters (n<10) appeared to depend on their size [93]. For a Pt cluster size $3 \leq n \leq 7$ vertical planar adsorption was stable, and for $n \geq 7$ adsorption as a parallel planar was energetically favorable. Their calculations showed that the interaction energy decreased as cluster size increases. Yamakawa et al. modeled Pt nucleation on graphene using a Phase-field method coupled with first principles calculations [94]. They demonstrated that as the coordination between Pt atoms increases, the interaction between Pt and graphene decreases. Their results support a Volmer-Weber (island) growth mode, which occurs when adsorbate-adsorbate interaction overcomes adsorbate-substrate interaction combined with lattice mismatch that cannot be compensated by structural relaxation alone [95]. They also point out that obtaining a uniform size distribution depends on the competing nucleation and growth. Instantaneous nucleation leads to homogeneous particle growth while progressive nucleation leads to heterogeneous particle growth. This has been experimentally supported by Zoval et al. [96] who employed non-contact AFM and TEM to analyze Pt particles deposited on clean HOPG by pulsed potentiostatic deposition. They discovered that spontaneous deposition of Pt was taking place onto HOPG without application of any voltage. Moreover, most of the observed deposition was concentrated at step edges. According to the authors, the spontaneous reduction was caused by reducing equivalents such as aldehydes, alcohols and ketones on defect and edge sites. They also found that preoxidation of HOPG decreases the amount of Pt deposited by spontaneous reduction. This led the authors to anodically protect their
electrode during pulsed electrodeposition, which resulted in a narrow particle size distribution, though the distribution broadened as the average particle size increased from 2.6 to 7.2 nm. Jinnouchi et al. showed that not only does the binding energy per Pt atom between graphene and Pt decrease as the particle size increases; the d-band center also lowers with respect to Fermi level. The lowering of the d-band center was also correlated with an increase in the dissolution potential [97]. Toyoda et al. correlated the d-band center of Pt particles ranging from 6.8 Å to 31.4 Å deposited on a glassy carbon electrode using an arc plasma gun to their specific ORR activity [98]. As the Pt size increases, the d-band center increases or moves away from Fermi level and ORR activity increases accordingly (Figure 1.4). This was also verified by X-ray photoelectron spectroscopy (XPS) as the binding energies of the Pt valence band and core 4f became closer to that of polycrystalline Pt as the particle size increased, though a perfect fit with the theoretical prediction was not obtained which the authors ascribed to final state effects.

1.4 Nitrogen-Doped Carbon as Pt support for ORR Activity

Though enhancements in stability have been reported, none of these supports have been shown to increase interaction or bonding with the catalyst support. This is problematic since an improved catalyst-support interaction is required to increase ORR activity through modification of electronic structure of the Pt nanoparticles (NPs) [25]. As an alternative, heteroatom (N, B) doped carbon has shown potential to manipulate the d-band center of the catalyst through enhanced interaction via surface heteroatoms and is relatively cost effective [99]. In this regard, N-doped carbon nanostructures have been most studied.
Figure 1.4 ORR polarization curves of Pt with different sizes on glassy carbon electrode (a) and relation Pt cluster size and d-band center. Reproduced with permission from Ref. [98].
Nitrogen provides a suitable alternative to oxygen group to enhance Pt dispersion. The most common method to enhance Pt activity and dispersion on carbon supports is oxidative pre-treatment [100, 101]. Typically, oxygen functional groups are introduced to the carbon surface by heat treating the carbon supports in a caustic environment: HNO$_3$, H$_2$SO$_4$, H$_3$PO$_4$, H$_2$O$_2$, KMnO$_4$, O$_3$, etc. By controlling the amount and type of the oxygen functional groups, Pt dispersion can be enhanced. However, oxidative pre-treatment of carbon supports also introduces defects to the supports, which leads to higher carbon corrosion rate. If possible, these defect sites should be avoided since carbon corrosion is one of the leading causes for PEMFC performance degradation over time [25]. Therefore, nitrogen has been proposed as an alternative. N-doped carbons have been shown to have higher resistance against corrosion [18, 102, 103] and better Pt dispersion [21].

In 1996, Roy et al. reported enhancement in ORR activity of Pt NPs when carbon black (Vulcan XC-72R) support was doped with sulfur and nitrogen [104]. They attributed this enhancement to the decrease in Pt particle size. However, the data they reported has wide margin of error. A series of papers by Ye et al. around the same time reported ORR activity for Pt on carbon aerogel made from PAN which had significant N-content (22 wt%) [105-109]. Based on a XPS study of N 1s peak, they suggested formation of charge transfer complex between Pt and pyridinic-N although they did not observe any shift in Pt 4f peak [108]. Also, they did not suggest that such an interaction might have an effect on Pt ORR activity.

Metal-free carbon nanostructures doped with nitrogen are ORR active. Hence it has also been suggested that in metal containing N-doped carbon, the metal may simply catalyze the formation of active N-containing active sites [110]. Gong et al. reported a breakthrough in this field by showing that N-doped vertically aligned carbon nanotubes (VACNTs) have higher ORR
activity and stability than the literature standard Pt/C catalyst [111]. Same group reported remarkable ORR activity and stability on N-doped graphene [112]. Similarly, a number of metal free N-doped carbon nanostructures have shown ORR activity [113]. Interestingly, activity is higher when the carbon nanostructure is highly graphitic and the electrolyte is alkaline. In acidic systems, activities are generally orders of magnitude lower than Pt/C, making raw N-doped carbons a poor option for the PEMFC cathode catalyst.

On the other hand, a fair amount of evidence currently exists for enhancing the dispersion and ORR activity of Pt clusters supported on several types of N-doped carbon. Well dispersed Pt clusters with a small mean Pt size of (ca. 2.4 nm) have been reported on N-doped carbon supports. Roy et al. (104) reported that Pt/N-containing Vulcan carbon showed higher ORR activity compared to raw Pt/C for direct methanol fuel cells (DMFCs); however, significant sulfur impurities were present in their carbons. Studies regarding the ORR in acidic electrolyte have been done for Pt clusters supported on functionalized highly ordered graphitic structures, such as CNTs (114, 115) and GO (116). Vijayaraghavan and Stevenson (115) reported an increase in ORR activity of dendrimer encapsulated Pt on N-doped CNTs compared to undoped CNTs. Moreover, the activity increased when the N-doping was increased from 4 to 7.5 at %. However, the mass-transfer-limited current density and mass activity of their most active catalyst fell short of Pt/C. Higgins et al. have shown that Pt on N-doped, bamboo like CNTs (ED-CNT) synthesized from ethylenediamine precursor have enhanced ORR activity than both undoped CNTs and Py-CNTs made from a pyrrole precursor (114). The ED-CNT had higher total nitrogen concentration (4.74 at %) than that of Py-CNT (2.35 at %), higher relative amount of pyridine-type nitrogen, more structural defects, smaller and rounder bamboo compartments as opposed to longer and rectangular compartments, increased Pt dispersion, and smaller Pt
nanoparticles, which resulted in higher ECSA than that of Pt/CNT or Pt/Py-CNT. This ex-situ observation was also supported by testing in a laboratory scale PEMFC. Jafri et al. (116, 117) reported Pt/N-functionalized graphene and Pt/N-functionalized multiwall carbon nanocoils with enhanced ORR activity performance in PEMFCs compared to their unfunctionalized counterparts.

Platinized, N-doped carbon composite and nanosphere catalysts were shown to have superior ORR activity to Pt/C by Li et al. (118) and Su et al., respectively (119). Li et al. prepared N-modified carbon composite (NMCC) from ethylene diamine, carbon black, and Co(NO$_3$)$_2$. At 0.9 V vs. RHE, the mass activity of Pt/NMCC was 0.16 A/mg$_{\text{Pt}}$, which was 33% greater than Pt/C. In addition, Pt/NMCC was more stable than Pt/C under both potentiostatic hold and electrochemical cycling in a PEMFC. At 100% relative humidity, 0.4 mgPt/cm$^2$ loading, and 0.7 V the specific activity of Pt/NMCC was 1.2 A/mg$_{\text{Pt}}$ while that of Pt/C was 0.6 A/mg$_{\text{Pt}}$. Similar enhancement in ORR activity vs. Pt/C was observed by Su et al. (119) for platinized N-doped porous carbon nanospheres.

O’Hayre showed that the Pt nucleation rate on N-HOPG was greater than that on pristine HOPG and Ar irradiated HOPG (Ar-HOPG), yielding well dispersed Pt clusters. In addition, Pt stability on N-HOPG was very high compared to both raw and Ar-HOPG (120). As shown in Figure 1.5, while Pt agglomeration was clear on undoped HOPG after 1000 potential cycles, Pt clusters on both N-HOPG and Ar-HOPG showed good stability. However, after 10,000 potential cycles only Pt clusters on N-HOPG were stable against agglomeration. This shows that while Ar irradiation produces defects and disordering, only N-containing defects are able to bring truly enhanced interaction between the Pt atoms and the graphitic substrate. The nitrogen defects also
**Figure 1.5** SEM images of Pt clusters after potential cycling: (a), (b), and (c) After 1000 cycles on undoped HOPG, Ar-HOPG, and N-HOPG, respectively; (d), (e), and (f) After 10,000 cycles on undoped HOPG, Ar-HOPG, and N-HOPG, respectively [120].
change the electronic structure of Pt and Groves et al. (121) showed that the binding energy between Pt and C atoms was a strong function of the N-site density.

Based on computational studies, nitrogen sites do not directly bond to Pt atoms but it disrupts the $\pi$-electron distribution in the graphene layer [14, 121]. Carbon atom near to this localized high electron density sites are localized electron density sites which interacts strongly with Pt. O’Hayre et al. experimentally correlated N cluster implanted on HOPG through ion implantation to supported metal catalyst using EELS on an aberration-corrected STEM [121]. This is believed to intrinsically enhance catalytic activity of Pt. The increase in dispersion of Pt on N-doped carbon due to enhanced nucleation rate is well established experimentally [21]. However, convincing rigorous experimental proof showing that the boost in ORR activity is due to strong Pt carbon interaction is outstanding. Besides, based on strong ORR performance of metal free N-doped carbon nanostructures, complementary co-catalyst role of N-group is speculated on Pt decorated N-doped carbon support [21].

1.5 Nitrogen-Doped Carbon for Supercapacitors

Natural sources of energy such as solar and wind power are inherently intermittent. Hence, there is a significant need to develop energy storage options that have high energy density, rapid charge/discharge capability and high efficiency. Electrochemical capacitors (ECs), also called supercapacitors or ultracapacitors, are one of the most promising technologies to meet this need. Though their energy density is lower than that of batteries, they can be used to complement or replace batteries in many applications because of their significantly larger power density. They are also uniquely suited for use in load-levelling and uninterruptible power supply applications. Two types of ECs exist: EDLCs and redox or pseudo-capacitors. EDLCs are
inherently more stable compared to pseudo-capacitors due to their non-faradaic charge storage mechanism [123, 124].

Activated carbon, with porosity controlled through selective oxidation, is the most popular carbon for use in EDLCs. During activation, pores are formed over three length scales, all of which play a different role in the double layer (DL) capacitance of these materials: micropores (< 2 nm), mesopores (2 to 50 nm) and macropores (> 50 nm). Since charge is stored in a double layer at the electrode/electrolyte interface, it is advantageous to have very large surface area, resulting from a large number of micropores. Previously, it was believed that pores smaller than 0.5 nm for hydrated ions and 1 nm for organic ions were too small to form the double layer because desolvation of ions would require a prohibitively large energy input [124]. However, it was shown that very high capacitance can be achieved with carbon materials exclusively comprised of micropores less than 1 nm [125] and complete or partial desolvation of ions has been shown to require less energy than expected [126, 127].

In addition to surface area and pore size, surface functional groups also influence capacitance. Oxygen functional groups seem to enhance capacitance, but they also increase internal resistance and carbon corrosion. N-doped carbon has been shown to be corrosion resistant [18, 128-130]. Many studies have shown that the carbons synthesized using various N-containing precursors have enhanced capacitance.

N-doped carbon for supercapacitors was first explored by Jurewicz et al [131] on ammodized young coke carbon. Since then, N-doping has been a popular way to increase capacitance of carbon nanostructures such as CNT [132], carbon aerogel [133], Carbon nanospheres [134], OMC [135], Graphene [137], etc. The enhanced capacitance due to N-doping was believed to be mostly due to electron donor tendency of nitrogen functionalities especially
N-6 having a lone pair of electrons [138] and pseudocapacitive behavior [ref]. Beguin et al. proposed that the pseudocapacitive behavior is due to redox behavior of nitrogen functionalities as pyrrole and pyridone shown in Equation 1.2 and 1.3 [139].

\[
\text{>C=NH} + 2 \text{e}^- + 2 \text{H}^+ \leftrightarrow \text{CHNH}_2 \quad 1.2
\]

\[
\text{>C-NHOH} + 2 \text{e}^- + 2 \text{H}^+ \leftrightarrow \text{CHNH}_2 + \text{H}_2\text{O} \quad 1.3
\]

Based on first principle calculation using DFT, Wang et al. proposed possible pathways which are shown in Figure 1.6 based on oxidation/reduction between pyridine and pyridone groups [140]. The proposed model was based on the results of charge distribution where N-6 showed reductive capabilities due to high negative charge and NO\textsubscript{x} showed oxidative capabilities due to high positive charge. However, pseudocapacitance is observed only in aqueous electrolyte and within a certain pH range [141]. Hence, various works have proposed enhancement in electronic properties of the carbon materials due to N-doping as a reason for improved capacitance. Tashima et al applied a pulsed electro acoustic method to map the space-charge distribution in a capacitor made by N-doped activated carbon in non-aqueous electrolyte [142]. They found that the space-charge distribution was uneven between the positive and negative electrodes of the capacitor and that the charge-density was higher when compared to non-doped carbon. Using scanning photoemission microscopy (SPEM) to locate N sites on graphene, XPS to find N states and DFT to calculate binding energy of N states to K\textsuperscript{+} ion, Jeong et al., found that N sites at the basal plane, especially N-6, contribute more to the increased capacitance than N sites at the edge planes, perhaps due to higher binding energy that would increase density of ions adsorbed during charging [141].
Figure 1.6 Path 1, redox between pyridine (N-6) and pyridone (N-6-OH) Path 2, redox between NO$_x$ and N-6 [140].
Zhang et al. correlated increased capacitance of N-doped graphene to an increase in quantum capacitance and suggested that the capacitivie effect of N-doping could be a modification in the electronic structure of graphene [143]. Xia et al first measured the quantum capacitance of the graphene and found the behavior similar to that of basal plane of graphite [144, 145]. Hence, they suggested that the interfacial capacitance of graphene could be due to quantum capacitance. Hence, they suggested that role of nitrogen could be to influence quantum capacitance by changing density of states at the electrode surface.

On carbon materials with complex microstructure, the capacitive effect of the N-doping is still not well understood in the literature. One of the reasons for this is that in many of these materials, the surface area and porosity could not be controlled. Since surface area and porosity play a major role in DL capacitance, the pure effect of surface chemistry and microstructure could not be extracted.

1.6 Ordered Mesoporous Carbon for Supercapacitors

OMC carbons are a popular choice for electrodes in supercapacitors due to their high surface area and tunable porosity. Lee et al. reported first the capacitance of OMC made from MCM-48 template from phenol resin [146]. The capacitance of CMK-3 made from sucrose precursor using SBA-15 as the template was shown by Zhou et al. [147]. However, carbon casted within the MCM-48 template does not have same symmetry as that of the template and controlling porosity is much more difficult with MCM-48 than SBA-15 [68]. Jurewicz et al. compared capacitive behavior of OMC made from propylene and sucrose made in MCM-48 or SBA-15 and found that the capacitance depended upon the carbon precursor used and the porosity (micropores/mesopores) developed from the templating procedure [148]. They also
suggested that the mesoporous structure helped in the diffusion of ions. In a similar study by Vix-Guterl et al., the advantage of a well-connected mesoporous system was underscored [149]. They found that the largest contribution to the electrochemical capacitance was from non-solvated ions charging within the ultramicropores (pores less < 0.7 nm). Due to a well-connected pore system, solvated ions can access these micropores compared to activated carbons where the path is tortuous. Other studies have highlighted the benefit of a mesoporous/microporous system from plots showing the dependence of capacitance as a function of frequency [150, 151]. They show that by modulating the mesopore size, OMC can maintain capacitance at high frequency better than that of activated carbons. By doping with N, the capacitance of the OMC could be further enhanced. This has been reported by various groups [135, 136, 152, 153].
CHAPTER 2

EFFECTS OF N-DOPING ON THE PHYSICAL PROPERTIES OF CARBON

The electronegativity of the nitrogen atom (3.04 PU) is larger than that of carbon atom (2.55 PU) which means that it can draw electrons from carbon atom creating a dipole moment [154]. Moreover, nitrogen has 5 valence electrons compared to 4 of carbon which can lead to doping effect similar to phosphorous doping in Si producing n-type Si. Hence, due to such electronic effects, N-doping can be expected to change physicochemical properties of carbon. What are these physicochemical changes? and what are its effects? are discussed in the following sections.

2.1 Effect of N-Doping on the Microstructure of Carbon

In an aromatic compound, the bond length of C-N bond is 134 pm (in pyridine) or 137 pm (in pyrrole) while that of C-C bond is 140 pm (in Benzene) [155]. As the C-N bond is only slightly smaller than C-C bond, incorporation of nitrogen into a graphene matrix should be feasible. Therefore, at low atomic concentration of nitrogen, graphene should maintain its 2D planarity. However, at high concentration of N, the small difference in bond lengths could accumulate to give significant distortion in 2D planar structure.

Helgren et al. saw a transition from a graphite-like structure to a fullerene structure when nitrogen concentration was varied from 5 to 15 at% in carbon nitride films [156]. The transition to the fullerene type structure was attributed to formation of pentagonal like defects facilitated by high nitrogen content. The pentagonal defects cause the graphene plane to bend which could now
crosslink through \( \text{sp}^3 \) bonds. The curving of basal planes have been clearly observed in 2D carbon nanostructures such as graphene after N-doping [157, 158].

Hence, the microstructure of the carbon changes due to N-doping. N-doped carbon is expected to have greater basal plane distortions than that of non-doped carbon. It also implies that, if we want to locate nitrogen on a carbon, we should look at the distorted basal planes. These microstructural changes should be easily discernible in carbon nanostructures having only a few graphene layers such as graphene and CNT. But, on carbon nanostructures having several layers of graphene, these microstructural change might not significantly effect their nanostructure. However, such distortions might introduces faults and cracks in the graphitic structure where carbon atom with unsatisfied valence electron exists making the carbon more reactive.

One limitation of nitrogen heteroatom is their deletion at high temperature. At very high temperature, carbon becomes more graphitic i.e. the graphene planes become more planar and stacked uniformly with the distance between adjacent graphene layers approaching 3.354 Å. The N also becomes more reactive so that it has energy enough to combine to form \( \text{N}_2 \) and leave the carbon surface. Hence, nitrogen content and graphiticity are reciprocal properties with respect to the temperature. This has direct consequence during the preparation of N-doped carbon using N-containing carbon precursors; it would be impossible to obtain carbon with high graphiticity and nitrogen content at the same time by heating alone. Also, the types of N-groups would change during heating because more thermally reactive N-groups would leave while less thermally reactive N-groups would stay. As the N atoms become mobile at high temperature, one type of N-group can also transform into another more stable N-group. So the amount and type of N-groups would also change with temperature.
2.2 Effect of N-Doping on the Electronic Properties of Carbon

N-doping creates various nitrogen functional groups on carbon surface. Unfortunately, no one has reported a mechanism to independently control the N type and N content with high precision. This is not ideal because the surface properties of the carbon depends on the type of nitrogen functional groups. The most common nitrogen functional groups found in N-doped graphene are pyrrole, pyridine and quaternary or graphitic-N groups (Figure 2.1). In an ammonia molecule, the nitrogen atom has four sp\(^3\) hybridized orbitals. Three of the orbitals have one electron involved in \(\sigma\) bonds with the hydrogen atoms while remaining orbital has two electrons. The lone pair of electrons make ammonia molecule basic as these can be donated or shared with an electrophilic species such as H\(^+\) to form NH\(_4^+\). In pyrrole, the nitrogen atom has three sp\(^2\) orbitals, each containing one electron that forms \(\sigma\) bonds with neighboring carbon and hydrogen atoms. The remaining pair of electrons resides in \(\pi\)-orbitals of the aromatic system. Hence pyrrole does not have electron donating properties. In pyridine, two of the three sp\(^2\) orbitals occupy one electron each forming \(\sigma\) bonds with the adjacent carbon atoms. The third sp\(^2\) orbital has a lone pair of electrons which are localized and can be donated, similar to ammonia. Hence, pyridine is basic. The remaining electron is located in a \(\pi\)-orbital and contributes to the aromatic structure of pyridine. In graphitic-N, three sp\(^2\) orbitals have a single electron forming three \(\sigma\) bonds with the carbon atoms. One \(\pi\)-electron orbital is donated to the aromatic system. The remaining \(\pi\)-electron is located in an antibonding \(\pi\)-orbital and is delocalized. Therefore, from electronic configurations, we can say that pyrrole does not impart basic character to the carbon, and pyridine and graphitic-N groups are alkaline.
**Figure 2.1** Chemical structure of pyrrole, pyridine and graphitic-N. Vertical double-lobed structure denote $\pi$-orbitals in an aromatic system while dots represent the electrons. Carbon atoms and associated hydrogen atoms are not shown.
and play the biggest role in the surface properties of N-doped carbon. Indeed, it has been experimentally shown that N-doping increases the basic nature of the carbon which can be attributed to the pyridinic and/or graphitic-N [178, 182]. Graphitic-N is interesting because of its in-plane location. It is also uncertain whether graphitic-N donates an electron due to the delocalized π-electron or attracts an electron due to its electronegativity of N. Delocalization of the π-electron of graphitic-N is supported by the positive BE shift in XPS [13]. However, some DFT studies claim that graphitic-N is negatively charged due to higher electronegativity than that of carbon atoms [14, 99, 111].

### 2.2.1 Effect on catalysis

It is clear that N-doping creates sites with charge concentration as in the case of graphitic-N or basic sites with a lone pair of electron to give as in the case of pyridinic-N. These sites can act as adsorption sites. The electron donating or receiving nature of these adsorption sites has significant effect on metal deposition. For example, in a site specific adsorption, negatively charged metal ion complex (eg. [PtCl$_6$]$^{2-}$) would likely nucleate on a positive charge center and positively charged metal ion complex (eg. [Pt(NH$_3$)$_2$]$^{2+}$) would likely nucleate on a negative charge center or coordinate with available lone pair of electrons. And If the adsorption is strong enough to anchor the metal ion during deposition, high dispersion of metal could be expected. Compared to non-doped carbon, N-doped carbon should provide sites for strong interaction with the metal ion complex because of its N-groups which could result in uniform catalyst dispersion and this has been shown to be true for N-doped carbon in the literature [21]. It follows that the distribution of these N-groups is also an important factor for catalyst dispersion. Evenly distributed N-groups should yield an uniform catalyst dispersion. However,
no method exists in literature to effectively control the distribution of nitrogen on carbon surface. Also the nitrogen surface concentration should be dictated by the catalyst loading requirement; i.e. for a catalyst with high loading; low concentration of nitrogen would not give desirable result as it would yield large catalyst particles with low mass activity (activity per metal loading).

However, the intrinsic enhancement of metal depends on the nature of metal-support interaction. It is difficult to predict the nature of the interaction between metal and the N-doped carbon surface and therefore, the shift in the intrinsic catalyst activity beforehand without doing advanced calculations such as Density Functional Theory (DFT), which is outside the scope of this work.

Incorporation of nitrogen into carbon should also impact the wettability of carbon. Nitrogen forms hydrogen bonds with water molecules and introduces polarity into the carbon. Therefore, N-doped carbon is expected to be easily dispersed in polar solvents such as water. N-doped HOPG was shown to be more hydrophilic than its non-doped counterpart by Zhou et al. [120]. Since it is necessary to make carbon ink before applying it as an electrode in electrochemical devices, an increase in wettability would greatly enhance the dispersion of the carbon. Increase in wettability also helps catalyst deposition when using a hydrophilic solvent to disperse the catalyst ions. For example, a solution containing metal ions is mixed with carbon and then reduced in H₂ in impregnation methods. So, a hydrophilic carbon surface will help to wet the water-based catalyst solution and disperse the catalyst uniformly.

Also, N-doping enhances the activity of carbon itself [159]. This has been attributed mainly to the basic nature of N-doped carbon [159]. The basic nature of the N-doped carbon is due to pyridinic nitrogen and/or graphitic-N as discussed above. For example during ORR, the sites associated with these N-groups could make adsorption, reaction and dissociation of
molecules such as O$_2$ facile. Ni et al. has shown that the energy barrier for O$_2$ adsorption and dissociation decreases after doping graphene with nitrogen [160]. This could be the reason for superior ORR activity on the N-doped carbon compared to the non-doped carbon.

2.2.2 Effect on Capacitance

N-doping is expected to increase the DL capacitance of the carbon. This could be assigned to a pseudo-capacitive effect where charge is stored in a redox couple involving nitrogen functionalities as shown in Chapter 1 [139].

\[ \text{>C=NH + 2 } e^- + 2 H^+ \leftrightarrow \text{CHNH}_2 \]  
\[ \text{>C-NHOH+ 2 } e^- + 2 H^+ \leftrightarrow \text{CHNH}_2 + \text{H}_2\text{O} \]

N-doping could also increase capacitance due to non-faradaic effect. Since an extra electron is introduced into the graphene due to N-doping, the electron density increases, especially when the nitrogen functionality is graphitic, which truly dopes the carbon by delocalization of π-electron. The increase in electron density increases space-charge capacitance ($C_{SC}$) according to Equation 2.3 [145]. In effect, the surface that carries charges becomes thicker.

\[ C_{SC} = \left(2\varepsilon \varepsilon_0 e^2n_i / kT\right)^{1/2} \]  

Where $\varepsilon$ is dielectric constant, $\varepsilon_0$ is permittivity, $e$ is charge of an electron, $n_i$ is the number of electrons, $k$ is Boltzmann constant and $T$ is the temperature. The $C_{SC}$ is related to the total capacitance from the following Equation 2.4 [1];

\[ 1/C = 1/C_{SC} + 1/C_H + 1/C_{diff} \]  

Where $C_H$ is the Helmholtz capacitance and $C_{diff}$ is the capacitance in the diffuse double-layer.
Some works have shown that N-doped graphene has high specific capacitance [141,143]. The increase in specific capacitance was assigned to an increase in binding energy with the ions or quantum capacitance (similar to space-charge capacitance) due to N-doping. Although in bulk graphite such phenomena has not been shown till now in the literature, a similar effect should hold on bulk graphite as it is a surface phenomenon.

2.3 Effect of N-doping on Stability

Carbon corrosion is one of the major issues in carbon-based electrochemical devices. It takes place through the formation of surface oxides which eventually come out as CO$_2$ and CO [161]. Hence, carbon stability can be increased just by removing these oxygen containing surface groups. Heat treatment (>600 °C) is often carried out during N-doping. By doing so, oxygen content decreases which increases resistance towards corrosion. Also, there are other beneficial effects of heating such as replacement of thermally unstable acidic oxygen containing species such as carboxyl and hydroxyl groups with more thermally stable basic pyrone-like structures [1] and increase in surface homogeneity of graphene plane which also increases stability as corrosion starts at defects.

In Table 2.1, the combustion enthalpy of oxygen and nitrogen containing model aromatic compounds with one benzene ring are listed. A suitable model compound representing graphitic-N could not be found, but DFT studies have shown that the C-N bond in graphitic-N is just 0.002 nm less than C-C bond [162] meaning that their bond strengths are almost equal. Also, graphitic-N might not affect the carbon corrosion as they are not located at defect sites. The table shows that benzoic acid, benzaldehyde and phenol compounds are thermodynamically less stable towards oxidation than pyrrole and pyridines. This indicates that the N-doped carbon is
thermodynamically more stable than the non-doped carbon. However, since solid carbon is more complex than aromatic compound, advanced theoretical work is needed to truly predict the thermodynamic stability of N-doped carbon.

The increase in corrosion resistivity in N-doped carbon is also attributed to the basic nature of N-doped carbon. The basic N-doped carbon is reductive in nature due to delocalized $\pi$ electrons of graphitic-N. It is proposed that N-doped carbon reduces adsorbed $O_2$ molecules to superoxide radical ($O_2^-$) which can react with water to form $H_2O_2$ instead of surface oxides [18]. $H_2O_2$ decomposes 10 to 100 times faster on the N-doped carbon than on the non-doped carbon [159]. Thus, reduction of $O_2$ in the presence of water is more kinetically favorable than formation of surface oxides, which are intermediates during carbon corrosion. Hence, the N-doped carbon show higher resistance towards corrosion.
Table 2.1 Combustion enthalpy of some oxygen and nitrogen-containing molecules.

<table>
<thead>
<tr>
<th>Species</th>
<th>Enthalpy of combustion (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen containing species</td>
<td></td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>-3272.0 (liquid), -3228.0 (solid)</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>-3526.0 (liquid)</td>
</tr>
<tr>
<td>Phenol</td>
<td>-3058.0 (solid)</td>
</tr>
<tr>
<td>Nitrogen containing species</td>
<td></td>
</tr>
<tr>
<td>Pyrrole</td>
<td>-2350.5 (liquid)</td>
</tr>
<tr>
<td>Pyridine</td>
<td>-2761.0 (liquid)</td>
</tr>
</tbody>
</table>
CHAPTER 3

EXPERIMENTAL

In this study, N-doped mesoporous carbon (NMC) was synthesized on modified or pristine SBA-15. Modification of SBA-15 was carried out to optimize the pore structure of NMC for its use as a Pt support. The NMC were heat treated to various temperatures to change the N-content and graphiticity. To study, the performance of NMC as a Pt support, Pt deposition was carried out using modified polyol process. The Pt deposited NMC and naked NMC were characterized using various techniques such as \( \text{N}_2 \) adsorption isotherm analysis, transmission electron microscopy (TEM), Raman spectroscopy, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA) The electrochemical properties were investigated by casting a thin-film of the Pt/NMC or NMC over a glassy carbon disk electrode. Details of each synthesis and experimental procedure are detailed below. Materials used throughout this work are listed in Table 3.1 on page 47 and equipments used throughout this work are listed in Table 3.2.

3.1 Synthesis of SBA-15

SBA-15, was synthesized from Pluronic® P 123 (BASF) triblock copolymer and tetraethyl orthosilicate (TEOS) according to the method outlined by Zhao et al [163]. The Pluronic® P 123 was dissolved in a solution of 180 mL of 2 M HCl and 45 mL of deionized (DI) water (18 M\( \Omega \)). 13.6 mL of TEOS was added to the mixture and the reaction was carried out for 20 h at 45 °C and then for 24 h at 100 °C. TEOS, after being hydrolyzed by HCl, interacts with
PEO head groups to form the walls of globular micelles while PPO head groups form the core [164]. These globular micelles associate to form flocs that precipitate with 2-D hexagonal packing driven by repulsive forces due to adverse entropic interaction between overlapping EO chains and the attractive forces due to hydrophobic attraction between condensing silica and EO chains. The SBA-15 template was recovered after washing and filtering with copious amount of ethanol and DI water. It was then dried under vacuum and calcinated at 500 °C for 3 h.

3.2 Modification of SBA-15

The pore size of the SBA-15 template was manipulated by additive silicate treatment (Figure 3.1). To accomplish this, 3.5 g of the SBA-15 was introduced into a fresh solution of 180 mL of 2 M HCl and 45 mL of DI water. Different amounts of TEOS (4 mL, 8 mL, and 12 mL) were added to the mixture at 45 °C and stirred for 48 h. The TEOS treated templates (SBA-15-0, SBA-15-4, SBA-15-8 and SBA-15-12 for the 0, 4, 8 and 12 mL additions, respectively) were filtered, washed and calcined at 500 °C for 3 h.

3.3 Synthesis of N-Doped Mesoporous Carbon

3 mL of pyrrole (Py) monomer (C₄H₅N, 99% Acros Organics) was incorporated into 1.0 g of SBA-15 by vacuum impregnation for 24 h. The vacuum helps to fill the SBA-15 pores with pyrrole monomer through capillary action [165]. The impregnated pyrrole was polymerized to polypyrrole (PPy) in 0.25 M FeCl₃ for 24 h. After polymerization, PPy containing SBA-15 was washed with DI water several times until the filtrate was clear, signaling complete removal of FeCl₃. Although Fe assists the graphitization process [166], it can also form catalytically active macrocyclic compounds at high temperature [167]. Therefore, Fe was removed before
Figure 3.1. Schematic of hydrolysis and condensation of tetraethyl orthosilicate (TEOS) on the walls of SBA-15.
carbonization to study the neat N-functionalized graphitic surface. The polypyrrole/SBA-15 was heated to 800 °C at 3 °C/s and pyrolyzed for 3 h under N₂ atmosphere. Finally, the silicate template was removed in hot (120 °C) 10 M KOH for 48 h followed by filtering and washing with acetone and DI water. The sample was dried and analyzed by X-ray photoelectron spectroscopy (XPS), which confirmed that all of the Fe was removed. A schematic for the preparation of N-functionalized mesoporous carbon (NOMC) is presented in Figure 3.2.

Carbon casted on unmodified SBA-15 will be referred to as CPPy-0. Carbon casted on modified SBA-15 are denoted as CPPy-0, CPPy-4, CPPy-8 and CPPy-12 for the 0, 4, 8 and 12 mL additions of TEOS to the templating procedure, respectively. In Chapter 5, CPPy-0 was reheated without the template at 800, 1000, 1200 or 1400 °C for 3 h to change N-content and graphiticity without changing the pore structure. The heating rate was 3 °C/min from RT to 800 °C and 1.5 °C/min from 800 °C to the target temperature. The NOMCs are denoted as CPPy-0-X, where X represents the final heating temperature. In Chapter 6, polypyrrole/SBA-15-8 were again carburized in N₂ atmosphere at 800 °C, 1000 °C, and 1200 °C to make CPPy-8-800, CPPy-8-1000, and CPPy-8-1200 respectively to change N-content and graphiticity. To prepare CPPy-8-1400, the template-free CPPy-8-800 was heated to 1400 °C to avoid the formation of silicon carbide. In this work, Vulcan Carbon (VC) XC-72R (Cabot Corp.) was used as a reference material.

3.4 Pt deposition

Pt was deposited using a modified polyol process [168, 169] for experiments in Chapter 6 and 7. 120 mg of NaOH was added to 25 mL of ethylene glycol (EG) and stirred until it dissolved completely. Next, CPPy-800 was introduced into the solution and ultrasonicated for
**Figure 3.2** A schematic for the synthesis of nitrogen-functionalized ordered mesoporous carbon.
30 min. Then the platinum precursor, hexachloroplatinic acid (H₂Cl₆Pt·6H₂O, Sigma-Aldrich), was added to the mixture and refluxed at 160 °C for 3 h in N₂ atmosphere. After cooling for 1 h, the N₂ atmosphere was changed to air and the pH was adjusted to 1.5 using 0.5 M H₂SO₄. The concentrations of glycolate and hydroxyl anions are dependent upon pH, which in turn determines the particle size and loading of Pt particles [170]. After 48 h, the platinum deposited NMC was filtered and washed with acetone and deionized water. Similarly, Pt was deposited on VC for comparative study.

The target Pt loading was 50 wt% in this study. When the Pt loading is low, better dispersion and size distributions can be obtained on even low surface area carbon support. Hence, only at high Pt loading, ability of carbon support to have uniform Pt dispersion and size distribution can be truly measured. In addition, major advantage of high Pt loading is that the thickness of catalyst layer on PEMFCs is less than that of low Pt loading to obtain same performance. Thin catalyst layer is helpful in overcoming mass-transfer problems. Hence, for practical applications, catalyst with high wt% Pt is desired.

3.5 Physical characterization

N₂ adsorption isotherms of CPPY-X were obtained at 77 K. The samples were degassed at 300 °C for 3 h in inert atmosphere before the isotherms were collected. The Brunauer-Emmett-Teller (BET) specific surface area (S_{BET}) was calculated using the N₂ adsorption isotherm between relative pressures (P/P₀) of 0.04 and 0.2 [171]. The total pore volume (V_{tot}) was measured by converting the amount of gaseous nitrogen adsorbed at relative pressure 0.99 (V_{0.99}) to the volume of liquid nitrogen adsorbate (V_{tot} = 0.0015468 \times V_{0.99}). The Kruk-Jaroniec-Sayari correction (KJS), built into the ASAP 2020 V3.04 operating software, was employed to
determine the pore size distribution (PSD). The $\alpha_s$ plot was calibrated against a macroporous silica reference [172] (LiChrospher Si-1000, $S_{\text{BET}} = 25.1 \, \text{m}^2/\text{g}$, $V_{0.4} = 9.1248 \, \text{cm}^3 \text{STP/g}$) for SBA-15 and non-graphitized carbon [173] (Cabot BP 280 $S_{\text{BET}} = 40.2 \, \text{m}^2/\text{g}$, $V_{0.4} = 14.70 \, \text{cm}^3 \text{STP/g}$) for the carbon supports.

Transmission electron microscopy (TEM) was conducted in a JEOL 2010 FasTEM with a 200 kV thermionic ion source. Sample preparation was carried out by dispersing samples in acetone/ethanol by ultrasonication, followed by deposition and drying on Holey carbon/copper grids.

Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) was performed with an iS10 spectrometer (Thermo Scientific). PPy, CPPy-0 or VC XC-72R was mixed with KCl at a ratio of 1/300 (by wt) and grinded thoroughly with a mortar and pestle. The samples were scanned 50 times from 650 cm$^{-1}$ to 4000 cm$^{-1}$ at a resolution of 4 cm$^{-1}$.

X-ray photoelectron spectroscopy (XPS) was used to investigate the surface composition of the support materials. XPS was performed using a PHI Multiprobe System with twin anode X-ray photoelectron spectrometer using unmonochromatised Al $K\alpha$ radiation (1486.6 eV) operating at 250 W and 15 kV. The pressure in the analysis chamber was always $\sim 10^{-8}$ torr or less. Full survey were taken at 100 eV pass energy with a scan rate of 1 eV/s and high resolution scans were conducted at 25 eV pass energy with a scan rate of 0.1 eV/s. The spectra were calibrated with respect to the graphitic carbon 1s electron band at 284.6 eV [174]. The background signals were determined using Shirley-type background correction and the curves were fitted with Gaussian/Lorentzian product functions.

Raman spectra were taken with a Renishaw 2000 Spectrometer Ramanscope operated by the Wire 2.0 Service pack 5 software. The peak at 521 cm$^{-1}$ from Si was taken as the standard
reference. All data were taken using a 514 nm laser. Peak fitting was performed using GRAMS/AI (7.01) software using mixed Gaussian and Lorenztian functions.

X-ray diffraction (XRD) was performed on a conventional θ-2θ diffractometer with a Cu anode and Ni filter. The instrument was a Bruker D8 Advance Diffractometer System. The Kα₂:Kα₁ intensity ratio was 0.5. The XRD spectra were collected from 5° to 90° in steps of 0.02° with 3s per step. Samples were compressed and leveled in a 0.5 mm deep sample holder. The collected spectra were stripped of Kα₂ using the Rachinger method built into DIFFRAC\textsuperscript{plus} EVA software. Average size of the Pt crystallites and height of the carbon crystallite were calculated from the Scherrer equation [175].

\[ t = \frac{0.9\lambda}{w \cos \theta} \]

3.1

The weight (wt) % of Pt NPs on carbon was found by thermogravimetry with a TA Instruments model TGA Q-500 instrument. All samples put on the Pt pan for analysis were ca. 7.5 mg. Temperature was increased at 2 °C/min from room temperature to 900 °C in dry air (20% O₂, Airgas) flowing at a rate of 60 mL/min. From 0 to 160 °C, the weight loss was assumed to be due to loss of adsorbed water. From 160 to 600 °C, the weight loss was attributed to the gasification of carbon. There was less than 3 % increase in weight from 600 to 900 °C due to Pt oxide formation. Using this method the calculated wt % of Pt/VC (BASF) matched to that of BASF’s measurement within 0.1 wt %.

3.6 Electrochemical characterization

All ex-situ electrochemical measurements were performed with an Autolab PGSTAT302N Potentiostat in a custom-built (Adams & Chittenden), thermostated three-compartment electrochemical cell with a Luggin capillary (Figure 3.3). The counter electrode
(CE) was a Pt flag and the reference electrode (RE) was a K$_2$SO$_4$ saturated Hg/Hg$_2$SO$_4$ electrode. The working electrode was a thin cast of sample on a glassy carbon disk electrode (Pine Instruments) mirror finished with a 0.05 µm alumina suspension (Buehler). Before each experiment, the reference electrode was calibrated against a hydrogen reference electrode (eDAQ Inc, Hydroflex). All data is reported with respect to the reversible hydrogen electrode (RHE). For capacitance experiments the electrolyte was N$_2$ saturated 0.5 M H$_2$SO$_4$ at 25 °C while for oxygen reduction reaction, the electrolyte was N$_2$ or O$_2$ saturated 0.1 M HClO$_4$ at 25 °C.

3.6.1 Capacitance

In Chapter 4, CPPy-0 or VC XC-72R was ultrasonicated for 0.5 h with DI water to make 0.3 mg/mL dispersions. 20 µL of the suspension was applied to an inverted 5 mm GCE. The water was evaporated from the suspension by rotating the electrode at 600 RPM in air. The dry samples were fixed onto the GCE by dropping 20 µL of diluted DE-520 Nafion® solution (1/100, 5 wt %, DuPont).

In Chapter 5, above procedure was slightly modified. Approximately 10.0 mg of the CPPy-0-Xs was dispersed in a mixture of 21 mL deionized (DI) water (18 MΩ, Millipore), 4 mL isopropanol and 100 µL of 5-6 % Nafion® DE-520 dispersion (DuPont) by ultrasonicating for 1 h. After ultrasonication, 30 µL of the carbon ink was pipetted onto the GCE. The carbon ink was dried in air by rotating at 500 RPM for 1 h. The carbon loading was ca. 47 µg/cm$^2$. Finally, the electrode was stabilized by scanning the electrode potential between 0.05 to 1.4 V at 200 mV/s for 40 cycles.
Figure 3.3 Schematic of custom-built three-compartment electrochemical cell.
3.6.2 Oxygen reduction reaction

To prepare the working electrodes for Chapters 6 and 7, approximately 18.5 mg of the Pt/NMC or Pt/VC was dispersed in 25 mL of 24% (by volume) isopropanol solution with 100 µL of Nafion® DE-520 dispersion (DuPont) [176]. The mixture was ultrasonicated for 1 h. Immediately after sonication, a 12.6 µL aliquot was pipetted onto a rotating ring disk electrode (RRDE) with a glassy carbon disk (Area = 0.2472 cm²), which was polished to a mirror finish with a 0.05 µm alumina suspension (Buehler). The catalyst ink was dried by rotating the ink covered electrode at 700 RPM in air [177] and the resulting electrode was transferred, covered by a drop of water, to deaerated 0.1 M HClO₄. The thin film was subjected to potential cleaning by scanning between 0.05 and 1.4 V at 200 mV/s for 40 cycles. To investigate the oxygen reduction reaction (ORR), the electrolyte was saturated with UHP oxygen (Airgas) for at least 1 h and polarization curves were taken at different rotation rates at a scan rate of 5 mV/s between 0.05 and 1.06 V at 25 °C.

The polarization curves were corrected for electrolyte resistance and DL capacitance. To correct for the double layer, CVs were taken in N₂ saturated 0.1 M HClO₄ with a scan rate of 5 mV/s and subtracted from the polarization curves. The illustration of polarization curves before and after background or DL current is corrected is shown in Figure 3.4a. The shift in current at the open circuit potential region is conspicuous as shown in the enlarged figure of the region, however, the starting of the ORR is the same and also, the shift in current at the potential less than 1 V is negligible.

Electrolyte or ohmic resistance was obtained from the X-intercept of the Nyquist plot after it was fitted with a linear regression. These polarization curves were corrected for ohmic resistance by using following equation;
Figure 3.4a Polarization curves before and after background subtraction. Background currents were obtained at the same scan rate as that of polarization curves in N₂ saturated electrolyte. The most significant effect of background correction is highlighted in the enlarged section.
Figure 3.4b Polarization curves before and after ohmic correction. The electrolyte resistance was measured from the X-intercept of the nyquist plot taken at 0.3 V.
Where $V$ is the voltage, $I$ is the current and $R$ is the ohmic resistance. The example of polarization curve corrected for ohmic resistance is shown in Figure 3.4b. At regions where current is constant ($V < 0.4 \text{ V}$) or very small ($V < 0.9 \text{ V}$), the ohmic resistance has negligible effect. It should be kept in mind that while DL correction is of current, Ohmic correction is of voltage.

### 3.6.3 Accelerated degradation test (ADT)

The resistance of CPPy-0 against corrosion was investigated in nitrogen saturated 0.5 M $\text{H}_2\text{SO}_4$. Accelerated degradation test (ADT) was conducted by applying potential square waves for 500 cycles. In each cycle, the WE was potentiostated at 1.4 V for 140 s and at 0.1 V for 30 s consecutively[178]. Twenty cyclic voltammograms (CV) were recorded after every 100 cycles from 0 V to 0.8 V vs. NHE at 50 mV/s scan rate.

### 3.7 Fuel Cell Test

#### 3.7.1 Membrane electrode assembly (MEA)

Nafion® 117 membrane was treated in 5% $\text{H}_2\text{O}_2$ and 0.5 M $\text{H}_2\text{SO}_4$ subsequently for 24 h each and dried under a heavy load so as to avoid deformation. PTFE-treated Toray gas diffusion layer (GDL) of 5 cm$^2$ area was painted with a catalyst ink prepared by ultrasonicating 30 mg of the Pt/carbon, 270 µL of 5% Nafion, 150 µL IPA, and 1.2 mL DI, for 2 h and stirring overnight. The painted GDL was dried for 10 min at 80 °C between subsequent coatings and for 30 min after target loading of 0.4 mgPt/cm$^2$ was achieved. At anode, 50 wt% Pt/Vulcan XC-72R (BASF)
was used as the electrocatalyst. The catalyst coated GDLs (CCG) were hot pressed to a pressure of 0.75 metric ton for 5 min at 136 °C with Nafion® 117 membrane in-between. So prepared membrane electrode assembly (MEA) was sandwiched between Teflon gaskets such that the pinch was 1 mil and assembled in a single fuel cell stack with a graphitic bipolar plate with a serpentine flow channel by applying 35 in-lb of torque in three successive steps.

### 3.7.2 Fuel cell performance

The single stack PEM fuel cell was tested with a 850e Multi-Range Fuel Cell Test Station (Scribner Associates Inc.). At anode, hydrogen was flown at constant stoichiometric flow rate of 30 s. At cathode, ultra high purity oxygen (Airgas) was flown at load based fuel rate of 20 s with minimum stoichiometric flow rate of 20 at \( \leq 0.2 \text{ A/cm}^2 \). The cell was conditioned for 24 h at 20 mA/cm\(^2\), 100 mA/cm\(^2\), and 200 mA/cm\(^2\), 8 h at each current density at 35 °C and 100% humidity at both the cathode and the anode. After conditioning, the N\(_2\) was flown at the cathode, the voltage was left to reach equilibrium, and ECSA was determined at a scan rate of 50 mV/s. The anode with H\(_2\) flowing served as both reference and counter electrodes for this measurement. The fuel cell performance test was done at ambient pressure, 80 °C cell temperature, 100% anode humidity, and 82% cathode humidity. At each current density, the cell was stabilized for 3 min and 6 data points (cell potential) were taken during that time which were averaged and plotted against the current density to obtain the polarization curves.
Table 3.1 List of materials used in this work

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Table 3.2 List of equipments used in this work

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CHAPTER 4

PROPERTIES OF N-DOPED ORDERED MESOPOROUS CARBON PREPARED USING POLYPYRROLE PRECURSOR

4.1 Objective

In this study, the synergistic effect of the physical and the chemical modification of carbon is used advantageously for electrochemical applications [130, 179]. N-functionalized ordered mesoporous carbon is synthesized using SBA-15 as the template and polypyrrole (PPy) as the N-containing carbon precursor. Capacitance, oxygen reduction activity, and electrochemical stability of such physically and chemically modified carbon are reported.

4.2 Results and Discussion

4.2.1 Pore structure of SBA-15

2D TEM micrographs of SBA-15 show cylindrical tubes arranged in a highly ordered honeycomb structure (Figure 4.1). The average pore diameter estimated from the micrographs is 6.0 nm and the wall diameter 3.0 nm, indicating a mesoporous structure.

The N$_2$ adsorption isotherm of the SBA-15 shows a Type IV isotherm, which is consistent with the results obtained in the literature for mesoporous SBA-15 (Figure 4.2a) [180]. The isotherm has a capillary condensation hysteresis loop extending from 0.4 to 0.8 P/P$_o$. The extended loop indicates mesopores with varying sizes because the capillary condensation pressure depends on the pore size [181]. From the PSD plot, the mesopores show a narrow
distribution from ca. 4 nm to 10 nm (Figure 4.2b). The maximum of the PSD is located at 7.2 nm, which agrees with the average pore diameter obtained from TEM. The unresolved half peak (< 4 nm) observed at the beginning of the PSD plot is due to the interconnecting pores which have shifted towards the mesoporous region [68]. The structural robustness of the carbon formed by templating SBA-15 depends on the presence of these interconnecting pores. Hence, the mesoporous interconnecting pores are beneficial as they increase order in the carbon replica.

4.2.2 Pore structure of CPPy-0

Like SBA-15, the N\textsubscript{2} adsorption isotherm of CPPy-0 shows a type IV isotherm (Figure 4.2a). However, the capillary condensation step is not as steep as SBA-15 and lengthens further towards higher relative pressure. The pores at lower relative pressures can be assigned to the mesopores formed from the replica of the template and the pores at the higher relative pressures can be assigned to the mesopores formed due to partial pore filling [182, 183]. These two distinct pore formations are also evident from the PSD plot where two peaks are observed - a sharp peak centered at 3.3 nm representing the pores formed by replicating the pores of SBA-15 and a flat and broad arm extending up to 50 nm representing the pores formed by incomplete pore filling (Figure 4.2b). The pore characteristics of SBA-15, CPP-0 and Vulcan XC-72R (VC) are listed in Table 4.1.

From Figure 4.3, CPPy-0 appears to be a good negative replica of the template. Long carbon nano-rods are observed, which are arranged in a regular pattern and form a single ordered structure. The average diameter of the carbon rods is 4.7 nm based on the TEM image, less than the pore diameter of SBA-15. This is expected due to sintering of the carbon during pyrolysis.
Figure 4.1 TEM images of SBA-15: (a) cross-section and (b) longitudinal section view of SBA-15.
Figure 4.2a $\text{N}_2$ adsorption isotherms of SBA-15 and CPPy-0
Figure 4.2b PSD of SBA-15 and CPPy-0.
Figure 4.3 TEM images of CPPy-0: (a) a particle of CPPy-0 and (b) longitudinal section of CPPy-0.
Table 4.1 Pore characteristics obtained from N$_2$ adsorption isotherm.

<table>
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<tr>
<th>Sample</th>
<th>Pore diameter (nm)</th>
<th>$S_{\text{ext}}$ (m$^2$/g)</th>
<th>$S_{\text{BET}}$ (m$^2$/g)</th>
<th>$V_{\text{tot}}$ (cm$^3$/g)</th>
<th>$V_{\text{me}}$ (cm$^3$/g)</th>
<th>$V_{\text{mi}}$ (cm$^3$/g)</th>
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<td>SBA-15</td>
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<td>387</td>
<td>700</td>
<td>0.66</td>
<td>0.59</td>
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<tr>
<td>CPPy-0</td>
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<td>324</td>
<td>544</td>
<td>0.52</td>
<td>0.40</td>
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<tr>
<td>VC</td>
<td>-</td>
<td>78.7</td>
<td>163</td>
<td>0.31</td>
<td>0.27</td>
<td>0.04</td>
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</table>
These carbon nano-rods are separated by an average distance of 3.3 nm, matching with the size of the mesopores due to complete pore filling obtained from N\textsubscript{2} adsorption isotherm.

### 4.2.3 Surface chemistry of CPPy-0

The ATR-FTIR spectra of PPy, CPPy-0, and VC are presented in Figure 4.4. The peak at 1560 cm\textsuperscript{-1} is assigned to C=C/C-C stretching and the peak at 1474 cm\textsuperscript{-1} is assigned to C-N stretching [184, 185]. The ratio of intensities of these peaks represents the effective mean π conjugation length. The other characteristic peak of polypyrrole is located at 1189 cm\textsuperscript{-1} which is due to breathing vibration of the pyrrole ring. Presence of these characteristic peaks shows that polypyrrole was successfully synthesized. After pyrolyzation, these peaks disappear, suggesting the deformation of the polypyrrole chain and the spectrum of polypyrrole after pyrolyzation is similar to that of VC. No significant peaks are observed in carbonized polypyrrole and VC for the absorption band as these functional groups would have been shadowed by the high absorbance of carbon in the mid-infrared region (400-4000 cm\textsuperscript{-1}) [186]. Hence, the ATR-FTIR method is limited in its ability to provide meaningful insights about the composition of the carbon materials. For detailed analysis on the presence of functional groups and composition, XPS was employed.

From XPS, it was observed that an unusually high N-content was retained in CPPy-0; the C/N (atomic %) ratio is 8.3. N-functionalized carbon through other processes such as ammonia treatment at 800 °C have yielded average C/N ratio of 25.4 [187, 188]. This could be attributed to the fact that the precursor material had high initial N-content as well as the fact that the SBA-15 pores act as nanoreactors, providing confined space for reactions that helps to keep the C/N ratio low by allowing the N-containing volatiles to react again with the
Figure 4.4 The ATR-FTIR spectra of PPy, CPPy-0, and VC.
carbon. Hence, the carbonization of polymers containing the desired functionalities may be a good method to introduce surface functionality into graphene layers.

In the literature, four binding energies (BE) for different N-groups are reported as: pyridinic (N-6) at 398.3-398.8 eV, pyrrolic (N-5) at 400.0-400.7 eV and quaternary (N-Q) at 401.0-401.6 eVs [13, 189-191]. The peak at the higher B.E. 402.0-405.0 eV has been assigned to a number of functional groups such as N-oxides, nitro or nitroso groups, and shake-up satellites; it is denoted as N-X [13, 190, 191]. The deconvolution of high resolution XPS spectra of the N 1s region shown in Figure 4.5a for CPPy-0 reveals three types of nitrogen functional groups: N-6 at 398.8 eV (36 at.%), N-Q at 400.8 eV (39 at.%), and N-X at 402.1 eV (25 at.%). The B.E. for N-Q is close to B.E. for N-5, though studies done on synthetic chars produced by heat treating acridine, carbazole, and polyacrylonitrile (PAN) in argon find that N-5 starts decomposing to N-6, N-Q, and N-X above 600°C [13]. At 800 °C, complete conversion of N-5 to N-6, N-Q, and N-X is expected [13]. Therefore, assigning the peak at 400.8 eV to N-Q is justified. The chemical structure of N-6 suggests that it is a surface edge group and contributes only one \( \pi \)-electron to the aromatic ring but has a lone pair of electrons to share. A high amount of N-6 (C/N-6 = 23) is favorable as it suggests the presence of many surface edges that contain the active sites for chemical reactions. Though the exact nature of N-Q is unknown, it is accepted as a nitrogen atom with a positive formal charge greater than that of N-6. The graphitic-N is stable at higher temperature and is an in-plane functional group [13]. Therefore, it provides better coordination with carbon atoms, stabilizing the nitrogen bonded carbon structure.
Figure 4.5 (a) XPS spectra of deconvoluted N 1s peak: (1) N-6, (2) N-Q, and (3) N-X and (b) XPS spectra of deconvoluted C 1s peak: (1) graphitic C, (2) defect, (3) C-OH, C-O-C, or C-N, (4) COOH or COOR, and (5) $\pi$-$\pi^*$ transition.
The polypyrrole backbones were converted to mostly graphitic carbon with sp$^2$ hybridization, which is represented by the peak at 284.6 eV (44 at.%) in Figure 4.5b. Graphitic carbon imparts electrical conductivity because of the mobile $\pi$-electrons on the graphene layers. The peak at 285.5 eV (27 at.%) is identified as the peak correlating with the defects or faults in the graphene layers [192]. The defect peak is assumed to have sp$^3$ or partial sp$^2$/sp$^3$ hybridization. Carbon in hydroxyl (C-OH), ether (C-O-C) or amine (C-N) groups appears at 286.5 eV (4.6 at.%). While the peak at 288.2 eV (8.3 at.%) is recognized as the carbon present in carboxyl (COOH) or ester (COOR) group, and the peak at 290.6 eV (16.31 at.%) is due to $\pi$-$\pi^*$ transition [174, 191, 192].

4.2.4 Electrochemical properties of CPPy-0

The CVs of CPPy-0 from 0 to 0.8V at different scan rates are given in Figure 4.6. Clearly, the charge/discharge current is dependent upon the scan rate. A CV curve of ideal electrochemical DL capacitance from pure electrostatic attraction between a charged surface and the ions is rectangular. A non-rectangular CV with reversible peaks, as in Figure 4.6, is caused by pseudocapacitance of the electrode material [6]. The peak observed at 0.6 V in the oxidation sweep is caused by the quinine/hydroquinone redox couple [193]. Hence the electrical double layer capacitance ($C_d$) was determined at potentials less than 0.6 V using Equation 4.1 [194].

\[ i = \nu \cdot C_d \]  

4.1
Figure 4.6 CVs of CPPy-0 at different scan rates in N₂ saturated 0.5 M H₂SO₄ at 25 °C.
Where \( i \) is the current and \( \nu \) is the scan rate. Reduction currents between 0 and 0.5 V were considered for calculation as the currents at this range are almost independent of voltage, similar to the ideal DL capacitance. When such currents are plotted against the scan rates (\( \geq 5 \text{ mV/s} \)), a linear fit was obtained, which is presented in Figure 4.7. It is known that at very low scan rates, capacitance can increase considerably due to the loss of the hydration shell enveloping ions so that microporous surface areas are available for DL capacitance [195]. At the high scan rates such as applied here, which represent the performance of an operating capacitor, the DL capacitance should be mainly due to the surface area of mesopores. In addition, the time constant of charge/discharge is very high for micropores [24, 136]; hence they will have very small contribution at such high scan rates. The specific capacitance of CPPy-0 was 182.5 F/g or 33.5 \( \mu \text{F/cm}^2 \). This is very high compared to the specific capacitance of VC, 11.6 F/g or 7.1 \( \mu \text{F/cm}^2 \). The literature standard for the capacitance of the carbon is 5-20 \( \mu \text{F/cm}^2 \) [124]. Hence, the capacitance of VC falls within the literature standard while that of CPPy-O exceeds the literature standard value for carbon materials.

Theoretically, pores larger than 0.5 nm are easily accessible to aqueous electrolytes [196]. Hence, in NOMC where mesopores contribute 77 % of the total pore volume and form a regular ordered structure, all of the mesopores contribute in charging/discharging. Due to these mesopores and a higher affinity of nitrogen modified carbon towards water, pore wetting should not be a problem [197]. However, it should also be noted that the capacitance in N-functionalized carbon is not a lone function of its pore characteristics. Studies on carbon with similar pore characteristics but different N-content found that capacitance increased for higher N-content [198, 199]. Although, this effect was credited to pseudocapacitance due to Faradaic redox reaction of edge nitrogen edge structures such as pyridine and pyridone [139],
Figure 4.7 The dependence of current on the scan rate taken in N\textsubscript{2} saturated 0.5 M H\textsubscript{2}SO\textsubscript{4} at 25 °C.
no clear experimental evidence exists. Also, peak representing N-induced pseudocapacitance could not be identified (Figure 4.6). Hence, the role of nitrogen in DL capacitance is still an open question.

The high capacitance could also be due to electron delocalization due to graphitic-N [111, 200], which produces a high surface charge, shrinking the electric double layer thickness, d, and increasing $C_d$ by:

$$C_d = \frac{\varepsilon A}{d}$$

4.2

Where A is the surface area accessible to the electrolyte, and $\varepsilon$ is the dielectric constant of the electrolyte. The electron delocalization could induce polarization and decrease ion transport resistance. Or, as mentioned in Chapter 2, space-charge capacitance could play a role. This theme is explored more in Chapter 5.

Polarization curves (Figure 4.8) for VC and CPPy-0 were obtained in oxygen saturated 0.5 M H$_2$SO$_4$ at 1600 RPM with a scan rate of 5 mV/s. The dry Nafion® film thickness was ca. 0.2 µm, calculated assuming a film density of 2.0 g/cm$^3$ on GCE [201]. The mass-transfer resistance and the effect on kinetics due to retention of O$_2$ can be ignored of the Nafion® film thickness is less than 0.2 µm. It is clear from Figure 4.8 that CPPy-0 exhibits higher activity for ORR than VC. The activation overpotential for the ORR on NOMC is 300 mV lower than that of VC. This agrees with the literature where Subramanian and coworkers observed increased ORR on N-doped carbon prepared by pyrolyzing N-containing resin and carbon black together [202]. As mentioned in Chapter 2, this could be due to basic nature of N-doped carbon where oxygen adsorbs strongly to form superoxide radical and then hydrogen peroxide. Gong et al. also suggested that oxygen molecule adsorb side-on on the carbon sites adjacent to nitrogen and the O-O bond is weakened, facilitating oxygen reduction [111].
Figure 4.8 ORR polarization curves recorded at 1600 RPM with a 5 mV/s scan rate in O$_2$ saturated 0.5 M H$_2$SO$_4$ at 25 °C
4.2.5 Stability of CPPy-0

Here a simple ADT designed by Shao et al. was applied to study the degradation of VC and CPPy-0 [178]. In this test, the system under study is subjected to a high potential step (1.4 V for 140 s) followed by a brief low potential step (0.1 V for 30 s) for many cycles (500 here). It is believed that the oxidation of carbon to oxygen containing surface species and rapid reduction of these species creates active surface sites for re-oxidation [178]. In addition, rapid reduction causes removal of protective HSO$_4$/$SO_4^-$ layer, exposing sites for oxidation [178]. A slightly different explanation based on two-site model has been put forward by Gallagher et al [203]. They suggest that there are two types of sites on the carbon surface: an active site that takes part in rate determining step and a passive site for surface oxide and eventually CO$_2$ formation such that during potential cycle surface oxides are reduced decreasing the passive sites and increasing active sites. A simple pathway for formation of surface oxides and CO$_2$ evolution is given below where C* represents surface active carbon [6, 204].

\[
\begin{align*}
R-C^* + H_2O &= R-C^*-OH + H^+ + e^- & 4.3 \\
R-C^*-OH &= R-C^*=O + H^+ + e^- & 4.4 \\
R-C^*=O + H_2O &= R-C^*OOH + H^+ + e^- & 4.5 \\
R-C^*OOH &= C^*O_2 + R-H & 4.6
\end{align*}
\]

The results of ADT are presented in Figures 4.9 and 4.10 where the time is corrected to overlap currents before and after ADT. Both the oxidation and reduction currents after ADT have increased for VC. The reasons behind the anomalous increase in current are not known, but repeated experiments gave similar results. Under the same test, there are no changes in oxidation and reduction currents for CPPy-0 although the oxidation and reduction currents before ADT
Figure 4.9 Chronoamperometric curves before and after ADT at potential 1.4 V vs NHE in N$_2$ saturated 0.5 M H$_2$SO$_4$. 

Figure 4.10 Chronoamperometric curves before and after ADT at potential 0.1 V vs NHE in N$_2$ saturated 0.5 M H$_2$SO$_4$. 


match with VC. Based on these results, it can be concluded that CPPy-0 is more resistant to corrosion than VC.

The stability of CPPy-0 compared to VC confirms to what we described in Chapter 2. Nitrogen coordinates with C atoms and given the fact that the C-N bond is stronger than the C-C bond, the carbon atoms surrounding nitrogen atoms are strongly held. Also, N-doped carbon circumvents the formation of surface oxides, crucial for corrosion, by reductively adsorbing oxygen. All of these mechanisms likely contribute to the enhanced stability of CPPy-0 compared to carbons without any surface nitrogen functionality.

4.3 Summary

NOMC was successfully synthesized from pyrrole using a SBA-15 template. CPPy-0 had two types of mesopores: one due to complete pore filling and another due to incomplete pore filling, which was evidenced by the PSD. Hence, pore filling must be improved to obtain a more homogeneous structure. The size of the mesopores due to complete pore filling was dependent on the walls of SBA-15 and the shrinkage of polymer during polymerization. However, a more thorough study is required to clarify the dependence.

Compared to VC, CPPy-0 had higher capacitance and enhanced ORR activity. Besides better pore characteristics, the nitrogen functional groups play important role in capacitance although their role is not clear. The presence of nitrogen functional groups also enhances the ORR due to delocalization of electrons, though the exact mechanism is not known. Hence further work is needed to understand the role of nitrogen in capacitance and ORR activity. NOMC was more resistant to corrosion than VC. This was ascribed to strong C-N bonds and reducing character of N-doped carbon.
Thus, by tuning the nitrogen functionality and its population, it may be possible to make a highly resistant yet active carbon material. The properties of NOMC investigated here are relevant for electrochemical devices such as batteries, supercapacitors, and fuel cells. Hence, NOMC represents a promising next generation material for electrochemical applications. These results clearly signal the need for more work to understand the increase in capacitance and ORR activity on N-doped carbon.
CHAPTER 5

EFFECT OF SURFACE CHEMISTRY ON DOUBLE LAYER CAPACITANCE OF N-DOPED ORDERED MESOPOROUS CARBON

5.1 Objective

The objective of this work is to isolate and elucidate the effect of nitrogen heteroatoms on the DL capacitance of carbon [205]. The N-content was varied between 0 and 8.2 atomic % by heating N-doped carbon to different temperatures. The change in graphiticity with the temperature was also characterized. To allow for precise control over surface area and pore structure, this study focused on ordered mesoporous carbon (OMC) synthesized from a SBA-15 template. Since the carbon surface area and pore structure largely depends on the template, the surface area and pore structure of the carbon was set by controlling the template structure.

5.2 Results and Discussions

5.2.1 Pore Characteristics

The pore structure of SBA-15 has been well characterized [180]. It has a honeycomb-like pore structure with 2D hexagonal \( p6mm \) symmetry. It also has secondary pores located in its walls. When carbon is cast in SBA-15, the carbon structure does not collapse; the carbon nanorods formed in the primary pores are held together by carbon spacers formed in the secondary pores. Therefore, the carbon is exact inverse replica of the template with the same \( p6mm \)
symmetry. However, depending on the carbon precursor, infiltration of the SBA-15 pores could be incomplete leading to a wide pore size distribution (PSD) [182, 183].

The PSDs for the SBA-15 template and the resulting carbons are shown in Figure 5.1. The SBA-15 template had a narrow single peak centered at 10 nm. The N-free templated carbon, CS-900, showed a single narrow peak centered at 3.9 nm. The CPPy-0-X samples also possessed a narrow peak centered at 3.9 nm; however, they also had a small shoulder peak indicating a bimodal or extended PSD. The difference in PSD between CS-900 and CPPy-0-X was likely due to differences in pore filling. The walls of the SBA-15 are populated with hydrophilic hydroxyl groups, which make the capillary action more facile for sucrose dissolved in water than that of hydrophobic Py in SBA-15. However, the PSD profiles of all of CPPy-0-X samples were alike, and the overall structure appeared to be the identical to CS-900.

The pore size, BET surface area ($S_{BET}$) and total pore volume ($V_{tot}$) for all of the carbon samples are summarized in Table 5.1. $S_{BET}$ and $V_{tot}$ of CPPy-0-1000 to CPPy-0-1200 were similar; ca. 593 m$^2$/g and ca. 0.78 cm$^3$/g. CPPy-0-800 had slightly higher $S_{BET}$ (622 m$^2$/g) and $V_{tot}$ (0.80 cm$^3$/g). The decrease of $S_{BET}$ and $V_{tot}$ were expected as some micropores collapse at higher temperatures [1]. However, the differences in $S_{BET}$ and $V_{tot}$ among CPPy-0-X were less than 5%. On the other hand, because of better pore filling, the $S_{BET}$ of CS-900 was significantly higher (913 m$^2$/g) although $V_{tot}$ was lower (0.68 cm$^3$/g).

5.2.2 Raman spectroscopy

Raman spectra of CP-X and CS-900, showing both G and D peaks, are presented in Figure 5.2. The G peak is signified as a graphitic peak and is a main first order band at
Figure 5.1 Pore size distribution curves of the SBA-15 template, CPPy-0-Xs and CS-900.
Table 5.1 Pore diameter, BET surface area ($S_{\text{BET}}$) and pore volume ($V_{\text{tot}}$) of the SBA-15 template, the nitrogen-doped carbons heated at different temperatures (CP-X), where X represents temperature and non-doped carbon (CS-900).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pore Diameter (nm)</th>
<th>BET surface area (m$^2$/g)</th>
<th>Pore volume (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15</td>
<td>10</td>
<td>815</td>
<td>1.15</td>
</tr>
<tr>
<td>CPPy-0-800</td>
<td>3.9</td>
<td>622</td>
<td>0.808</td>
</tr>
<tr>
<td>CPPy-0-1000</td>
<td>3.9</td>
<td>591</td>
<td>0.778</td>
</tr>
<tr>
<td>CPPy-0-1200</td>
<td>3.6</td>
<td>591</td>
<td>0.773</td>
</tr>
<tr>
<td>CPPy-0-1400</td>
<td>3.9</td>
<td>594</td>
<td>0.791</td>
</tr>
<tr>
<td>CS-900</td>
<td>3.9</td>
<td>913</td>
<td>0.678</td>
</tr>
</tbody>
</table>
1582 cm\(^{-1}\) on pure crystalline graphite [206, 207]. The D peak is signified as a disordered peak and is a main first order band at 1332 cm\(^{-1}\) on a pure crystalline diamond [206, 207]. Hence, the presence of G and D peaks suggest that the microstructure is compromised of both crystalline and amorphous carbon structures. From the peak height ratio of G and D peaks, the basal plane size of the carbon crystallites, \(L_a\), can be calculated [208]. A third peak, commonly referred to as the A peak, representative of an amorphous graphitic phase, was added to obtain a precise fit [209]. The positions of G, D and A peaks, and \(L_a\) are reported in Table 5.2.

As the carbonization temperature increased, the G and D peaks of the CPPy-0-Xs were better articulated. The separation between G and D peaks also increased with temperature, which can be caused by the removal of defects with increased graphiticity [210]. Another indicator of increasing graphiticity and decreasing defect density with temperature was \(L_a\), which increased with the heat treatment temperature. Hence, at higher temperature, the average size of basal plane of carbon crystallites increased. However, the separation between G and D peaks, and \(L_a\) of CS-900 was larger than that of the CPPy-0-Xs implying that it had fewer defects and wider basal planes than that of the CPPy-0-Xs. This could be attributed to different precursors for CPPy-0-X and CS-900. In addition, N-doped carbon has been shown to have more defects than its non-doped counterpart [18, 19].

### 5.2.3 XRD Analysis

XRD spectra of the CPPy-0-Xs and CS-900 are shown in Figure 5.3. Several peaks representing reflections such as (102), (004), (103), (110), (112), and (006) present in XRD spectra of graphitized carbon were expectedly missing [211]. This confirmed the partial amorphous nature of the carbons in this work observed by Raman. Like the Raman spectra, the
Figure 5.2 Raman spectra of the carbon samples showing D and G peaks.
Table 5.2 Peak positions of G, D and A peaks obtained after fitting Raman peaks of the nitrogen-doped carbons heated at different temperatures (CP-X) and non-doped carbon (CS-900). $D_{G-D}$ is the distance between the G and D peaks. $L_a$ is the average size of the basal planes of the carbon crystallites.

<table>
<thead>
<tr>
<th>Samples</th>
<th>G peak (cm$^{-1}$)</th>
<th>A peak (cm$^{-1}$)</th>
<th>D peak (cm$^{-1}$)</th>
<th>$L_a$ (nm)</th>
<th>$D_{G-D}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPPy-0-800</td>
<td>1604</td>
<td>1520</td>
<td>1373</td>
<td>3.5</td>
<td>231</td>
</tr>
<tr>
<td>CPPy-0-1000</td>
<td>1597</td>
<td>1510</td>
<td>1367</td>
<td>3.8</td>
<td>230</td>
</tr>
<tr>
<td>CPPy-0-1200</td>
<td>1597</td>
<td>1514</td>
<td>1358</td>
<td>4.2</td>
<td>239</td>
</tr>
<tr>
<td>CPPy-0-1400</td>
<td>1598</td>
<td>1524</td>
<td>1352</td>
<td>4.2</td>
<td>245</td>
</tr>
<tr>
<td>CS-900</td>
<td>1601</td>
<td>1528</td>
<td>1343</td>
<td>4.4</td>
<td>257</td>
</tr>
</tbody>
</table>
Figure 5.3 XRD spectra of the carbon samples.
Table 5.3 Peak position ($2\theta$) and full-width at half-maximum (FWHM) of the (002) reflection of the carbon samples obtained from the XRD spectra. Carbon d-spacing and the average stack height of the carbon crystallites ($L_c$) were calculated using $2\theta$ and FWHM of the (002) reflection.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$2\theta$ (002)</th>
<th>Carbon d-spacing (Å)</th>
<th>FWHM (002)</th>
<th>$L_c$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPPy-0-800</td>
<td>25.7</td>
<td>3.46</td>
<td>5.18</td>
<td>1.57</td>
</tr>
<tr>
<td>CPPy-0-1000</td>
<td>24.2</td>
<td>3.68</td>
<td>5.41</td>
<td>1.50</td>
</tr>
<tr>
<td>CPPy-0-1200</td>
<td>24.6</td>
<td>3.62</td>
<td>5.37</td>
<td>1.51</td>
</tr>
<tr>
<td>CPPy-0-1400</td>
<td>24.8</td>
<td>3.59</td>
<td>4.79</td>
<td>1.70</td>
</tr>
<tr>
<td>CS-900</td>
<td>19.2</td>
<td>4.62</td>
<td>4.78</td>
<td>1.69</td>
</tr>
</tbody>
</table>
XRD peaks of the CPPy-0-Xs became better defined at higher temperatures, which implied that the degree of crystallinity increased as the temperature increased. The (002) peak positions were used to calculate the d-spacing in the CPPy-0-Xs (distance between graphene planes in a carbon crystallite) from Bragg’s law, which are presented in Table 5.3. The average d-spacing of the CPPy-0-Xs was ca. 3.59 Å, which was larger than 3.35 Å of graphite [1] suggesting a turbostratic nature; i.e. a lack of alignment between graphitic planes. It also showed that the heating temperature was not enough to obtain a full graphitization. Contrary to the CPPy-0-Xs, CS-900 had a very wide peak of (002) reflection, though the (100) and (101) reflections were comparable. Kim et al. obtained similar XRD spectra for carbonized sucrose templated in SBA-15 [212]. This could suggest that the stacking between the graphitic planes in CS-900 was highly disordered. In the work of Kim et al., the crystallinity of carburized sucrose collapsed under pressure compared to that of the carburized acenaphthene and furfuryl alcohol [213]. Hence, the crystalline nature in CS-900 was not as developed as in the CPPy-0-Xs.

5.2.4 Surface Chemistry

As shown above, the porosity among the CPPy-0-Xs was quite similar; however, XPS showed significant changes in surface composition among the CPPy-0-Xs. The atomic (at) % of C, N and O were determined from C 1s, N 1s and O 1s peaks of full survey spectra and are summarized in Table 5.4. In CPPy-0-X, the N-content decreased from 8.2 at % (800 °C) to 0.5 at % (1400 °C) while the oxygen content decreased from 6.2 at % (800 °C) to 3.1 at % (1400 °C). In fact, at 1400 °C, the N-content was within the error limit of the XPS (< 1 %). The lessening in the number of heteroatoms was expected, since at high temperatures the carbon surface undergoes surface reconstruction to increase graphiticity. For example, there is an
increase in the sp² hybridized carbon atoms on the graphene plane by “smoothing” the surface and removing surface defects. The increase in the degree of graphitization at higher temperatures was supported by Raman and XRD analyses. In addition, because oxygen is more reactive than nitrogen, oxygen was more prevalent than N at high temperatures.

### 5.2.5 Effect of Potential

Cyclic voltammograms (CVs) with increasing threshold potentials at a scan rate of 10 mV/s were collected, which are shown in Figure 5.4a for CPPy-0-800 and Figure 5.4b for CS-900. The behavior depicted in Figure 5.4a was typical for all CPPy-0-Xs. As seen in Figure 5.4, as the upper potential limit was increased, the magnitude of the negative current increased while the magnitude of the positive current remained constant for both doped (CPPy-0-800) and non-doped (CS-900) carbons. This could be ascribed to the formation of surface oxides at higher potential during positive-going scan that were reduced during negative-going scan. Indeed, thermodynamically favored carbon oxidation begins at 0.2 V [1]. Another significant observation in CVs with upper potential thresholds above 0.5 V, a peak at ca. 0.6 V was apparent in CS-900, signifying the formation of surface oxides such as the well-known quinine/hydroquinone redox couple [6, 193], but were almost absent in PPy-0-800 despite comparable oxygen content in CPPy-0-800 (6.2 at %) compared to CS-900 (5.3 at %). This is likely due to N-groups in CPPy-0-800 that suppressed the formation of oxygen redox couples perhaps due to association of oxygen with N-groups to form oxides such as pyridine-N-oxides and NOₓ.

To visualize the dependence of the negative current on the upper potential limit of the CVs, the negative currents measured at 0.3 V are plotted with respect to upper potential limits for both doped and non-doped carbons are plotted in Figure 5.5. The data were fitted with second
Figure 5.4a Cyclic voltammograms of CPPy-0-800 with increasing upper potential limits at a scan rate of 10 mV/s in N$_2$ saturated 0.5 M H$_2$SO$_4$ at 25 °C.
Figure 5.4b Cyclic voltammograms of CS-900 with increasing upper potential limits at a scan rate of 10 mV/s in N₂ saturated 0.5 M H₂SO₄ at 25 °C.
**Figure 5.5** Negative currents of the cyclic voltammograms taken at 0.3 V plotted against their upper potential limit for the carbon samples. The data are fitted with a second degree polynomial.
degree polynomial functions and the curvatures were calculated from the second derivative of the polynomial functions. The fitting of a second degree polynomial was in agreement with the observation in the literature that DL capacitance of graphite has an approximately parabolic relationship with electrode potential [1]. 0.3 V was selected since it was located near the minima of the parabolic curves, and the CVs were always nearly symmetrical at 0.3V when the threshold potential was < 0.5 V, indicating that 0.3 V was close to the potential of zero charge (PZC).

A consistent correlation was found between the decreasing curvatures with increasing temperatures. Here, the curvatures simply represent the rate of increase of reduction current with an increase in potential. Since the reduction current was enhanced by the formation of surface oxides, it could be deduced that as the temperature increased, the ability of the carbon to form oxides decreased in the CPPy-0-Xs. This could be due to a reduction in the number of surface defects, which are the most likely active sites for oxide formation. CS-900 possessed curvature in-between that of CPPy-0-1200 and CPPy-0-1400. This was despite CS-900 having higher initial oxygen content and than that of CPPy-0-1200 and CPPy-0-1400 (Table 5.4). This implied that not only the temperature but the carbon precursor may dictate the rate of formation and types of surface oxides with potential.

5.2.6 Double Layer Capacitance

The DL capacitance is greatly influenced by surface area, pore size and pore connectivity [1]. However, these factors could be ruled out in this work. Since CPPy-0-X and CS-900 were mostly mesoporous, the delay in charge/discharge processes due to microporosity could be ignored [1]. Also, in the CPPy-0-X (Figure 5.6a to 5.6d) and CS-900 (Figure 5.6e) CVs, the transition from positive current to negative current and vice versa at potential ends were vertical.
Figure 5.6a Cyclic voltammograms of CPPy-0-800 taken at different scan rates in N\textsubscript{2} saturated 0.5 M H\textsubscript{2}SO\textsubscript{4} at 25 °C.
Figure 5.6b Cyclic voltammograms of CPPy-0-1000 taken at different scan rates in N$_2$ saturated 0.5 M H$_2$SO$_4$ at 25 °C.
Figure 5.6c Cyclic voltammograms of CPPy-0-1200 taken at different scan rates in N$_2$ saturated 0.5 M H$_2$SO$_4$ at 25 °C.
Figure 5.6d Cyclic voltammograms of CPPy-0-1400 taken at different scan rates in N₂ saturated 0.5 M H₂SO₄ at 25 °C.
Figure 5.6e Cyclic voltammograms of CS-900 taken at different scan rates in N$_2$ saturated 0.5 M H$_2$SO$_4$ at 25 °C.
indicating no lag in the charge/discharge rate [6]. As the pore sizes in all carbons were analogous, the pore size effect could also be neglected. Lastly, since all the pores in OMC are interconnected, the inaccessibility of primary mesopores could be ignored. Hence, the behavior of DL capacitance found in the CPPy-0-Xs and CS-900 could be studied on the basis of their surface physicochemical properties, namely basal plane/edge structures and surface chemistry.

The CVs of the CPPy-0-Xs showed a nearly rectangular shape; they were slightly skewed due to IR resistance. Although, the CVs of CS-900 (Figure 5.6e) were asymmetrical about the x axis, likely due to pseudocapacitive effect; no such effect was observed in CVs of the CPPy-0-Xs. The average magnitude of negative and positive currents at 0.3 V was plotted vs. the scan rate for CPPy-0-X and CS-90, which is shown in Figure 5.7. Since the data was approximately linear, the DL capacitances for the CPPy-0-Xs and CS-900 were obtained from the slopes of the linear plots using Equation 4.1 [1] and are tabulated in Table 5.4.

The area-specific capacitance ($C_A$) for CS-900 was 10.6 μF/cm$^2$, similar to that of carbon black and active carbon [1]. In contrast, the $C_A$ of CPPy-0-800 was 25.1 μF/cm$^2$. The mass-specific capacitance ($C_M$) of CPPy-0-800 (156.0 F/g) was also higher than that of CS-900 (97.0 F/g). This ca. 150 % increase in $C_A$ signaled a fundamental increase in DL capacitance due to the presence of surface nitrogen, irrespective of pore structure and pore size as these parameters were alike in both carbons. Among the CPPy-0-Xs, a gradual decrease in both $C_A$ and $C_M$ was obtained with an increase in temperature. The decrease in $C_A$ and $C_M$ with temperature was in good correlation with the decrease in N-content instead of oxygen content as 95.2 % loss of $C_A$ was in accordance with was in accordance with ca. 100 % decrease in N-content rather than 50 % decrease in oxygen content. This is visualized in Figure 5.8. The dependence of $C_A$ on N-content could be fit with a straight line that almost passes through the origin. But the dependence
Figure 5.7 The dependence of current on the scan rates taken in N\textsubscript{2} saturated 0.5 M H\textsubscript{2}SO\textsubscript{4} at 25 °C. The current was obtained by averaging magnitude of current at 0.3 V from the anodic and cathodic scans of the cyclic voltammograms taken at different scan rates.
Table 5.4 The mass-specific capacitance ($C_M$) and area-specific capacitance ($C_A$) of the carbon samples obtained from the slopes of the lines in Figure 5.7. The oxygen content, nitrogen-content and total heteroatom content were obtained from the full survey of the XPS spectra of carbon samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$C_M$ (F/g)</th>
<th>$C_A$ (µF/cm²)</th>
<th>O content (atomic %)</th>
<th>N content (atomic %)</th>
<th>O + N content (atomic %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPPy-0-800</td>
<td>156.0</td>
<td>25.1</td>
<td>6.2</td>
<td>8.2</td>
<td>14.4</td>
</tr>
<tr>
<td>CPPy-0-1000</td>
<td>35.2</td>
<td>6.0</td>
<td>5.8</td>
<td>3.5</td>
<td>9.3</td>
</tr>
<tr>
<td>CPPy-0-1200</td>
<td>20.5</td>
<td>3.5</td>
<td>3.7</td>
<td>1.3</td>
<td>5.0</td>
</tr>
<tr>
<td>CPPy-0-1400</td>
<td>7.1</td>
<td>1.2</td>
<td>3.1</td>
<td>0.5</td>
<td>3.6</td>
</tr>
<tr>
<td>CS-0-900</td>
<td>97</td>
<td>10.6</td>
<td>5.3</td>
<td>NA</td>
<td>5.3</td>
</tr>
</tbody>
</table>
of $C_A$ on oxygen content appeared asymptotic. This suggests that by increasing the N-content, a proportional increase in $C_A$ could be achieved while increasing oxygen content may have little or no effect in DL capacitance above a certain limit.

The capacitance of basal planes of carbon has been explained by Yeager by treating the graphite as a semiconductor along the perpendicular direction to the basal plane [145]. At the PZC, where the capacitance is the least, the DL capacitance of the basal plane depends on the capacitance of the space-charge layer inside the graphite [1]. According to Yeager, the space-charge capacitance was due to charge carrier following Boltzmann statistics [145] while according to Gerischer, the space-charge capacitance ($C_{SC}$) was due to low electronic density of states near Fermi level of graphite [214]. As several studies have shown that, nitrogen can modulate the electronic properties in carbon nanostructures such as carbon nanotubes (CNTs) and graphene, imparting semiconducting or metallic properties [15, 16, 215], it is possible that N-doping could change the electronic density of states or perhaps the charge carrier concentration. As discussed in Chapter 2, increase in electronic density of states or charge carrier concentration, thickens the space-charge layer. This could dramatically increase the $C_{SC}$ of the basal planes, which could be the cause for the high area-specific capacitance in CPPy-0-800 with very high nitrogen concentration [141-144]. In addition, nitrogen functional groups exhibit a functional charge center that may facilitate charge donation or even undergo electrostatic interaction with the electrolyte.

Our data also suggests that the nitrogen functional groups impact the microcrystallinity of the carbon itself. From XRD and Raman analysis, it was shown that the size of carbon crystallites was larger in CS-900 compared to the CPPy-0-Xs, and within the CPPy-0-X
Figure 5.8 The area-specific capacitance of the carbon samples plotted against their nitrogen (■) or oxygen content (▲). The filled markers represent nitrogen-doped carbons (CPP-0-Xs) and the empty marker represents non-doped carbon (CS-900). The relationship with nitrogen-content is shown with a linear fit and that of oxygen is shown with a logarithmic fit.
materials, the crystallite size increased with increasing with temperature. Thus, the presence of N-groups is also an indicator of an increased number of defect sites and reduced graphiticity, which is expected to increase the edge plane:basal plane ratio, which results in an increase in \( C_A \) because the edge plane capacitance is larger than the basal plane capacitance [1]. This may even explain the linear relationship with N-content compared to oxygen as in Figure 5.8.

### 5.3 Summary

In this work, NOMCs made from Py/SBA-15 were heat treated to different temperatures, allowing for the N-content to be directly controlled while preserving the overall pore structure of the carbon. Maintaining a constant nanostructure while controlling the surface N and O content of the carbons allowed the contribution of the surface functional groups to be isolated and investigated. After calculating the DL capacitance, it was found that both the \( C_A \) and \( C_M \) increased linearly with the N-content while there was little increase with oxygen content. This indicated that nitrogen plays a greater role in enhancing the DL capacitance of NOMCs than oxygen, likely through a modulation of the local electronic structure, which can enhance the space-charge capacitance of the basal planes of carbon, which typically have a notoriously low DL capacitance. In addition, comparing with CS-900, it was shown that nitrogen introduces more defects and makes the carbon crystallites smaller, exposing a greater number of high capacitance edge planes. Thus, nitrogen affects the DL capacitance by changing both the electronic properties and crystalline microstructure of the carbon.
CHAPTER 6

PORE ORDER EFFECTS OF N-DOPED MESOPOROUS CARBON ON PT ORR ACTIVITY

6.1 Objective

The objective of this work is to study the impact of the pore microstructure of NMC support on the dispersion, structure, and ORR activity of Pt NPs [216-218]. In this work, we have modified the pore microstructure of NMC keeping the amount and type of nitrogen functional groups constant. To accomplish this, we chose a template (SBA-15) based method to synthesize N-doped mesoporous carbon. Literature suggests that the surface chemistry of NMC depend mainly on carbonization temperature and the precursor. Hence, the surface chemistry was controlled by maintaining same carbonization temperature (800 °C) and precursor (Pyrrole) while the pore microstructure was varied by template modification. The physicochemical properties of such N-doped carbon, Pt deposited on N-doped carbon and their ORR activities are presented and discussed below.

6.2 Results and discussion

6.2.1 Pore characteristics

SBA-15 has a honeycomb-like ordered pore structure [163]. In this study, SBA-15 was treated with TEOS to modify its pore size and structure. Figure 6.1 shows the pore size distributions and the corresponding $\alpha_s$ plots (inset) for the SBA-15-Xs templates where X
represents the volume of TEOS added to 3.5 g SBA-15. The pore size of the SBA-15-Xs decreased with increased TEOS exposure, which indicated that the condensation of silica occurred on the walls of SBA-15 as illustrated in Figure 3.1. The pore area and volume of the templates decreased with increasing concentration of TEOS, which are shown in Table 6.1. The loss of pore area and volume was likely due to filling of primary mesopores. Here, the primary mesopores are defined as the mesopores forming the ordered pore structure [219]. This was concluded from the $\alpha_s$ plot (Figure 6.1, inset) in which the volume of N$_2$ adsorbed by material under analysis is plotted against the standard reduced adsorption ($\alpha_s$) for the reference solid. Standard reduction adsorption is the volume of N$_2$ adsorbed at relative pressures 0 to 1, which are normalized to the volume of N$_2$ adsorbed by the reference solid at relative pressure 0.4 [172]. At $\alpha_s = 1.4$ in the $\alpha_s$ plot in the inset of Figure 6.1, a step was observed for SBA-15-0 to SBA-15-12 signifying the filling of primary mesopores. This step was smaller for modified SBA-15-4 to SBA-15-12 compared to SBA-15-0 which indicated that modified SBA does not have as many primary mesopores as that of SBA-15-0. This could have occurred due to blockage or filling of the ordered pores in SBA-15-0 during modification by TEOS. The $\alpha_s$ plot also indicates that most of the surface area comes from mesopores, not micropores, due to a lack of a significant step at low relative pressures.

One interesting observation was that further increase in the TEOS treatment to 12 mL (SBA-15-12) did not result in a further decrease in pore diameter compared to SBA-15-8. This is most likely due to the underlying mechanism for the modification of the SBA-15, which involves the hydrolysis of TEOS and condensation of silica. Hydrolysis is faster than condensation at low pH [220]. Therefore, hydrolysed alkoxy silanes can access pores and condense on the walls of the SBA-15-0. However, hydrolysis and condensation also occur on the outer surface of the
Figure 6.1 Pore size distribution of 3.5 g of SBA-15 modified with 0, 4, 8 and 12 mL of tetraethyl orthosilicate and their $\alpha_s$ plots (inset).
template, forming clusters. These clusters are more likely to be prevalent at high TEOS concentrations, which would provide both kinetic and steric hindrance towards the condensation and growth inside of the SBA-15 pores. This suggests that there may be a critical concentration above which external clustering and internal wall growth compete, reducing the effectiveness of the silicate additive method as a pure pore modifier. Since SBA-15-12 did not show further pore modification compared to SBA-15-8, it was not extensively studied.

One of the attractive features of SBA-15 as a template is that the resulting carbon is a faithful inverse replica; in other words, the carbon has same $p6mm$ symmetry as SBA-15 [60, 62]. Therefore, the carbon replica of the TEOS-modified SBA-15 would be expected to have increasing pore diameters, corresponding to the increasing wall thickness of the template. However, the PSD of the carbon replica in Figure 6.2 shows little change in the primary pore diameter. In addition, the PSD shows some peak broadening with increasing TEOS concentration. Earlier we hypothesized that the condensation of hydrolyzed silica into clusters took place on the pore entrances based on the lack of change in PSD for SBA-15-12. This phenomenon, though very prominent in SBA-15-12, should occur in all modified templates at different rates depending on the SBA-15/TEOS ratio. Hence the increase in widening of PSD may be due to carbon formed on silicate clusters at the external surface or pore entrance. This also might be the cause for the decrease in BET surface area of CPPy-4 and CPPy-8 compared to CPPy-0 (Table 6.1) as the SBA-15 were not completely filled with the pyrrole precursor. This resulted in the systematic decrease of the pore order with increasing TEOS treatment.
Figure 6.2 Pore size distribution of the carbonized polypyrrole carbons (CPPy-X) synthesized by templating on SBA-15 tailored with TEOS and their α_s plots (inset).
Table 6.1 Pore diameter, BET surface area ($S_{\text{BET}}$) and total pore volume ($V_{\text{tot}}$) of templates and carbons obtained from $N_2$ adsorption isotherm.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pore diameter (nm)</th>
<th>$S_{\text{BET}}$ (m$^2$/g)</th>
<th>$V_{\text{tot}}$ (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-0</td>
<td>10.0</td>
<td>815</td>
<td>1.15</td>
</tr>
<tr>
<td>SBA-4</td>
<td>8.3</td>
<td>651</td>
<td>0.77</td>
</tr>
<tr>
<td>SBA-8</td>
<td>7.2</td>
<td>782</td>
<td>0.97</td>
</tr>
<tr>
<td>SBA-12</td>
<td>7.8</td>
<td>778</td>
<td>0.74</td>
</tr>
<tr>
<td>CPPY-0</td>
<td>4.3</td>
<td>873</td>
<td>1.3</td>
</tr>
<tr>
<td>CPPY-4</td>
<td>4.7</td>
<td>698</td>
<td>0.85</td>
</tr>
<tr>
<td>CPPY-8</td>
<td>3.7</td>
<td>519</td>
<td>0.64</td>
</tr>
<tr>
<td>VC</td>
<td>-</td>
<td>163</td>
<td>0.31</td>
</tr>
</tbody>
</table>
TEM images of the templates showed that all SBA-15-X had an ordered pore structure (Figure 6.3). Contrarily, the resulting carbons, CPPy-X, showed various degrees of order until CPPY-8, which showed an amorphous structure. This could be due to small pore size of SBA-15-8 and obstruction due to formation of silica cluster at the pore entrance helped by the partial pore filling [182, 183]. In addition, our results suggested that there is gradual increase in growth of silica structures at the pore entrances with increasing TEOS treatment which could also be seen on TEM images of SBA-15-4 and SBA-15-8. The difficulty in pore filling increases with smaller pore size. Both factors give rise to amorphous structures at the walls of the ordered carbon structure. Thus, the amount of external amorphous carbon increased from CPPy-0 < CPPy-4 < CPPy-8.

6.2.2 Raman analysis

As already mentioned in Chapter 5, disordered graphite shows two sharp Raman peaks, one around 1580-1600 cm\(^{-1}\) called the “G peak” relating to main first order band at 1582 cm\(^{-1}\) of pure crystalline graphite and another around 1350 cm\(^{-1}\) called the disorder-induced or “D peak” relating to main first order band at 1332 cm\(^{-1}\) of pure crystalline diamond. In the literature, Raman analysis of the carbon microstructure focuses mainly on these G and D peaks [206, 207]. The G and D peaks for the CPPy-X supports, with curve fitting, are shown in Figure 6.4. Peak fitting was accomplished by introducing third peak, the “A peak”, to capture the amorphous graphitic phase of the supports [209]. The G and D peaks were not clearly separated. The separation of G and D peaks was more distinct in VC than in CPPy-X.
Figure 6.3 Transmission electron microscope (TEM) pictures of the templates (a) SBA-15-0, (b) SBA-15-4, (c) SBA-15-8 and their respective nitrogen-doped mesoporous carbons (d) CPPy-0, (e) CPPy-4, (f) CPPy-8.
Figure 6.4  Raman spectra of the carbons used in this study. The curves at wavenumber 1000-2000 cm\(^{-1}\) are fitted with D, A and G peaks using mixed Gaussian and Lorentzian functions with linear baseline correction.
The distances between the G and D peaks were measured and it was found that the distance was largest for VC (Table 6.2). Among CPPys, the separation decreased from CPPy-0 ≈ CPPy-4 > CPPy-8. In a study by Jorio et al., when point defects are introduced in small amounts on a pure crystalline graphene which has a single G peak, two new peaks arose at 1345 cm\(^{-1}\) and 1626 cm\(^{-1}\), which are the D and D\(^\square\) peaks [210]. The D\(^\square\) peak appears as a shoulder of the G peak and fuses with it and the D peak as more disorder is introduced. Hence, the shift of D peaks towards G peaks typically suggests the intensity of disorder. This indicates that CPPys did not have the same degree of crystallinity as that of VC. On calculating \(L_\text{a}\) (average size of basal planes) from relative intensities of D to G peak [208], it was larger for the VC compared to the CPPy-X. The difference in the size of the basal planes suggested differences in microcrystallites in carbons. To further study such microstructural modification, the carbon samples were analyzed with XRD.

6.2.3 XRD analysis

The microstructural differences in CPPYs with increasing pore disorder were observed by d-spacing and \(L_\text{c}\) (average stack height) measured from (002) reflection of XRD spectra in Table 6.3 from Figure 6.5. VC had the largest d-spacing, 3.63 Å, which agreed well with the literature reported value (3.60 Å) [1] while graphite has a d-spacing of 3.354 Å. Such large d-spacing in VC shows its turbostratic nature; i.e. there is a lack of 3D order in its microcrystallites. In comparison, CPPYs had smaller d-spacing than VC. \(L_\text{c}\) (002) measured using Scherrer equation (Table 6.3) [1] revealed that the crystalline height decreased from VC to CPPys. Hence, \(L_\text{c}\) from XRD and \(L_\text{a}\) from Raman indicated that the carbon crystallites in VC are larger than that of CPPys with CPPy-8 probably having the smallest of all the samples. So, there
**Table 6.2** Peak positions of G, D and A peaks fitted on Raman spectra of carbons. $L_a$ is the average size of basal planes of carbon crystallites calculated from $L_a = 4.4 \text{ nm} \times \frac{I_G}{I_D}$ [1] where $I$ is the peak intensity. $D_{G-D}$ is the distance between G and D peaks.

<table>
<thead>
<tr>
<th>Samples</th>
<th>G peak (cm$^{-1}$)</th>
<th>D peak (cm$^{-1}$)</th>
<th>A peak (cm$^{-1}$)</th>
<th>$D_{G-D}$ (cm$^{-1}$)</th>
<th>$L_a$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VC</td>
<td>1590</td>
<td>1363</td>
<td>1506</td>
<td>227</td>
<td>4.5</td>
</tr>
<tr>
<td>CPPy-0</td>
<td>1592</td>
<td>1373</td>
<td>1509</td>
<td>219</td>
<td>3.3</td>
</tr>
<tr>
<td>CPPy-4</td>
<td>1587</td>
<td>1366</td>
<td>1465</td>
<td>221</td>
<td>3.9</td>
</tr>
<tr>
<td>CPPy-8</td>
<td>1586</td>
<td>1380</td>
<td>1497</td>
<td>206</td>
<td>3.2</td>
</tr>
</tbody>
</table>
Figure 6.5 XRD spectra of the CPPy-Xs showing their graphitic nature.
Table 6.3 Parameters obtained from XRD analysis. Tabulated are the peak position and full-width-half-maximum (FWHM) of (002) peaks of carbon. D-spacing was calculated from (002) peaks. $L_c$, the stack height of the carbon crystallites, was calculated using Scherrer equation [1].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carbon d-spacing (Å)</th>
<th>$2\theta$ (002) (°)</th>
<th>FWHM (002) (°)</th>
<th>$L_c$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VC</td>
<td>3.63</td>
<td>24.49</td>
<td>4.68</td>
<td>1.8</td>
</tr>
<tr>
<td>CPPy-0</td>
<td>3.51</td>
<td>25.32</td>
<td>8.97</td>
<td>0.9</td>
</tr>
<tr>
<td>CPPy-4</td>
<td>3.53</td>
<td>25.20</td>
<td>8.26</td>
<td>1.0</td>
</tr>
<tr>
<td>CPPy-8</td>
<td>3.49</td>
<td>25.48</td>
<td>10.29</td>
<td>0.8</td>
</tr>
</tbody>
</table>
seemed to be a gradual trend of not only the pore order but some microcrystallinity among CPPys.

6.2.4 Surface chemistry

XPS showed that the C/N atomic % ratio in this work was between 8 and 10, which is consistent with our previous work [130]. The N 1s peaks in CPPys were deconvoluted into 4 peaks. The peaks at 398.3 eV and 400.7 eV were assigned to pyridinic (N-6) and pyridone (N-5) N-groups [13]. The peak at 400.7 could also be due to quaternary nitrogen (N-Q) which has also been suggested to be protonated N-6 through formation of H-bridge with nearby hydroxyl or carboxyl groups [13]. The peak at 403.1 eV was likely to be pyridine-N-oxides and the peak at 405.6 could be NOx [13, 191]. The BEs and surface atomic compositions of CPPys were very similar. This implied that the chemical state and composition of nitrogen functionalities were a function of temperature. The N-groups compromised mostly of edge structures, N-5 and N-6 which is advantageous as these edge and defect sites can act as active sites for metal nucleation and growth.

6.2.5 Platinum on carbon

Figure 6.6 shows TEM images of 50 wt % Pt deposited on VC and CPPys. It should be mentioned here that both pre-surface-activation and post-heat-treatment steps, which leads to better dispersion of NPs [101, 221] were avoided during the deposition process. Despite the lack of surface treatment, Pt/CPPys showed very good dispersion compared to Pt/VC. On VC, Pt NPs
Figure 6.6 TEM images of Pt NPs on various carbons used in this study (a) Pt/VC, (b) Pt/CPPy-0, (c) Pt/CPPy-4 and (d) Pt/CPPy-8.
were concentrated between the carbon nanoparticles instead of uniformly covering them. On the contrary, Pt NPs were evenly distributed in CPPys.

The sizes of Pt NPs were estimated using the Scherrer equation from the Pt (111) XRD peak (Table 6.4). The volume averaged size of Pt NPs on VC was significantly larger than that of Pt NPs on CPPys. The smaller Pt NPs and their better dispersion on CPPys could be linked to their higher surface area and N surface functional groups. High surface area cannot alone ensure good dispersion; surface defects and edges play significant role in particle dispersion. N groups on carbon surface assist in dispersion by introducing electron deficient centers at nearby carbon atoms which can strongly interact with Pt atoms [14, 111, 121]. Also, N sites on carbon act as defect sites that also can provide centers for nucleation [14]. When the Pt/VC (in-house) was compared with commercial Pt/VC (50 wt %) from BASF, the Pt NPs size and peak position of (111) reflection were similar, but the d-spacing of Pt NPs on Pt/VC (BASF) was smaller than that of PtNPs on Pt/VC (in-house), which was closer to that of bulk Pt (2.265 Å). This smaller d-spacing could signify strain in Pt NPs, which could enhance its catalytic activity [222]. Despite the sizes of Pt NPs on CPPys being small, the d-spacing was slightly higher than that of Pt NPs on VC. This was surprising and could be due to effect of nitrogen functionalities on CPPys. The d-spacing of Pt NPs on commercial Pt/VC (BASF) was 2.19 Å, smaller than that of Pt/VC prepared in-house.

The C1s and N1s XPS peaks of Pt deposited VC and CPPy-X were deconvoluted and compared with similar peaks of bare VC and CPPys. The BE and the atomic % of various chemical states of C and N elements were indistinguishable from each other within the error limit. The BEs of Pt$^0$ 4f$_{7/2}$ state in both Pt/VC (in-house) and Pt/VC (BASF) was 71.2 eV, identical to that of bulk Pt 4f$_{7/2}$ (71.2 eV) [223]. For Pt/CPPy-0 and Pt/CPPy-4, the BEs of Pt$^0$
Table 6.4 Parameters obtained from XRD analysis. Tabulated are the peak position and full-width-half-maximum (FWHM) of (111) peaks of Pt. D-spacing was calculated from (111) peaks. Pt size were calculated using Scherrer equation [1].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pt d-spacing (Å)</th>
<th>2θ (111) (°)</th>
<th>FWHM (111) (°)</th>
<th>Pt size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/VC (in-house)</td>
<td>2.26</td>
<td>39.77</td>
<td>2.44</td>
<td>3.5</td>
</tr>
<tr>
<td>Pt/CPPy-0</td>
<td>2.32</td>
<td>38.87</td>
<td>6.72</td>
<td>1.3</td>
</tr>
<tr>
<td>Pt/CPPy-4</td>
<td>2.30</td>
<td>38.69</td>
<td>5.80</td>
<td>1.5</td>
</tr>
<tr>
<td>Pt/CPPy-8</td>
<td>2.29</td>
<td>38.93</td>
<td>5.67</td>
<td>1.5</td>
</tr>
<tr>
<td>Pt/VC (BASF)</td>
<td>2.19</td>
<td>39.76</td>
<td>2.28</td>
<td>3.7</td>
</tr>
</tbody>
</table>
4f_{7/2} states were 71.6 eV and 71.8 eV respectively. This agrees with observations by Toyoda et al., who observed a positive shift (ca. 71.2 eV $\rightarrow$ 71.7 eV) in the Pt 4f_{7/2} core level BE with a decrease in Pt particle size (3.14 nm $\rightarrow$ 0.86 nm) on GCE [98]. However, for Pt/CPPy-8, a negative shift (ca. 0.8 eV) in Pt 4f_{7/2} core level relative to Pt/CPPy-0 and Pt/CPPy-4 was found despite a similar Pt size (Figure 6.7, Table 6.5), which is discussed below.

BE shifts observed by XPS with changes in particle size can be attributed to both initial and final state effects [224, 225]. Initial state effects can be attributed to lattice strain, which reduces bond distance and influences d-hybridization. Final state effects are attributed to the relaxation energy due to core-hole screening. As particle size decreases, the BE shifts positive to the bulk value [98]. Specifically, the decrease in bond distance leads to enhanced d-orbital hybridization, strengthening the bonding between the metal atoms but weakening the bond between metal atoms and adsorbates [224, 226]. Therefore, the negative BE shift in Pt/CPPy-8 suggests that the strong d-orbital hybridization between Pt atoms was overcome by the interaction between Pt NPs and CPPy-8. This interaction could arise because of the synergistic effect from small Pt size, high N content, and amorphous carbon structure. High N content likely facilitates aggregation of N sites, as shown by DFT studies [121], which creates strong centers of concentrated charge. Very small Pt size creates greater specificity between surface N atoms and catalyst particles. And, if it is assumed that each carbon crystallite was an atom in a crystal structure, amorphous structured CPPy-8 has more coordinatively highly unsaturated sites than other more ordered CPPy-X i.e. more free active sites. Indeed, it is the high number of coordinatively highly unsaturated sites that makes Ni-based amorphous alloy catalysts more active than their crystalline counterpart [227].
Figure 6.7 Pt 4f XPS spectra of Pt NPs deposited on VC and CPPY-X. The peaks were fitted with doublet of of Pt$^0$, Pt$^{2+}$ and Pt$^{4+}$ peaks.
Table 6.5 Peak positions and atomic % of C, N and Pt states acquired after deconvolution of C 1s, N 1s and Pt 4f peaks respectively using mixed Gaussian and Lorentzian functions after Shirley background correction.

<table>
<thead>
<tr>
<th>Pt 4f states</th>
<th>Pt/VC (in-house)</th>
<th>Pt/VC (BASF)</th>
<th>Pt/CPPy-0</th>
<th>Pt/CPPy-4</th>
<th>Pt/CPPy-8</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BE (eV)</td>
<td>at %</td>
<td>BE (eV)</td>
<td>at %</td>
<td>BE (eV)</td>
</tr>
<tr>
<td>Pt⁰ 4f_7/2</td>
<td>71.2</td>
<td>21.1</td>
<td>71.2</td>
<td>36.9</td>
<td>71.6</td>
</tr>
<tr>
<td>Pt⁰ 4f_5/2</td>
<td>74.5</td>
<td>16.3</td>
<td>74.5</td>
<td>27.7</td>
<td>74.9</td>
</tr>
<tr>
<td>Pt⁺ 4f_7/2</td>
<td>72.0</td>
<td>22.5</td>
<td>73.3</td>
<td>19.7</td>
<td>72.8</td>
</tr>
<tr>
<td>Pt⁺ 4f_5/2</td>
<td>75.3</td>
<td>16.9</td>
<td>76.4</td>
<td>14.7</td>
<td>76.1</td>
</tr>
<tr>
<td>Pt⁺⁺ 4f_7/3</td>
<td>74.6</td>
<td>13.2</td>
<td></td>
<td></td>
<td>75.8</td>
</tr>
<tr>
<td>Pt⁺⁺ 4f_5/3</td>
<td>77.9</td>
<td>9.9</td>
<td></td>
<td></td>
<td>79.1</td>
</tr>
</tbody>
</table>
6.2.6 Electrochemical behavior

Cyclic voltammograms (CVs) for Pt supported on VC and CPPys in N$_2$ saturated HClO$_4$ are shown in Figure 6.8. The CVs were well defined and clearly showed all of the characteristics of polycrystalline Pt [228]. The region (0.05 to 0.3 V) before the DL was associated with Pt-H oxidation/adsorption while the region (0.45 to 1.2 V) after the DL was consistent with Pt-oxide formation/reduction. The H-adsorption/desorption region featured multiple peaks indicative of H-adsorption/desorption on different crystal facets of cubo-octahedral Pt crystallites [201]. The Pt-oxide formation started at ca. 0.6 V during the forward scan (0.05 $\rightarrow$ 1.2 V) and Pt-oxide and oxygen reduction peak occurred at ca. 0.7 V during the reverse scan (1.2 $\rightarrow$ 0.05V). The CV of Pt/CPPy-X mirrored the CV of Pt/VC in shape and position of different peaks except for the marked difference in the DL region (0.3 to 0.45 V) where the DL current of Pt/CPPy was significantly higher than that of Pt/VC. Pt/CPPys have significantly higher DL capacitance than VC due to their higher surface area of CPPys and pseudocapacitance or electron delocalization due to surface N atoms [130, 139, 200].

Another piece of information that can be obtained from Figure 6.8 is ECSA of the Pt NPs. Assuming one platinum atom adsorbs one hydrogen atom and that the current due to hydrogen evolution makes up for the charge required to complete partial monolayer coverage, ECSA can be calculated from the area under the Pt-H oxidation/formation peaks (0.05 V – 0.4 V) after the DL region correction using Equation 6.1 [228].

$$ A_{Pt} = \frac{Q_H}{210 \mu C/cm^2 \times L_{Pt}} $$
Figure 6.8 Cyclic voltammograms of Pt NPs deposited on VC and CPPy-X recorded in N\textsubscript{2} saturated 0.1 M HClO\textsubscript{4} at 25 °C with a scan rate of 20 mV/s.
Where \( Q_H \) is the charge under the Pt-H oxidation/formation peaks and \( L_{Pt} \) is the Pt loading on the working electrode. From the \( A_{Pt} \) values listed in Table 6.6, it was clear that Pt/CPPy catalysts had a higher active surface area than Pt/VC (BASF) despite similar Pt loadings. Pt/CPPy (83 m\(^2\)/g\(_{Pt}\)) showed the highest improvement in ECSA, almost 4 times that of Pt/VC (BASF) (21.4 m\(^2\)/g\(_{Pt}\)). This remarkable enhancement was due to nominal agglomeration and uniform dispersion of Pt NPs on CPPy-X, which could be subscribed to high surface area and N surface atoms on CPPy as discussed earlier. Among CPPys, Pt/CPPy-0 had the highest ECSA and Pt/CPPy-8 had the lowest ECSA. Here, CPPy-0 had the highest structural order while CPPy-8 had the least and the Pt NPs on CPPys were less than 2 nm (Table 6.4). This suggests that Pt NPs on Pt/CPPy-8 were less accessible than those on Pt/CPPY-4 which could be assigned to its lower structural disorder.

### 6.2.7 Oxygen reduction activity

Positive (0.1 → 1.1 V) going linear sweep voltammograms of Pt/CPPys and Pt/VC (BASF) at 1600 RPM in 0.1 M HClO\(_4\) at 25 °C with a scan rate of 5 mV/s are shown in Figure 6.9. To extract the true kinetic current density \( (j_k) \), the total current density \( (j) \) was corrected using the mass-transfer limited current density \( (j_d) \) using Equation 6.2.

\[
j_k = \frac{j \times j_d}{j_d - j}
\] 

6.2
Table 6.6 The Pt wt % in the catalyst ($W_{Pt}$), and parameters from the thin-film RDE experiment, where $L_{Pt}$ is the Pt loading in the thin-film, ECSA is the electrochemically active surface area, $I_s$ is the specific activity at 0.9 V, $I_m$ is the mass-specific activity at 0.9 V and $n$ is the number of electrons in an oxygen reduction reaction.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$W_{Pt}$ (wt %)</th>
<th>$L_{Pt}$ (µg/cm$^2$)</th>
<th>ECSA (m$^2$/g$_{Pt}$)</th>
<th>$I_s$ (µA/cm$^2$$_{Pt}$)</th>
<th>$I_m$ (A/mg$_{Pt}$)</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/VC (BASF)</td>
<td>48.1</td>
<td>18.2</td>
<td>21.4</td>
<td>297</td>
<td>0.055</td>
<td>3.7</td>
</tr>
<tr>
<td>Pt/CPPy-0</td>
<td>42.6</td>
<td>16.0</td>
<td>83.0</td>
<td>123</td>
<td>0.102</td>
<td>3.7</td>
</tr>
<tr>
<td>Pt/CPPy-4</td>
<td>44</td>
<td>16.3</td>
<td>55.1</td>
<td>208</td>
<td>0.115</td>
<td>3.5</td>
</tr>
<tr>
<td>Pt/CPPy-8</td>
<td>44.2</td>
<td>16.7</td>
<td>30.5</td>
<td>226</td>
<td>0.069</td>
<td>3.5</td>
</tr>
</tbody>
</table>
Figure 6.9 The oxygen reduction reaction (ORR) polarization curves (positive sweep) at 1600 RPM in O₂ saturated 0.1 M HClO₄ at 25 °C with a scan rate of 5 mV/s and Tafel plot calculated after mass-transfer correction of the catalysts used in this study (inset).
The mass-transfer limited current density can be taken as the current density at 0.4 V. However, one must first verify that this $j_d$ is within the theoretical boundary-layer diffusion limited current density at 1600 RPM which can be calculated from the Levich equation [194]:

$$j_d = 0.62nFD_O^{2/3} \omega^{1/2} v^{-1/6} C_0^*$$

Where F is the Faraday’s constant, $D_O$ is the $O_2$ diffusivity, $\omega$ is the rotation rate, $v$ is the kinematic viscosity, and $C_0^*$ is the bulk $O_2$ concentration. At room temperature, the theoretical diffusion limited current density is 6.04 mA/cm$^2$ assuming a 4e$^-$ ORR [229]. The mass-transfer limited region (<0.6 V) in Figure 6.9 was within 10% of this theoretical value which points out that the ORR occurred primarily through a 4 e$^-$ process. To confirm this, polarization curves were taken at different rotation rates and the current densities at 0.4 V normalized by $0.62D_O^{2/3} v^{-1/6} C_0^*$ at different rotation rates were plotted against the $\omega^{1/2}$ as in Figure 6.10 for Pt catalysts. The linearity of the plot meant that the diffusion limited current can be modeled after the Levich equation. The slopes were used to find $n = 3.5-3.7$ for Pt/CPPy-X (Table 6.6).

Then, the log of $j_k$ was plotted against the electrode potential to make the Tafel plots, which are shown in the inset of Figure 6.9. The Tafel plots of the Pt/VC and Pt/CPPy-X almost overlap each other signifying a similar ORR mechanism and kinetics for Pt regardless of the support. The experimental plots were fitted linearly in the low overpotential region (>0.9 V) and high overpotential region (<0.85 V). The Tafel slopes in both regimes agreed well with literature values for bulk Pt and Pt/C: -60 mV/dec and -120 mV/dec at low overpotential and high overpotential (Table 6.7), respectively in HClO$_4$ [230] Thus, the rate determining step (RDS) was the first electron transfer step notwithstanding the support.
Figure 6.10 Plot of current densities at 0.4 V normalized by $0.62D_o^{2/3}v^{-1/6}C_o^*$ at different rotation rates with respect to $\omega^{1/2}$ where $F$ is the Faradays constant, $D_o$ is the $O_2$ diffusivity, $v$ is the kinematic viscosity, $C_o^*$ is the bulk $O_2$ concentration and $\omega$ is the rotation rate. The plot was fitted linearly.
Table 6.7 Tafel slopes (TS) calculated at different potential ranges.

<table>
<thead>
<tr>
<th>sample</th>
<th>TS (mV/dec) for E&gt;0.85 V</th>
<th>TS (mV/dec) for E&lt;0.85 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/VC (BASF)</td>
<td>63</td>
<td>119</td>
</tr>
<tr>
<td>Pt/CPPy-0</td>
<td>60</td>
<td>121</td>
</tr>
<tr>
<td>Pt/CPPy-4</td>
<td>62</td>
<td>113</td>
</tr>
<tr>
<td>Pt/CPPy-8</td>
<td>62</td>
<td>129</td>
</tr>
</tbody>
</table>
After normalizing the current density to the specific active surface area ($A_{Pt}$) and catalyst loading ($L_{Pt}$), $j_k$ at 0.9V gives specific ($I_s$) and mass activity ($I_m$) of Pt (Table 6.6). The $I_s$ and $I_m$ of Pt/VC (BASF) were 297 µA/cm$^2_{Pt}$ and 0.055 A/mg$_{Pt}$, respectively. Gasteiger et al. have reported 190-200 µA/cm$^2_{Pt}$ and 0.062-0.069 A/mg$_{Pt}$ for 40 wt % Pt/VC (ETEK) which were measured in O$_2$ saturated 0.1 M HClO$_4$, 60 °C at 5 mV/s scan rate [231]. Although both catalysts have an identical support, there were not enough details about the Pt deposition method and Pt NP characteristics to make a true comparison possible. Besides, the Pt loading and reaction temperatures for their experiments are different from those presented in this work. Nevertheless, Gasteiger et al. showed that the mass activity of Pt/VC (ETEK) decreases from ca. 0.14 A/mg$_{Pt}$ to ca. 0.065 A/mg$_{Pt}$ when Pt wt % increases from 20 to 40, which makes 0.055 A/mg$_{Pt}$ for 50 wt % Pt/VC (BASF) a reasonable result.

Compared to Pt/VC (BASF), Pt/CPPys had lower specific activities but higher mass activities. The higher mass activities of Pt/CPPys compared to Pt/VC (BASF) might be the result of the better Pt NPs dispersion. Among Pt/CPPYs, Pt/CPPy-4 had the highest $I_m$, 0.115 A/mg$_{Pt}$. The difference in mass activities among Pt/CPPys was likely due to different specific surface areas and the specific activities. An increasing order from Pt/CPPy-0 (123 µA/cm$^2_{Pt}$) to Pt/CPPy-8 (226 µA/cm$^2_{Pt}$) was found with regard to specific activities. The difference between these catalysts was the structural disorder among CPPy-X and XPS showed strong interaction between the catalyst and the support in Pt/CPPy-8. These results implied that the enhanced interaction between the catalyst and the support could be achieved through the structural disorder in N-doped mesoporous carbon. Very high specific activity of Pt/CPPy-8 among Pt/CPPy-X could be result of such interaction between the Pt and CPPy-8. Likewise, it could be deduced that
Pt/CPPy-4 had the second highest activity as CPPy-4 had structural disorder in-between CPPy-0 and CPPy-8.

### 6.2.8 Fuel Cell Performance

The single stack PEM fuel cell polarization curves are shown in Figure 6.11. The figure showed that Pt/VC performed better than all of the Pt/CPPy-X catalysts. At low current densities (<100 mA/cm²), the polarization curves overlapped. However, at higher current densities (> 100 mA/cm²), the polarization curves of the Pt/NMCs digressed relative to Pt/VC, indicating poor performances. Among the Pt/NMCs, Pt/CPPy-0 was the worst performing NMC while Pt/CPPy-8 was the best performing NMC.

To further elucidate the underlying cause for the lower than expected performance of the Pt/NMCs, their polarization curves were deconvoluted to determine the influence of kinetics, ionic conductivity and reactant mass-transfer in the Pt/supports on the observed fuel cell performance. The overpotential or voltage loss in fuel cell is mainly due to (i) kinetic overpotential (\( \eta_{\text{ORR}} \)) as a result of sluggish ORR kinetic at the cathode, (ii) ohmic overpotential (\( \Delta E_{\text{ohmic}} \)) due to proton conduction resistance through the membrane and electronic contact resistance, and (iii) mass-transfer overpotential (\( \eta_{\text{tx}} \)) as a result of mostly O₂ transport. The cell voltage can be expressed as [231]:
Figure 6.11 Fuel cell test polarization curves at 80 °C cell temperature, 100% anode humidity and 82% cathode humidity.
where $E_{\text{rev}}$ is the thermodynamic cell potential, which is a function of partial pressures of hydrogen and oxygen, and temperature. It was determined to be 1.168 V under operating conditions applied in this study from following equation [232].

$$E_{\text{rev}} = 1.23 - 0.9 \times 10^{-3} (T - 298) + 2.3RT/4F \times \log \left( \frac{P_{\text{H}_2} P_{\text{O}_2}}{P_{\text{H}_2} P_{\text{O}_2}} \right)$$

The ohmic resistance was found by galvanostatic impedance where the intercept at very high frequency was taken as the ohmic resistance. Now, cell voltage corrected for the ohmic resistance can be written as;

$$E_{\text{IR-corrected}} = E_{\text{cell}} + \Delta E_{\text{ohmic}} = E_{\text{rev}} - \eta_{\text{ORR}} - \eta_{\text{tx}}$$

And assuming that at high potential or at low current density, mass-transfer is negligible, IR-corrected cell voltage is only dependent on ORR kinetic loss ($\eta_{\text{ORR}}$) [231], which can be fitted according to the relation;

$$\eta_{\text{ORR}} \propto b \log \left( i_{\text{eff}} \right)$$

where $b$ is the Tafel-slope and $i_{\text{eff}}$ is the H$_2$ cross-over corrected current. Hence, by utilizing above equation, polarization curves devoid of mass-transfer and ohmic effects can be obtained for each catalyst by extrapolating $E_{\text{IR-corrected}}$ at low current density. Now $\eta_{\text{tx}}$ can be calculated from Equation 6.4.

The three voltage losses were plotted against the current density and are shown in Figures 6.12a-c. From Figure 6.12a, it was clear that the ohmic losses among the four fuel cells were equivalent, which was expected since the same fuel set-up and membrane were used for each fuel cell test and ohmic loss depends upon contact resistance and proton conduction through the membrane. This established the consistency in our fuel cell assembly and test conditions. However, considerable differences can be seen in Figure 6.12b which plots $\eta_{\text{ORR}}$ vs. current.
Figure 6.12a Activation overpotential (\(\eta_{\text{ORR}}\)) plotted against current density after deconvolution of the fuel cell polarization curves in Figure 6.11.
Figure 6.12b Ohmic overpotential ($\Delta E_{\text{ohmic}}$) plotted against current density after deconvolution of the fuel cell polarization curves in Figure 6.11.
Figure 6.12c Mass-transfer overpotential ($\eta_{tx}$) plotted against current density after deconvolution of the fuel cell polarization curves in Figure 6.11.
density. Tafel-slopes were extracted between 0.85 to 0.9V and were all approximately 70 mV/dec, consistent with the values reported in the literature for Pt/C fuel cell, (20) confirming that the ORR mechanisms were same on both Pt/VC and Pt/NMCs. Despite similar Tafel slopes, the $\eta_{\text{ORR}}$ increased as Pt/CPPy-8 < Pt/CPPy-4 < Pt/VC < Pt/CPPy-0. There was a loss of 11 mV with Pt/CPPy-0 and a gain of 42 mV with Pt/CPPy-8 at 500 mA/cm$^2$, which is at 0.6V for Pt/VC (Figure 6.12a). This showed that ORR activity on Pt/CPPy-8 was superior to Pt/VC or other Pt/CPPy. From Figure 6.12c, it was clear that mass-transfer was the dominating loss in fuel cell performance for the Pt/NMCs and was significant as early as 100 mA/cm$^2$. Among Pt/NMCs, Pt/CPPy-8 had the lowest transport loss and Pt/CPPy-0 had the highest $\eta_{\text{tx}}$. The mass-transfer overpotential increased from Pt/CPPy-0 to Pt/CPPy-8. Hence, the disordered pore structure of CPPy-8 was actually more efficient in mass-transfer than the ordered structure of CPPy-0.

6.2.9 Pt Stability

The stability of Pt NPs was investigated using an accelerated degradation test (ADT) where the catalyst was cycled for 1000 cycles between 0 and 1.4 V vs. NHE in 0.1 M HClO$_4$ at 25 °C with a scan rate of 50 mV/s. Pt/CPPy-8 and Pt/VC were subjected to ADT and the CVs after every 100 scans are presented in Figure 6.13. Decrease in area of Pt-H adsorption/desorption peaks of both catalysts could be observed as the number of scans increases. The ECSA decreased as a result of potential cycling. For Pt/VC (BASF), the ECSA decreased by 32.9 % while for Pt/CPPy-8, the ECSA decreased by 70.3 %. The final ECSA of Pt/CPPy-8 was 48% of the final ECSA of Pt/VC (BASF). This was unexpected as stronger interaction with the support was expected to increase electrochemical stability of Pt NPs. Also as NMC was shown to be more electrochemically stable than that of VC in Chapter 4 makes this
Figure 6.13a Cyclic voltammograms of Pt/VC (BASF) in N$_2$ saturated 0.1 M HClO$_4$ at 25 °C with a scan rate of 50 mV/s for 1000 cycles for accelerated degradation test (ADT).
Figure 6.13b Cyclic voltammograms of Pt/CPPY-8 in N$_2$ saturated 0.1 M HClO$_4$ at 25 °C with a scan rate of 50 mV/s for 1000 cycles for accelerated degradation test (ADT).
result surprising. **Figure 6.14** shows the TEM image of Pt/CPPy-8 after ADT. The average size of Pt NPs was 3.6 nm. Although some agglomeration was observed, it was very mild.

The loss of active surface area in Pt/VC (BASF) is attributed to coarsening of Pt NPs [233]. However, there can be several mechanisms behind the coarsening of Pt NPs such as Ostwald ripening, Pt migration, detachment from carbon support and Pt dissolution and redeposition [233]. It also has been shown that Pt catalyzes carbon corrosion through a water-gas type reaction [234], which will be more severe with high Pt loading and high support surface area as in the Pt/CPPy used in this study. Besides, Raman studies suggested that CPPy is not as graphitic as VC. Hence the loss of ECSA could be primarily due to Pt catalyzed carbon corrosion. This is also supported by decrease in DL current, which is directly proportional to surface area of charging and discharging, of Pt/CPPy-8 which reduced by 43.0 % compared to 15.5 % in Pt/VC (**Figure 6.9**). However, to fully elucidate the mechanism more extensive work is needed.

### 6.3 Summary

In this work, the pore structure of NMC was optimized to enhance the ORR activity of the catalyst supported by it. NMC with varying structural disorder were synthesized by controlling the pore filling in the SBA-15 template which were modified with TEOS. This resulted in CPPy-X with different pore structures, from ordered (CPPy-0) to amorphous (CPPy-8) as revealed by TEM analysis. However, by keeping the carbonization temperature constant, the atomic percentage and types of surface C and N functionalities were equivalent in all of the CPPy-X. Thus, the surface chemistry was controlled and any variation in interaction between Pt and CPPy-X could only have been due to the structural differences. In addition, Raman and XRD
**Figure 6.14** Transmission electron microscope picture of Pt/CPPY-8 after undergoing accelerated degradation test.
indicated that in addition to pore structure, the microcrystallinity was also different in CPPy-X with CPPy-8, perhaps having the smallest carbon crystallites. Therefore, we could conclude that beside the pore structure, template based carbon synthesis also allowed for control of the microcrystalline nature of the carbon.

The effect of this structural disorder among CPPy-X on interaction its with Pt was underscored by the shift in BE of Pt in Pt/CPPy-8. Hence, structure based interaction between catalyst and support was established. Also, small Pt size and N content were thought to be critical in highlighting this structure-based interaction as small Pt size increases specificity with the support and the high N-content introduces highly active centers through aggregation of nitrogen functionalities. This interaction had a significant impact on the ORR activity of Pt as demonstrated by varying specific activity in Pt/CPPy-X. The results showed that structural disorder in CPPy increases interaction with Pt, thereby increasing its intrinsic activity. Moreover, this shows that the structural effect has to be in the discussion when comparing various carbon nanostructures as catalyst supports.
CHAPTER 7

TEMPERATURE CONTROLLED SURFACE CHEMISTRY OF N-DOPED MESOPOROUS CARBON AND ITS INFLUENCE ON PT ORR ACTIVITY

7.1 Objective

In previous study, the pore structure of NMC was optimized for Pt support. It was shown that the disordered pore structure enhances the Pt support interaction. However, the role of nitrogen was still unanswered. Therefore, the purpose of this study was to investigate the effect of N content on Pt dispersion and ORR activity [234]. The N content was varied through heat treatment at several temperatures while the pore structure was controlled by templating, which allowed for the influence of the support surface chemistry to be studied in the absence of structural effects. The change in Pt dispersion and ORR activity was studied in terms of nitrogen surface functional groups and the graphiticity of the NMC.

7.2 Results and Discussions

8 mL of TEOS was added to decrease pore size of 3.5 g SBA-15. The NMC casted in this template (SBA-15-8) was referred to as CPPy-8. In this work, the CPPy-8-X were synthesized on the SBA-15-8 template where X represents the heat treatment temperature. The SBA-15-8/PPy composites were heat treated to 800, 1000 and 1200 °C. Thenafter, the template was removed. To prepare CPPy-8-1400, CPPy-8-800 was reheated to 1400 °C so as to avoid formation of unknown material which was obtained when SBA-15-8/PPy composite was directly heated to 1400 °C.
7.2.1. N$_2$ Adsorption

The pore size distribution (PSD) plots for CPPy-8-X are shown in Figure 7.1. The PSD plot showed that the CPPy-8-X carbons possessed a narrow PSD signaled by a single peak in the mesoporous range (2 to 50 nm). The positions of the PSD peaks were centered at ca. 3.7 nm. This was expected as the same template was used to cast all of the CPPy-8-Xs. However, the PSD peaks were asymmetric; they were wider towards the higher mesoporous range (6 nm to 35 nm). This is likely due to incomplete pore filling, which led to the formation of some larger mesopores in all of the samples [182, 183].

Pore sizes, BET surface areas ($S_{BET}$) and pore volumes ($V_{tot}$) for SBA-15-8 and the CPPy-8-Xs, obtained from the N$_2$ adsorption isotherms, are listed in Table 7.1. Heat treating to 1000 °C increased $S_{BET}$ of CPPy-8-800 by 172 m$^2$/g. Upon heat treatment to temperatures above 1000 °C, $S_{BET}$ of CPPy-8-X decreased. The initial increase until ca. 1000 °C followed by a decrease of $S_{BET}$ has also been reported in carbon blacks [1]. The initial increase could be attributed to the loss of surface heteroatoms in the form of volatiles such as HCN, H$_2$, NH$_3$, CO$_2$, CO, and CH$_4$ [236], which allowed access to micropores [237]. Above 1000 °C the loss of surface area is likely due to closing of the micropores as the length of the graphite domains increased.

7.2.2 Transmission electron microscopy

The TEM images of the CPPy-0-Xs in Figures 7.2a-d showed that the nanostructure of the CPPy-8-Xs was indeed amorphous; i.e. a particular shape could not be ascribed to the
Figure 7.1 Pore size distributions of the CPPy-8-Xs.
Table 7.1 Pore diameter, BET surface area ($S_{\text{BET}}$) and pore volume ($V_{\text{tot}}$) of the tetraethyl orthosilicate modified SBA-15 template (SBA-15-8) and the templated nitrogen-doped carbons synthesized at different temperatures (CPPy-8-X).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pore diameter (nm)</th>
<th>$S_{\text{BET}}$ (m$^2$/g)</th>
<th>$V_{\text{tot}}$ (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15-8</td>
<td>7.2</td>
<td>782</td>
<td>0.97</td>
</tr>
<tr>
<td>CPPy-8-800</td>
<td>3.7</td>
<td>519</td>
<td>0.64</td>
</tr>
<tr>
<td>CPPy-8-1000</td>
<td>3.7</td>
<td>691</td>
<td>0.79</td>
</tr>
<tr>
<td>CPPy-8-1200</td>
<td>3.4</td>
<td>653</td>
<td>0.66</td>
</tr>
<tr>
<td>CPPy-8-1400</td>
<td>3.7</td>
<td>494</td>
<td>0.61</td>
</tr>
</tbody>
</table>
Figure 7.2 Transmission electron microscopy images of CPPy-8-800 (a, e), CPPy-8-1000 (b, f), CPPy-8-1200 (c, g) and CPPy-8-1400 (d, h) showing amorphous nanostructure (a, b, c, d) and graphitic planes (e, f, g, h).
nanostructure. The formation of an amorphous nanostructure was attributed to the silica cluster formation on the surface of SBA-15 due to high TEOS concentration and purposeful limiting of pore filling by constriction as hydrolysis and condensation of TEOS made the pore walls of the template thicker. In the high resolution TEM pictures of CPPy-8-Xs (Figures 7.2e-h), the graphitic planes of carbon were clearly observed. These graphitic planes were more prominent at higher temperatures, especially in CPPy-0-1400. This suggested an increase in graphiticity at higher temperatures. Thus, the TEM showed that all of the CPPy-0-Xs had the intended disordered pore structure.

7.2.3 Raman Spectroscopy

As mentioned in Chapters 5 and 6, two main Raman transitions in disordered graphite are G peak (~1600 cm\(^{-1}\)) and D peak (~1350 cm\(^{-1}\)) showing contributions from both graphitic (sp\(^2\)) and non-graphitic (sp\(^3\)) transitions respectively. From the peak height ratio of G and D peak, \(L_a\), which is the basal size of the graphitic basal planes in the carbon crystallites, can be calculated [208]. The relative peak position of the G and D peaks could be correlated with the number of defects in a pure crystalline graphene [210].

Figure 7.3 presents the Raman spectra of the raw CPPy-8-X supports showing both G and D peaks. The observations and trend obtained for CPPy-8-X from the figure are in agreement with that of CPPy-0-X in Chapter 5. From Figure 7.3, it seems that as the carbonization temperature increased, the G and D peaks became better resolved. The G and D peaks of CPPy-8-1400 were more discernible than the G and D peaks of CPPy-8-800. Another way, proposed in Chapter 5, to abstract information about the graphiticity was to calculate the distance between the G and D peaks which are tabulated in Table 7.2. The separation between
Figure 7.3 Raman spectra of the CPPy-8-Xs showing D and G peaks.
increased with at higher carbonization temperature. Relating the increase in separation of G and D peaks to work by Jorio et al., it could be said that fewer defects were present at higher temperature. Also, the increase in $L_a$ implied that the average basal size of the carbon crystallites enlarged at higher temperature.

From Table 7.2, the increase in separation between the G and D peaks was primarily due to a positive shift in D peaks. Also, the intensity of the D peaks decreased with temperature as suggested by increase in $L_a$ which is directly proportional to the peak ratio height of G to D peak. Hence, we can say that if CPPy-8-X were perfect graphite, D peak would get smaller and farther relative to the G peak by extrapolation. This correlates well with the assignment of the peak at 1350 cm$^{-1}$ to the D peak. This also suggests that it should be possible to look and quantify the evolution of graphiticity in carbon using these parameters.

7.2.4 XRD Analysis

In agreement with the Raman results, the XRD peaks of the CPPy-8-Xs were better resolved at higher temperatures (Figure 7.4). As in previous chapters, the peak position and full width at half maximum (FWHM) for the carbon (002) reflection were utilized to calculate d-spacing (distance between graphene planes in a carbon crystallite) from Bragg’s law and $L_c$ (average thickness of carbon crystallites) from Scherer equation, which are given in Table 7.3. The observations made coincide well with that of the Chapter 5. The d-spacing of the CPPy-8-Xs was on average ca. 3.53 Å which was slightly larger than that of graphite (3.354 Å), [1] suggesting a lack of alignment between graphitic planes or a turbostratic nature. Also, Table 7.3 showed that the heat treatment was ineffective in increasing the alignment between the graphitic planes as the d-spacing did not change with temperature. Similar to $L_a$, an increase in $L_c$ was
Table 7.2 Peak positions of G, D and A peaks obtained after fitting Raman peaks of the CPPA-Xs. \(D_{G-D}\) is the distance between G and D peaks and \(L_a\) is the average size of the basal planes of the carbon crystallites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>G peak(cm(^{-1}))</th>
<th>D peak(cm(^{-1}))</th>
<th>A peak(cm(^{-1}))</th>
<th>(D_{G-D}) (cm(^{-1}))</th>
<th>(L_a) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPPy-8-800</td>
<td>1586</td>
<td>1380</td>
<td>1497</td>
<td>206</td>
<td>3.2</td>
</tr>
<tr>
<td>CPPy-8-1000</td>
<td>1600</td>
<td>1371</td>
<td>1516</td>
<td>230</td>
<td>3.8</td>
</tr>
<tr>
<td>CPPy-8-1200</td>
<td>1605</td>
<td>1358</td>
<td>1541</td>
<td>247</td>
<td>4.0</td>
</tr>
<tr>
<td>CPPy-8-1400</td>
<td>1599</td>
<td>1353</td>
<td>1525</td>
<td>245</td>
<td>4.0</td>
</tr>
</tbody>
</table>
Figure 7.4 XRD spectra of the CPPy-8-Xs.
Table 7.3. Peak position ($2\theta$) and full-width at half-maximum (FWHM) of the (002) reflection of the CPPA-Xs obtained from the XRD spectra. Carbon d-spacing and the average stack height of the carbon crystallites ($L_c$) were calculated using $2\theta$ and FWHM of the (002) reflection.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carbon d-spacing (Å)</th>
<th>$2\theta$ (002)</th>
<th>FWHM (002)</th>
<th>$L_c$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPPy-8-800</td>
<td>3.53</td>
<td>25.18</td>
<td>8.66</td>
<td>0.9</td>
</tr>
<tr>
<td>CPPy-8-1000</td>
<td>3.50</td>
<td>25.44</td>
<td>8.39</td>
<td>0.9</td>
</tr>
<tr>
<td>CPPy-8-1200</td>
<td>3.53</td>
<td>25.18</td>
<td>5.43</td>
<td>1.4</td>
</tr>
<tr>
<td>CPPy-8-1400</td>
<td>3.53</td>
<td>25.20</td>
<td>4.34</td>
<td>1.8</td>
</tr>
</tbody>
</table>
found with increasing heat treatment temperature. However, the increase in $L_a$ was significant from 800 to 1200 °C, while the increase in $L_c$ was significant from 1000 to 1400 °C.

It is widely known that the graphiticity of carbon is enhanced by treating it at high temperature in inert conditions [1]. In this work, we have shown how the graphiticity increases in N-doped mesoporous carbon in terms of absence of defects or increase in size of carbon crystallites from Raman and XRD analysis. These changes in microcrystallinity are expected to affect Pt NPs nucleation and growth depending on the method of deposition as defects and edge sites serve as the nucleation and growth centers. Few defect and edge sites usually results in large Pt NPs and agglomeration. Moreover, the presence of oxygen or nitrogen at these sites is likely to determine how these Pt NPs nucleate, grow and interact with the carbon surface.

### 7.2.5 Surface Chemistry

The surface composition of the CPPy-8-Xs was analyzed using XPS. The atomic (at) % of C, N and O atoms were calculated from the C 1s, N 1s and O 1s peak areas from the full XPS surveys of CPPy-8-X (Figure 7.5) and are tabulated in Table 7.4. In general, a decrease in N (10.5 to 0.5 at %) and O (8.4 to 0.3 at %) was observed with an increase in the carbonization temperature as in Chapter 5. It should be mentioned that the nitrogen (0.5 at %) and oxygen content (0.3 at %) of CPPy-8-1400 were within the detection limit of the XPS (< 1 %).

In N-doped carbons, nitrogen functional groups are thought to be more involved in dictating the ORR activity of supported Pt NPs than oxygen functional groups. This might be due to the fact that N-doped carbons are better catalysts than carbons with oxygen groups only [113]. Also, the nitrogen functional groups may be more effective than oxygen in modulating the electronic structure of local carbon, which could lead to the smaller Pt NP sizes and narrow
Figure 7.5 Full survey XPS spectra of the CPPy-8-Xs.
Table 7.4. The atomic % of carbon (C 1s), nitrogen (N 1s) and oxygen (O 1s) in the CPPA-Xs (in bold) obtained from the full survey of the XPS spectra. The binding energy and relative atomic % (in bracket) of different carbon and nitrogen states in the CPPA-Xs obtained from the high resolution scans.

<table>
<thead>
<tr>
<th></th>
<th>CPPy-8-800</th>
<th>CPPy-8-1000</th>
<th>CPPy-8-1200</th>
<th>CPPy-8-1400</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s</td>
<td>81.1 %</td>
<td>90.0 %</td>
<td>93.2 %</td>
<td>99.2 %</td>
</tr>
<tr>
<td>Graphitic</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-OH, C-O-C, C=N</td>
<td>284.6 (70.3 %)</td>
<td>284.6 (68.6 %)</td>
<td>284.6 (70.3 %)</td>
<td>284.6 (71.8 %)</td>
</tr>
<tr>
<td>C=O</td>
<td>288.0 (7.4 %)</td>
<td>288.3 (7.3 %)</td>
<td>288.2 (7.0 %)</td>
<td>287.9 (5.6 %)</td>
</tr>
<tr>
<td>COOH, COOR</td>
<td>290.0 (3.4 %)</td>
<td>290.4 (4.3 %)</td>
<td>290.3 (5.5 %)</td>
<td>289.8 (5.3 %)</td>
</tr>
<tr>
<td>C-X</td>
<td>292.6 (2.4 %)</td>
<td>292.6 (2.2 %)</td>
<td>292.6 (3.0 %)</td>
<td>291.6 (4.2 %)</td>
</tr>
<tr>
<td>N 1s</td>
<td>10.5 %</td>
<td>4.3 %</td>
<td>1.9 %</td>
<td>0.5 %</td>
</tr>
<tr>
<td>N-6</td>
<td>398.3 (37.5 %)</td>
<td>398.4 (21.7 %)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-Q</td>
<td>400.8 (53.7 %)</td>
<td>400.9 (61.3 %)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyridine-N-Oxides</td>
<td>403.2 (7.2 %)</td>
<td>403.9 (11.3 %)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NOx</td>
<td>405.7 (5.9 %)</td>
<td>406.6 (5.7 %)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O 1s</td>
<td>8.4 %</td>
<td>5.7 %</td>
<td>4.9 %</td>
<td>0.3 %</td>
</tr>
<tr>
<td>O+N</td>
<td>18.9 %</td>
<td>10.0 %</td>
<td>6.8 %</td>
<td>0.8 %</td>
</tr>
</tbody>
</table>
size distributions reported in the literature [21] compared to non-doped carbons. Hence, the states of nitrogen on the carbon surface may be of more interest than their oxygen counterparts.

To further understand the states of nitrogen in CPPy-8-X, high resolution N 1s peaks were obtained. Unfortunately, the high resolution N 1s signals from CPPy-8-1200 and CPPy-8-1400 had poor signal to noise ratio and we were unable to perform a statistically significant deconvolution. Hence, the total N content was determined for all samples, though accurate peak positions and relative at % of distinct nitrogen states could only be determined for CPPy-8-800 and CPPy-8-1000 (Table 7.4). Peaks at 403.1 eV and 405.8 eV were assigned as pyridine-N-oxides and chemisorbed NO\textsubscript{X} groups, respectively [13, 191]. The peak at 398.3 eV represented N-6 groups while the peaks at 400.7 eV in CPPy-8-800 and 400.9 in CPPy-8-1000 were assigned as N-Q groups. N-Q is thought of as an in-graphene nitrogen substitute but also could be protonated N-6 through formation of H-bridge with nearby hydroxyl oxygen or carboxyl group [13].

Taking into account the relative content of nitrogen functionalities of CPPy-8-800 and CPPy-8-1000, it was clear that a significant reduction in atomic content of N-6 (37.5 to 21.7 at %) with concomitant increase of N-Q (53.7 to 61.3 at %) occurred. It has been reported that pyrrolic N-groups are less thermally stable than quaternary and pyridinic N-groups [13, 191]. Thus, the increase in N-Q could be due to the transformation of N-6 to N-Q. However, when we consider that the nitrogen at % decreased overall, the loss of edge groups like N-6 (3.9 to 0.9 at % overall, i.e. 76.9 % loss) was more than that of N-Q (5.6 to 2.6 at % overall, i.e. 53.6 % loss). Therefore, it was difficult to differentiate the amount of N-6 lost from the amount that transformed. Since there was also a clear loss of N-Q groups, it is possible that N-Q transformed into an edge structure similar to N-6 before breaking away from the carbon.
mechanism of evolution of nitrogen functionalities was not clear. Notwithstanding, it was apparent that at higher temperature, N-Q type groups were the dominating nitrogen functional group.

7.2.6 Platinum on Carbon

Pt deposition was carried out without oxidative pre-activation of the CPPA-Xs. Activation of carbon prior to Pt NPs deposition introduces oxygen functional groups and microporosity [53]. Without such pre-activation, Pt NPs on the CPPy-8-Xs were expected to be clustered, especially at high loadings such as 50 wt % which was the target loading in this work. In Figure 7.6e, such clusters of Pt NPs could be observed on Vulcan XC-72R (VC). Comparatively, high resolution TEM images of Pt/CPPy-8-800 and Pt/CPPy-8-1000 (Figure 7.6a and 7.6b) showed a uniform Pt particle size distribution. However, particles in Pt/CPPy-8-1000 were larger than that of Pt/CPPy-8-800; the average size of Pt NPs was 3.7 nm on Pt/CPPy-8-1000 while it was 1.5 nm on Pt/CPPy-8-800. Compared to Pt/CPPy-8-800 and Pt/CPPy-8-1000, agglomeration could be observed in Pt/CPPy-8-1200 and Pt/CPPy-8-1400 despite their high surface areas (Table 7.1). However, the size of Pt NPs on Pt/CPPy-8-1200 and Pt/CPPy-8-1400 were 2.9 and 3.3 nm respectively.

In this work, the differences in Pt NPs size distribution observed in the CPPy-8-Xs could be correlated to their surface properties. The surface area was high (> 500 m²/g) in all of the CPPy-8-Xs, but the surface functionalities and microcrystallinity were different and could be directly tied to the surface N content. The sizes of Pt NPs on Pt/CPPy-8-1000 to Pt/CPPy-8-1400 were comparable, which might suggest a threshold limit of amount of surface functionalities/edge sites per surface area in the CPPy-8-Xs, below which the Pt NPs size was
Figure 7.6 Transmission electron microscopy images of Pt/CPPy-8-800 (a), Pt/CPPy-8-1000 (b), Pt/CPPy-8-1200 (c), Pt/CPPy-8-1400 (d) and Pt/VC (e).
independent. In Pt/CPPy-8-1000, Pt NPs agglomeration was nominal while it was prominent in Pt/CPPy-8-1200 and Pt/CPPy-8-1400. On Pt/CPPy-8-1200 and Pt/CPPy-8-1400, the Pt NPs agglomeration could be assigned to lack of enough N-groups or edge/defect sites while on Pt/CPPy-8-1000, it seemed that the amount of N-groups or defect/edge sites were enough to maintain uniform Pt NPs size distributions. This is supported by observations on Pt/CPPy-8-800, which had the highest N-content (10.5 at %), where the Pt NPs size was the smallest and the Pt size distribution uniform. This suggests that very high N-content can influence Pt NPs size and distribution while moderate N-content can influence Pt NPs distribution only. Hence, a very intricate mechanism of Pt NPs nucleation and growth existed on Pt/CPPy-8-X which warrants a thorough study to assert the influence of nitrogen, oxygen, defects and microcrystallinity separately.

Pt 4f peaks were fitted with three pairs of peaks, pair representing Pt$^0$, Pt$^{2+}$ and Pt$^{4+}$ and their BE position and relative at % are shown in Table 7.5. There were no significant differences in BEs of these peaks among Pt/CPPy-8-X. The peak positions of Pt$^0$ in Pt/CPPy-8-X were similar to that of bulk Pt NPs (71.2 eV). On Pt/CPPy-8-X having Pt size $\geq$ 2.9 nm, this could be attributed to large Pt NPs size. While on Pt/CPPy-8-800, this could be assigned to specific interaction between Pt NPs and the carbon surface due to the carbon pore structure, high N-content and small Pt size (1.5 nm), which was discussed in detail in Chapter 6.

7.2.7 Electrochemical Behavior

Typical cyclic voltammograms (CVs) of the Pt/CPPy-8-Xs and Pt/VC (BASF) in N$_2$ saturated 0.1 M HClO$_4$ at 25 °C is shown in Figure 7.7. The H-adsorption/desorption region (0.0 to 0.4 V) showed characteristic peaks of hydrogen adsorption/desorption at different crystal faces.
Table 7.5. Binding energy (BE) and atomic (at) % of different Pt states in the Pt/CPPA-Xs obtained from deconvolution of high resolution scans of Pt 4f peaks.

<table>
<thead>
<tr>
<th></th>
<th>Pt/CPPy-8-800</th>
<th>Pt/CPPy-8-1000</th>
<th>Pt/CPPy-8-1200</th>
<th>Pt/CPPy-8-1400</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BE (eV)</td>
<td>at %</td>
<td>BE (eV)</td>
<td>at %</td>
</tr>
<tr>
<td>Pt° 4f$_{7/2}$</td>
<td>70.9</td>
<td>19.8</td>
<td>71.3</td>
<td>19.2</td>
</tr>
<tr>
<td>Pt° 4f$_{5/2}$</td>
<td>74.2</td>
<td>14.8</td>
<td>74.6</td>
<td>14.4</td>
</tr>
<tr>
<td>Pt° 4f$_{7/2}$</td>
<td>71.6</td>
<td>20.1</td>
<td>72.1</td>
<td>17.3</td>
</tr>
<tr>
<td>Pt° 4f$_{5/2}$</td>
<td>74.9</td>
<td>15.0</td>
<td>75.4</td>
<td>13.0</td>
</tr>
<tr>
<td>Pt° 4f$_{7/3}$</td>
<td>73.9</td>
<td>17.3</td>
<td>74.0</td>
<td>20.3</td>
</tr>
<tr>
<td>Pt° 4f$_{5/3}$</td>
<td>77.2</td>
<td>13.0</td>
<td>77.3</td>
<td>15.5</td>
</tr>
<tr>
<td>Pt° 4f$_{7/2}$</td>
<td>70.9</td>
<td>19.8</td>
<td>71.3</td>
<td>19.2</td>
</tr>
</tbody>
</table>
Figure 7.7 Cyclic voltammograms of Pt/CPPy-8-Xs and Pt/VC (BASF) in N\textsubscript{2} saturated 0.1 M HClO\textsubscript{4}, 25 °C with a scan rate of 20 mV/s.
of Pt. Pt-oxide formation/reduction was observed between 0.6 and 1.2V. There was no difference in peak positions of H-adsorption/desorption and Pt-oxide formation/reduction peaks among the Pt/CPPy-8-Xs and Pt/VC. The region between 0.4 V and 0.6 V was DL region. The DL region is dominated by the surface area of the carbon support. The thickness of DL regions varied among the catalysts since the surface areas of the carbon support and N-content were different as shown in Chapter 5. This also meant that DL correction in the polarization curves was necessary to make a fair comparison of the ORR activities.

One of the most important pieces of information that can be obtained from the CV is the ECSA of the supported Pt. The ECSA was determined from the area under the hydrogen adsorption/desorption peaks after correction for the DL using Equation 6.1. The ECSAs of the Pt/CPPy-8-Xs are given in Table 7.6. The ECSAs of the Pt/CPPy-8-Xs were higher than that of Pt/VC (BASF) probably due to better dispersion of Pt NPs in the CPPy-8-Xs (Figure 7.6). Although TEM indicated that Pt/CPPy-8-800 had the relatively better Pt NPs size distribution, it had comparatively low ECSA (31 m$^2$/g$_{Pt}$) probably due to poor accessibility because of the small Pt NPs size (1.5 nm) and the amorphous nanostructure. The PSD revealed that most of the pores in CPPy-8-800 were 3.7 nm wide (Figure 7.1) and the average Pt size was calculated to be 1.5 nm from XRD spectra. Since the Pt size is smaller than that of pores, the Pt NPs can reside inside the pores which will obstruct the movement of reactants and decrease accessibility. On top of that, amorphous structures at the surface would further impede the transfer of reactants. Hence, the Pt NPs taking part in ORR in CPPy-8-800 should mostly exist on the surface. This is also expected to decrease the mass activity of Pt/CPPy-8-800.

Pt/CPPy-8-1400 had even lower ECSA (25 m$^2$/g$_{Pt}$) than that of Pt/CPPy-8-800 (Table 7.1). This could be ascribed to the larger size and agglomeration of Pt NPs on Pt/CPPy-8-1400.
(3.3 nm) than that of Pt/CPPy-8-800. Despite large Pt NPs size (3.7 nm), Pt/CPPy-8-1000 had the highest ECSA (65 m²/gPt) because of nominal agglomeration of Pt NPs as discussed above in Section 6.2.2. In addition, CPPy-8-1000 had the highest surface area and pore volume (Table 7.1) compromised mostly of mesopores so that Pt NPs on CPPy-8-1000 could have the best accessibility to the electrolyte among Pt/CPPy-8-Xs. In addition, due to large size of Pt NPs of Pt/CPPy-8-1000 compared to that of Pt/CPPy-8-800, most of them would not reside deep into the pores which are of comparable size (3.7 nm).

7.2.8 Oxygen Reduction Reaction

To determine the specific and mass activities of the Pt/CPPy-8-Xs for the ORR, the Pt/CPPy-8-Xs or Pt/VC (BASF) working electrodes were immersed in O₂ saturated 0.1 M HClO₄ at 25 °C. The electrode potential was anodically scanned at 5 mV/s between 0.1 and 1.1 V vs RHE. The rotation speed of the electrode was modulated at 1600 RPM for all experiments. The ORR polarization curves are shown in Figure 7.8. The mass-transfer limited current at 0.4 V (ca. 5.6 mA/cm²) of the Pt/CPPy-8-Xs was within the 10 % limit of theoretical diffusion limited current, 6.04 mA/cm² at 25 °C which was calculated from the Levich equation (Equation 6.3) assuming a 4 e⁻ reduction [229], which supports the reliability of our experimental setup and methodology.

The RDE technique is a useful tool since the mass-transfer of reactants (O₂) is controlled by the rotation rate of the electrode and can be removed from the data in a straightforward way, yielding the pure kinetic current as a function of potential. The pure kinetic current was determined using Equation 6.2.
Figure 7.8 Anodic scan of Pt/CPPy-8-Xs and Pt/VC (BASF) in O₂ saturated 0.1 M HClO₄, 25 °C with a scan rate of 5 mV/s.
Table 7.6. The weight %, thin-film loading for rotating disk electrode ($L_{Pt}$), electrochemically active surface area (ECSA), specific activity ($I_s$) and mass activity ($I_m$) of the Pt/CPPA-Xs.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Pt wt %</th>
<th>$L_{Pt}$ (µg/cm$^2$)</th>
<th>ECSA (m$^2$/g$_{Pt}$)</th>
<th>$I_s$ (µA/cm$^2$ Pt)</th>
<th>$I_m$ (A/mg$_{Pt}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/VC (BASF)</td>
<td>48.1</td>
<td>18.2</td>
<td>21</td>
<td>297</td>
<td>0.055</td>
</tr>
<tr>
<td>Pt/CPPy-8-800</td>
<td>44.2</td>
<td>16.7</td>
<td>31</td>
<td>226</td>
<td>0.069</td>
</tr>
<tr>
<td>Pt/CPPy-8-1000</td>
<td>44.5</td>
<td>16.9</td>
<td>65</td>
<td>141</td>
<td>0.091</td>
</tr>
<tr>
<td>Pt/CPPy-8-1200</td>
<td>43.4</td>
<td>16.5</td>
<td>45</td>
<td>181</td>
<td>0.082</td>
</tr>
<tr>
<td>Pt/CPPy-8-1400</td>
<td>46.9</td>
<td>17.9</td>
<td>25</td>
<td>324</td>
<td>0.080</td>
</tr>
</tbody>
</table>
The specific mass activity \( (I_m) \) and the specific activity \( (I_s) \) of the Pt/CPPy-8-Xs or Pt/VC (BASF) catalyst which are given in Table 7.6. The \( I_s \) and \( I_m \) of Pt/VC (BASF) were 297 \( \mu \text{A/cm}^2_{\text{Pt}} \) and 0.055 \( \text{A/mg}_{\text{Pt}} \) respectively. These values were comparable to the accepted values, 190-200 \( \mu \text{A/cm}^2_{\text{Pt}} \) and 0.062-0.067 \( \text{A/mg}_{\text{Pt}} \), reported by Gasteiger et al. for 40 wt % Pt/VC (ETEK) measured at 60 °C [231].

All of the Pt/CPPy-8-Xs showed higher mass activity than that of Pt/VC (BASF) (Table 7.6). However, only Pt/CPPy-8-1400, which was relatively nitrogen and oxygen free showed better specific activity (324 \( \mu \text{A/cm}^2_{\text{Pt}} \)) than that of Pt/VC (BASF). Though mass and specific activities depend on various factors such as Pt NPs size and structure, dispersion, and interaction with the support, Gasteiger et al. showed that they can be related to the ECSA. On Pt/C catalysts, Studies have shown that the specific activity decreases with increasing ECSA while mass activity increases with increasing ECSA, reaching a shallow maximum [231, 238]. A similar relation between specific activity and mass activity, and ECSA of the Pt/CPPy-8-Xs is observed in Figure 7.9. This showed that the mass and specific activities trend observed in the Pt/CPPy-8-Xs was in accordance with that of Pt/C. However, the ECSA is an indicator of ORR activity, not a direct cause. The relation between ECSA and ORR activities points towards a complex mechanistic effect of Pt NPs size, distribution, and accessibility on ORR activity, although this effect is not completely understood in the literature. In this work too, the trend observed among Pt/CPPy-8-X regarding specific and mass activities suggested a complex synergistic effect dependent upon the Pt NPs themselves and their interaction with the support. Despite the complexity, a guideline to design next generation carbon support doped with nitrogen could be outlined by plotting Pt ORR activities, \( I_s \) and \( I_m \) vs. N-content, which is shown in Figure 7.10.

The data points with unfilled markers are that of Pt/VC (BASF). Figure 7.10A shows that as the
**Figure 7.9a** Specific activity of Pt/CPPy-8-Xs plotted against their electrochemically active surface area (ECSA).
Figure 7.9b Mass activity of Pt/CPPy-8-Xs plotted against their electrochemically active surface area (ECSA).
N-content decreased, the specific activity also decreased, passed through a minimum, then increased. Contrarily, Figure 7.10B shows that as N-content decreased the mass activity increased passing through a maximum and decreased. Since N-content and total heteroatom content are directly correlated, similar dependence of $I_s$ and $I_m$ on total heteroatom content could be deduced. Also, the same trend would be observed if the X-axis were carbonization temperature in Figure 7.10. In this work, one inherent limitation to our thermal preparation method is that at low temperature, the surface functionalities and edge defects are higher while at higher temperatures, the graphiticity is higher. From Figure 7.10A, it could be proposed that N-doped carbon with both high N-content and high graphiticity would enhance the intrinsic activity of supported Pt NPs. Having high graphiticity and N-content would also augment the mass activity because of the possible high intrinsic activity and high ECSA due to narrow size distribution of small Pt NPs. Therefore, future work should focus on preparation methods to decouple the support graphiticity and nitrogen content.

7.3 Summary

NMCs with a disordered pore structure were synthesized from a TEOS-modified SBA-15 template from a pyrrole precursor at temperatures of 800, 1000, 1200 and 1400 ºC. As the temperature increased from 800 to 1400 ºC, the N content decreased from 10.5 at % to 0.5 at %. On the other hand, the graphiticity of the NMCs increased with increasing temperature, evidenced by XRD and Raman studies. When Pt NPs were deposited on the NMCs, it was found that the Pt NPs dispersion improved with increasing N-content, even stabilizing 1.5 nm Pt particles at a loading of 50 wt % on Pt/CPPy-8-800 (10.5 at % N). Moreover, based on the XRD and TEM results, it was suggested that above a certain threshold, the N-content also determines
Figure 7.10a Specific activity of Pt/CPPy-8-Xs and Pt/VC (BASF) plotted against their nitrogen content. The temperatures indicate the carbonization temperatures of the CPPy-8-Xs. As temperature increases, the amount of surface functionalities (nitrogen and oxygen) decreases while the graphiticity increase (fewer defects, bigger carbon crystallites).
Figure 7.10b Mass activity of Pt/CPPy-8-Xs and Pt/VC (BASF) plotted against their nitrogen content. The temperatures indicate the carbonization temperatures of the CPPy-8-Xs. As temperature increases, the amount of surface functionalities (nitrogen and oxygen) decreases while the graphiticity increase (fewer defects, bigger carbon crystallites).
the Pt NPs size. The improvement in dispersion with N increasing content and stabilization of very small Pt particle sizes at high loading suggest a strong bonding of Pt with the N-modified surface.

The enhanced interaction between Pt and N-modified supports also significantly influenced the ORR activity of supported Pt nanoparticles. The ORR mass activity and the specific activity of Pt NPs supported on NMCs showed a reciprocal relationship. ORR mass activity was highest for the Pt/CPPy-8-1000. The ORR specific activities were very high for Pt/CPPy-8-800 and Pt/CPPy-8-1400 and the lowest for Pt/CPPy-8-1000. The high specific activity of Pt/CPPy-8-1400 is likely the result of the large Pt size (3.3 nm). Pt/CPPy-8-800 was expected to exhibit the lowest ORR specific activity because of the small Pt size (1.5 nm); however, the combination of high N-content in CPPy-8-800 and small Pt particle size led to an N-promoted enhancement in the specific ORR activity. Due to the high N-content, the interaction between the N-doped support and the catalyst was enhanced so that the activity increased despite non-optimal Pt NPs size. Therefore, by controlling the N-content, the Pt loading may be greatly decreased in future catalysts.
8.1 Conclusions

NOMC with high N-content was successfully synthesized from pyrrole using a SBA-15 template. Compared to Vulcan XC-72R, NOMC had higher capacitance and enhanced ORR activity. Most of all, NOMC was shown to be more resistant to corrosion than VC. This showed that a highly corrosion resistant and active N-doped ordered mesoporous carbon could be made from polypyrrole precursor and SBA-15 template.

The NOMCs were heat treated post-synthesis to different temperatures. There was a gradual decrease in N-content as the temperature increased. On the other hand, as the temperature increased graphiticity increased, which was indicated by an increase in basal plane area and stack height of carbon crystallites calculated from Raman and XRD spectra respectively. Moreover, the basal plane size of the heat treated NOMC were smaller than NOMC made from sucrose, which showed the defect-inducing effect of the doped nitrogen. However, there was no change in pore diameter and the decrease in BET surface area and pore volume was ca. 5%. Also, TEM images showed similar amorphous nanostructure. Hence, the pore structure was held constant. The DL capacitance was obtained at potential of zero charge where the effect of pseudocapacitance could be neglected and the DL capacitance can be said to be due to space-charge capacitance. The effect of nitrogen is to enhance the space-charge capacitance of the basal planes of carbon. The other effect of nitrogen was to introduce more defects and keep the carbon crystallites smaller, thus exposing a greater number of edge planes. The edge planes have
higher capacitance than the basal planes and could be the main reason for the decrease in capacitance with increasing temperature. Thus the effect of nitrogen was shown to be two-fold, creation of defects and changing electronic properties, which affects the DL capacitance.

For application of NOMC as a support for Pt nanoparticle electrocatalysts, alternative nanostructure was explored. The pore size of the template was reduced by hydrolysis and condensation of TEOS. The resulting NMC had ordered to amorphous nanostructure as revealed by TEM. There was change in microcrystallinity i.e. more defects were present in the NMC having amorphous nanostructure shown by Raman spectroscopy. However, the atomic percentage and types of surface C and N functionalities did not differ with the structure if the temperature was constant. When Pt was deposited, although the Pt size were similar, only NMC with amorphous nanostructure showed shift in BE as that of bulk Pt. Therefore, high N-content was important for small Pt size but the amorphous nanostructure was important for making the Pt NPs behave like bulk Pt. Not surprisingly, Pt NPs supported on NMC with amorphous nanostructure also showed higher intrinsic ORR activity. Hence, it was concluded that the amorphous nanostructure could enhance the effect of the nitrogen functionalities in establishing Pt support interaction, which increased its activity.

Next, the NMCs with amorphous nanostructure were synthesized at temperatures; 800, 1000, 1200 and 1400 °C. Again, a decrease in N-content and increase in graphiticity, indicated by increase in carbon crystallite size, was observed from XPS, Raman and XRD results. After deposition of Pt NPs, it was found that up to a certain threshold, N-content determines both particle size and dispersion, then it controls only dispersion. After that point, as the N-content decreases further, both Pt size and dispersion are not controlled by N-content. When talking about the effect of N-content, the effect of graphiticity should be thought to be reciprocal. The
ORR specific activities of Pt NPs went through minima when plotted against N-content or graphiticity. The high intrinsic activity of Pt NPs on NMC with the highest N-content was expected to exhibit the lowest ORR specific activity because of the small Pt size was unexpected. This also shows that both N-content and amorphous nanostructure were crucial in enhancing activity of highly dispersed small-sized Pt NPs. Thus, the intrinsic activity of Pt NPs could be increased by increasing both graphiticity and N-content. Therefore, control of Pt NPs size and dispersion, and stabilization of small Pt NPs (< 2 nm) through enhanced interaction aided by nanostructural modification was shown to be the role of N-doped in carbon for catalyst support.

8.2 Future work

In this work, the role of graphiticity and N-content were shown to be interdependent. Both of these properties have to be optimized to make the carbon better suited for electrochemical applications. However, this can be a hinderance if graphiticity and N-content has to be independently controlled. In this work, both capacitance and catalyst support high nitrogen content has been shown to be advantageous. In capacitance, the increase in edge planes is beneficial, but it does not mean that graphiticity has to be sacrificed. It just means that there should be a strategy to orient edge planes facing the electrolyte. In the case of ORR electrocatalysts support, higher graphiticity could lead to enhancement of nitrogen-induced surface catalyst-support interaction. However, the synthesis procedure applied in this work results in a reciprocal relationship between N-content and graphiticity. Hence, a better route to synthesize N-doped carbon with both high N-content and high graphiticity should be explored. In the literature, this is achieved through a post-synthesis treatment such as ion-implantation. A similar technique can be applied in NOMC. Highly graphitic nitrogen-free NOMC can be
synthesized using precursors such as furfuryl alcohol, mesophase pitch, etc. Such highly graphitic NOMC can also be synthesized by chemical vapor deposition of carbon precursors such as CH₄. However, in this approach, the microstructure modification due to N-doping would not be present. Hence a better approach might be to use a precursor yielding a high N-content such as aminoguanidine hydrochloride or use NH₃ and CH₄ as precursors in CVD and modulate N-content and graphiticity through heat.

One of the great mysteries in this field of N-doped carbon is how to control the state of nitrogen. Until now, temperature and precursors are the only tools to control the nitrogen functionalities. Hence, future studies should focus more on this using different precursors and synthesis route to better control the state of nitrogen. However, such strategy results more than one nitrogen functionality. In the literature, pyridinic-N is believed to be one of the most important surface N-groups. However, no strategy exists to synthesize N-doped carbons with just pyridinic N-groups. Even the location of pyridinic-N, edge vs basal planes is controversial. Although traditionally pyridinic-N is thought to be edge group, some believe that pyridinic-N can occur at basal planes in aggregation. The basal plane pyridinic-N might be more influential in determining properties of nitrogen-doped carbon than the edge plane pyridinic-N. Therefore, a more thorough experimental and theoretical work should resolve this issue.

Apart from understanding and improving physicochemical properties of N-doped carbon, the properties of the N-doped carbon could be enhanced with a superior nanostructure. The DL capacitance has been shown to increase when the pore size of the carbon is comparable to the ion size due to removal of the solvation layer. Thus, by modulating size of pores in NOMC, the DL capacitance could be enhanced. However, to accomplish this efficiently pore filling should be enhanced which can be done by surface functionalization of the SBA-15 or choosing a suitable
precursor. This should be accompanied by a decrease in the size of the monolith NOMC particle or create a hierarchal pore structure so that the diffusion of ions in the system is efficient.

Similarly, for real PEMFC application, the mass-transfer resistance should be lessened. Again, this could be achieved by making a mesoporous-macroporous hierarchal pore structure or decreasing particle size of the NOMC. The results show that the enhancement of catalyst-support interaction in N-doped carbon is also due to amorphous nanostructure. Based on the particle size, the surface area of 1.5 nm Pt NPs should have been 8 times more than the 3 nm Pt NPs assuming uniformly dispersed hemi-spherical particles. This was not the case which was due to inaccessibility due to small Pt NPs and 3D amorphous nanostructure. By proper design, accessibility to this small catalyst particle could be greatly improved. One of the novel designs to improve mass-transfer while maintaining amorphous nanostructure is presented in Figure 8.1. The mean free path of oxygen molecule at 80 °C and 1 atm is 83.6 nm [239]. Hence, a pore size of 83.6 nm will make the mass-transfer very efficient. However, in the interest of maintaining high surface area, the pore size should be in the mesoporous region (2-50 nm). In addition, loading and size of Pt NPs, ionomer to carbon ratio, MEA fabrication process and humidity complicates the estimation of the optimum pore size of advanced mesoporous carbon. Careful experimental and theoretical work is needed to predict the optimal pore size.
Figure 8.1 Novel designs to improve NOMC as catalyst support.
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