GENESIS AND EVOLUTION OF POROSITY AND MICROSTRUCTURE IN NANOPOROUS CARBON DERIVED FROM POLYFURFURYL ALCOHOL

A Thesis in
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by

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Rosalind Franklin first termed carbons derived from the pyrolysis of polymer precursors as either graphitizing or non-graphitizing. The classification was determined by the tendency of the amorphous carbon to convert to crystalline graphite when annealed at temperatures above 1000 °C. A unique property of non-graphitizing carbon is native nanoporosity, pores with widths less than 2 nm. The pores act as molecular sieves and are able to separate molecules based on size and shape. Nanoporous carbons (NPC) are utilized in gas separation membranes, catalysis, and electrical double layer capacitors. The disordered structure of the carbon is attributed to the presence of extensive cross-linking in its precursor.

Polyfurfuryl alcohol (PFA) is an example of a non-graphitizing carbon precursor. Numerous researchers have studied this polymer-carbon system and acquired extensive knowledge in the areas of polymerization, pyrolysis, activation, and high temperature treatment. Investigating the genesis and evolution of porosity in all aspects of carbon synthesis is critical to engineering the carbon to meet required design criteria, which include pore widths and volumes, surface area, and microstructure.

Four topics are examined herein: 1) Tuning of PFA polymerization and cross-linking in order to direct changes in carbon structure and porosity; 2) the autogenesis of porosity during pyrolysis; 3) the evolution of porosity and microstructure during annealing of non-activated and activated carbon; 4) the effectiveness of activated NPC as an electrode in an electrical double layer capacitor.
Efforts to modify the molecular weight and degree of cross-linking in PFA were successful; however the variations were not propagated to the carbon. The polymers were assimilated during pyrolysis due to the continued polymerization which occurred up to the point of decomposition. Thus bulk production of NPC could proceed from PFA synthesized by any method with the assurance that the properties of the product are consistent. The exception was carbon derived from mixtures of PFA and Triton X-100, a surfactant. With sufficient amount of the surfactant present, mesopores were generated in the nanoporous carbon. Pyrolysis, rather than polymerization, was the key step in the synthesis of purely nanoporous carbon.

The pyrolysis of polyfurfuryl alcohol was studied up to 600 °C. Nanopores appeared in the carbon as early as 300 °C along with significant amount of mesopores. As the pyrolysis temperature was increased, nanoporosity was retained, but the mesoporosity disappeared. At 600 °C the average pore width was 0.4-0.5 nm. Between 300 and 400 °C, both polyaromatic domains decorated with hydrogen and oxygen (hetero) atoms and partially decomposed polymer chains coexisted. The unreacted polymer and heteroatoms induced mesoporosity by buffering the nanopores created by polyaromatic domains. Raising the pyrolysis above 400 °C released the buffering material, thereby collapsing the mesopores.

A new pathway to synthesize a carbon with both nanoporosity and pre-graphitic structures was discovered by annealing a nanoporous activated carbon at 2000 °C. The activation process permitted the carbon to overcome its intrinsic barrier to graphitization. Prior to activation the nanopore walls were comprised of disordered graphene layers. Activation eliminated the barrier to graphitization by reducing the number of layers and
removing carbon material highly susceptible to oxidation. High temperature annealing at 2000 °C of a carbon activated to 84% burnoff induced the formation of pre-graphitic domains amongst the nanoporous carbon. The structures were termed pre-graphitic as order extended in two dimensions. (002) bands were identified and assigned to amorphous, turbostratic, and graphitic carbon. A nanopore volume of 0.50 cm³ gm⁻¹ was preserved after annealing. The product was heterogeneous, exhibiting both nanoporosity, a property of non-graphitizing carbon, and pre-graphite, a property of crystalline graphite.

Two electrode capacitors were fabricated utilizing activated nanoporous carbons. The performance of carbons derived from polymers synthesized in the presence of either the solvent tetrahydrofuran or surfactant Triton X-100 was compared. Triton X-100 acted as a mesopore former during pyrolysis. The initial mesoporosity influenced activation by allowing generation of additional mesoporosity at all burnoffs. Whereas, the carbon derived from polymer with tetrahydrofuran did not exhibit significant mesoporosity until a burnoff of 80%. Nanopore volumes as high as 0.98 cm³ gm⁻¹ at an average diameter of 0.82 nm were achieved. Constant current capacitances of 106 F gm⁻¹ and 109 F cm⁻³ were measured for carbon activated to just 15% burnoff with a nanopore volume of 0.28 cm³ gm⁻¹. The highest capacitance measured was 164 F gm⁻¹. The volumetric capacitance was 88 F cm⁻³ due to extensive activation and a lower bulk density. Polylurafurcetyl alcohol derived nanoporous carbon had tunable porosity and was an excellent material for capacitor electrodes.
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Chapter 1

Nanoporous carbon: an overview

1.1 Introduction

In 1951 Rosalind Franklin first classified non-graphitic carbons derived from the pyrolysis of organic polymers as either graphitizing or non-graphitizing depending on their tendency to undergo transformation from a disordered structure to highly ordered graphite when annealed at temperatures above 1000 °C [1, 2]. Non-graphitic carbons are amorphous, whereas the most thermodynamically favorable form of carbon is graphite. Non-graphitizing carbons remain amorphous at high temperature, and are inherently nanoporous, thermally stable, and resistant to chemical attack [3]. These unique properties have been attributed to the presence of extensive cross-linking in the precursor, which manifests as a disordered, chaotic misalignment of graphene layers in the carbon after pyrolysis [4]. The robust nature of non-graphitizing carbons has made them ideal candidates for a variety of applications including gas separation, catalyst supports, electrodes in lithium ion batteries, and electrical double layer capacitors. Investigating the genesis and evolution of porosity in all aspects of carbon synthesis, from polymerization, to pyrolysis, activation, and high temperature treatment, is critical to engineering the carbon to meet specific requirements of these applications. Design parameters include pore diameters and volumes, surface area, and microstructure. Over the last sixty years a wealth of knowledge has been accumulated with respect to the
structure and properties of non-graphitizing carbon, yet the intrinsic barrier to graphitization is still not entirely understood.

Polyfurfuryl alcohol (PFA) is an example of a polymer which upon pyrolysis decomposes to form a non-graphitizing carbon [5]. This material is termed nanoporous carbon (NPC). Understanding the complex structure of PFA and NPC requires attention to each step in the material’s synthesis. A review of publications relevant to polymerization, pyrolysis, activation, and high temperature treatment is provided. The utility of NPC in several applications is relayed, with special attention paid to electrical double layer capacitors. Finally, the specific objectives of the thesis are outlined.

1.2 Applications for nanoporous carbon

Polyfurfuryl alcohol pyrolyzed at 500-800 °C in an inert atmosphere yields 25-50% by weight carbon, which is inherently porous with a narrow distribution of pore widths centered at ~0.5 nm [6]. Pores less than 2 nm in width are defined as micropores by IUPAC [7], however recently the term nanopore has gained acceptance as it more appropriately describes the pore size dimension. The intrinsic pore volume is ~0.2 cm$^3$ gm$^{-1}$ [8]. In the past, mesoporosity has been incorporated in the carbon by simply blending polyethylene glycol (PEG) into the precursor [9-11]. Mesopores are defined as having diameters between 2 and 20 nm [7]. Macropores, >20 nm in diameter [7], can be controlled by varying the viscosity of the resin [12]. Skeletal densities of NPC are significantly less than graphite (2.25 gm cm$^{-3}$) and range from 1.4-1.8 gm cm$^{-3}$ [13].
Due to its narrow distribution of nanoporosity and chemical and thermal stability, NPC has been utilized in the areas of gas separation and catalysis. The nanoporosity gives rise to the property of molecular sieving, whereby molecules are separated, or excluded from pores, based on their size and shape [14]. Acharya et al. brush coated macroporous non-selective stainless steel discs with a commercially available PFA resin (Durez) and then pyrolyzed to from a supported NPC membrane [15]. Permeances for H₂, He, Ar, O₂, N₂, and SF₆ were measured. O₂/N₂ selectivity was 2-3. Disc membranes were also fabricated by a spray coating method [16]. Shifflett and Foley ultrasonically deposited thin films of PFA onto tubular supports to create NPC membranes with an ideal O₂/N₂ selectivity of 30.4, but permeance was low [17]. Merritt et al. have realized higher performance membranes by modification of the support with silica nanoparticles [18, 19]. A two order of magnitude improvement in permeance, compared to the previous studies, was reported with selectivity up to 6. An air stream was enriched to 48% O₂ by volume. Carbon molecular sieves for pressure-swing-adsorption were also developed based on PFA derived carbons [20].

Membrane reactors combine reaction and separation in a single unit operation, and thus provide the ability to enhance the product yield by continuous removal of products from the reactor [21]. This concept was utilized by Strano and Foley to decompose methyl tert-butyl ether (MTBE) into isobutylene and methanol [22]. A selective carbon membrane was prepared and doped with catalyst. In a semi-batch reactor the conversion of MTBE was 96.5% versus 64.1% for a non-selective membrane. Platinum nanoparticles were incorporated into a NPC membrane and propylene was selectively hydrogenated in a mixture including 1-butene and isobutylene [23].
Platinum has also been supported on bulk NPC derived from PFA [24]. Access to the active catalyst site was controlled by diffusion through the molecular sieving nanopores. Schmitt and Walker coated an activated carbon with a selective NPC skin [25-27]. The catalyst’s effectiveness was demonstrated by favorably hydrogenating 1-butene in the presence of 3-methyl-1-butene. Sintering of Pt nanoparticles at high temperatures is a problem in the case of metals supported on a surface; however entrapping the particles in the NPC matrix blocked sintering even after multiple heating cycles to 800 °C [28]. A TEM image of a Pt nanoparticle (4 nm diameter) embedded in NPC is shown in Figure 1.1, the image is reproduced from Ref. [28].

![Figure 1.1: Platinum nanoparticle embedded in nanoporous carbon.](image)

Carbon monoliths have been prepared according to a patent held by Hucke [29] and doped with iron particles [30]. Recently enzyme catalysts were supported as well [30].

Solid-base catalysts were synthesized by dispersing cesium metal in NPC [31-34]. Curiously, the cesium also caused spontaneous reorganization of the non-graphitizing carbon into polyhedra and other nanotube-like structures at temperatures as low as 50 °C.
[35, 36]. It has been confirmed that similar transformations occur with sodium, potassium, and rubidium metals.

1.2.1 Electrical double layer capacitors

Development of electrodes for electrical double layer capacitors (EDLC) based on carbon materials has recently garnered tremendous interest. Carbon is environmentally benign and exists in numerous forms; examples are powders, fibres, fabrics, and foams [37]. Within the operating temperature range of EDLCs carbon is thermally stable and also resistant to acid and base attack. Research in the field of EDLCs is fuelled by applications demanding high energy density, power density, and longevity [38]. Examples of technologies benefiting from EDLC research include hybrid vehicles, uninterruptible power supplies, solar energy storage, and rechargeable power supplies for consumer electronic devices [39].

Energy storage in an EDLC is based on separation of charged species in a double-layer formed at the electrode/electrolyte interface [37]. Thus an effective EDLC should be designed to maximize the area of the electrode contacting the electrolyte solution [39]. Activated carbons possess high surface areas; however maximum surface area does not necessarily correlate to maximum capacitance [40, 41]. Nanopores strongly contribute to a carbon’s surface area, yet small pores block entry of large solvated ions in the electrolyte and prohibit formation of the double-layer. Aqueous electrolytes are able to reach pores 0.5 nm in diameter [37]. Larger mesopores and macropores improve electrolyte transport, but do not contribute significantly to the carbon surface area. Their
presence decreases the bulk density of the carbon and negatively impacts the volumetric capacitance of the material. An ideal activated carbon electrode would have high surface area and pores in the range of 1-5 nm [42].

Numerous activated carbons have been investigated as potential EDLC electrode materials. Raymundo-Piñero et al. activated heat-treated bituminous coal with KOH to reach surface areas between 800 and 3000 m² gm⁻¹ and pore diameters in the range of 0.7-1.5 nm [43]. In an aqueous KOH electrolyte capacitance up to 286 F gm⁻¹ was reported. KOH-activated anthracite was utilized by Bleda-Martínez et al. who reported a maximum value of 321 F gm⁻¹ in a three-electrode cell [44, 45]. The authors also examined pitch and PAN-based carbon fibres, which depending on the KOH or NaOH activation conditions gave capacitances between 90 and 230 F gm⁻¹. Physical activation of the pitch-based fibres with either CO₂ or steam yielded 118-148 F gm⁻¹. Wang and Teng pulverized PAN-based fibres to prepare a material with a capacitance of 290 F gm⁻¹, again with respect to a reference electrode in sulphuric acid electrolyte [46]. Three electrode cells are not true capacitors and the values are greater than those measured in two electrode cells for the same materials.

Resorcinol-formaldehyde polymer-based carbons prepared by Zhang et al. had surface areas of ~800 m² gm⁻¹ and pore diameters of ~2 nm without activation [47]. Capacitances of ~200 F gm⁻¹ were measured in a two electrode system. Chmiola et al. have employed carbide derived carbons [48]. Templated mesoporous carbons were tested by Fuertes et al. [49, 50]. Mesoporous silica was impregnated by furfuryl alcohol and polymerized in-situ. Removal of the template left carbons with monodisperse mesopores
at 2.8 and 8 nm. In sulphuric acid capacitances between 127 and 199 F gm$^{-1}$ were realized.

### 1.3 Polymerization of furfuryl alcohol

Furfuryl alcohol (FA) monomer, Figure 1.2, is a natural reagent found in oat bran, sawdust, tobacco, and other biomasses [51]. Cationic polymerization of FA occurs in the presence of either a Bronsted or Lewis acid [52]. The reaction is highly exothermic and insufficient heat removal can lead to thermal runaway.

![Figure 1.2: Furfuryl alcohol.](image)

Dunlop and Peters determined that the early stages of polymerization were dominated by competitive head-to-tail and head-to-head condensations, as shown in Figure 1.3 [51]. Furan rings were connected by either methylene or ether bridges. The latter spontaneously decomposed to a methylene linkage by loss of formaldehyde. Increasing the reaction temperature or acidity of the solution reduced the instances of head-to-head condensation [53]. If the polymerization continued along these two simple pathways, a colorless, high molecular weight, linear polymer would have resulted. Instead the solution darkened to brown as cross-linking occurred and the molecules became highly branched. Cross-linking reactions were accelerated by high temperature or catalyst concentration and long reaction times. The nature of cross-linking has been
investigated by a number of researchers; none have given a definitive solution to the structure.

![Initial products of the linear condensation of furfuryl alcohol.](image)

**Figure 1.3**: Initial products of the linear condensation of furfuryl alcohol.

Conley and Metil characterized PFA catalyzed by ferric chloride, benzenesulfonic, p-toluenesulfonic (pTSA), oxalic, and sulfuric acids [54]. Thermal polymerization by heating the monomer in the absence of an acid was also analyzed. Irrespective of the initiation method, the infrared (IR) spectra of the resulting polymers were identical. During polymerization the mixture was blanketed by 460 mm nitrogen to prevent polymer oxidation and facilitate removal of water during the reaction. Water led to undesired hydrolysis of furan rings to form levulinic acid [51] or γ-diketone [54] species. Oxidative degradation also produced γ-diketones [55]. The resins were cured by mixing in additional benzenesulfonic acid and heating at 100-200 °C under flowing nitrogen. An examination of the IR spectra after curing indicated a reduction in the hydroxyl stretch and out-of-plane bending of the hydrogen at position 5 on the furan ring,
which was consistent with extended polymerization via head-to-tail condensation. An increase in the resin’s brittleness signified the occurrence of a cross-linking reaction. The authors concluded the most probable cross-linking mechanism was an attack by the active species on the methylene bridge between furan rings, but were unable to provide convincing spectroscopic evidence.

Chuang, Maciel, and Myers interpreted solid-state $^{13}$C NMR spectra of cured PFA resins as confirmation of the methylene bridge cross-linking mechanism [56, 57]. The structure of a methylene bridge cross-link is shown in Figure 1.4. A neutralized PFA resin was combined with 3% by weight BF$_3$·NH$_2$C$_2$H$_5$ (trifluoroboron ethylamine, TFBE), which is commonly used to accelerate curing of thermosetting resins, and heated at 100 °C under nitrogen. Spectra were collected at various times up to 160 minutes. Figure 1.5 is a reproduction of the Maciel et al. data. Major peaks were in agreement with other studies [58] and were assigned to the structure as follows: 150 ppm, 2- and 5-positions on the furan ring; 110 ppm, 3- and 4-positions of the furan ring; 28 ppm, methylene bridge. There were several notable peaks related to cross-linking phenomena. At 40 minutes a small peak appeared at 125 ppm. It was attributed to cross-links formed at the β-positions of the furan ring, but dismissed as a minor occurrence. The peak at 36-44 ppm, which appeared after 20 minutes and continued to grow significantly over time, was assigned to a CH species formed by cross-linking at the methylene bridge. A peak at 140 ppm, corresponding to –H terminated chains, appeared simultaneously. The TFBE complex was thought to fracture the polymer backbone and attach an ethylamine group to one fragment, although amine species were not detected in the $^{13}$C spectrum. The other segment was –H terminated, explaining the growth in the peak at 140 ppm. Several steps
were omitted; it is inferred the BF$_3$ species activated a methylene bridge by extraction of a hydride ion and the new carbocation displaced the ethylamine group to create a cross-link.

![Cross-link formed at a methylene bridge on the backbone of PFA.](image)

**Figure 1.4:** Cross-link formed at a methylene bridge on the backbone of PFA.

![Solid-state $^{13}$C NMR spectra of PFA resins collected after various times at 100 °C.](image)

**Figure 1.5:** Solid-state $^{13}$C NMR spectra of PFA resins collected after various times at 100 °C.
Choura, Belgacem, and Gandini conducted a more detailed study utilizing numerous model compounds in an effort to isolate specific reactions and explain the origin of cross-links in PFA [59]. Several mechanisms previously proposed to explain cross-linking were disproved. The possibility of branching at the $\beta$-position was clearly ruled out. It was shown that ring hydrolysis was not required to form cross-links. Most importantly, the authors demonstrated that the methylene bridges were inert to attack by the carbocation and not directly involved in the cross-linking reaction. The authors suggested cross-linking requires that mobile hydrogen atoms, present on the polymer backbone in the form of CH$_2$ groups, undergo a series of hydride ion abstraction and proton expulsion reactions, which leaves the polymer highly conjugated. The reaction scheme is elaborated in Figure 1.6. The active center of a propagating chain removes a hydride ion from a CH$_2$ group along the backbone a separate polymeric unit, distributing a positive charge between the two adjacent furan rings. To neutralize the charge a proton is expelled, forming a sequence of conjugated bonds. The propagating chain is terminated, the freed proton is able to initiate another monomer, and the conjugated polymer is eligible to undergo another series of the same reactions. A UV-visible spectrum of the polymer confirmed the presence of the unsaturated sequences.
Figure 1.6: Sequence of reactions leading to conjugation along the backbone of PFA.

Once conjugated, cross-linking was proposed to occur via attack on the unsaturated bridge carbon, shown in Figure 1.7, or a novel Diels-Alder condensation, shown in Figure 1.8. The unsaturated carbon in Figure 1.7 is more reactive towards an active center than the previous –CH₂ bridge. It must be inferred the active center is transferred to the neighboring –CH group by reforming the furan ring. Expulsion of a proton creates another conjugated sequence. In the Diels-Alder condensation the furan ring acts as a diene, while the conjugated sequence acts is a dienophile. Reagents comprised of furan rings are commonly utilized in Diels-Alder syntheses [60]. Conjugation was proven experimentally. Principe et al. have provided evidence of the methylene bridge mechanism [61], but the DA cross-linking mechanism is unproven.
The rate of polymerization and polymer molecular weight in cationic systems are affected by changes in the reaction medium [62]. High-polarity solvents promote the formation of free ions, rather than ion pairs. Free ions lead to an increased rate of propagation. Another determining factor is the reaction temperature. Chain transfer reactions in cationic polymerization are inhibited by polymerizing at lower temperature, thereby enabling propagation [62]. Time and catalyst concentration also increase the conversion of FA [63-69]. Several kinetic studies on the polymerization of FA have been conducted [70-72]. Based on NMR experiments Glowinkowski and Pajak confirmed the occurrence of extensive cross-linking as PFA was heated above 100 °C, but lower than its decomposition temperature [73]. Finally, Buchwalter polymerized furfuryl acetate to
obtain a polymer with a chemical structure analogous to PFA, but with higher molecular weight [74]. Cross-linking occurred more rapidly for polyfurfuryl acetate.

Following polymerization, the PFA is carbonized by pyrolysis to derive NPC. Prior work related to this process is elaborated in the next section.

1.4 Pyrolysis of polyfurfuryl alcohol

In order to understand the pyrolysis process, NPC formed by decomposition of PFA has been characterized over a range of temperatures by several techniques, which include infrared and Raman spectroscopy, x-ray diffraction, temperature programmed oxidation and NMR [75-80]. A Monte-Carlo simulation approach was undertaken by Kumar et al. [81]. Studies relating the development of porosity are summarized in detail in this section. Additionally, the pyrolysis mechanism of an analogous system is given.

Fitzer and Schafer utilized infrared spectroscopy (IR) to examine the pyrolysis of PFA [6, 82]. The furan ring was found to be stable up to 275 ºC. Between 300 and 400 ºC the furan ring ruptured and released CO, CO₂, and H₂O. Aromatic units appeared around 400 ºC as the fragments began to coalesce. At temperatures greater than 450 ºC a reaction of the remaining methylene bridges with water to form keto groups was proposed. In the same temperature range, formation of methane ceased due to the oxidation of methylene bridges and a significant amount of hydrogen was released. Liberation of CO and H₂ continued at higher temperatures as the carbonyl groups decomposed and aromatic domains coalesced. The final carbon was described as a highly unsaturated aromatic network. The authors speculated that in the intermediate
state between the polymer and the final carbon, open pores with diameters smaller than 100 Å must be present that allowed the transport of gaseous products formed during the pyrolysis. There was no experimental evidence given to prove this hypothesis.

Mariwala and Foley observed the development of porosity in NPC as a function of maximum pyrolysis temperature [4]. Uptake of CO$_2$ was utilized as a measure of porosity. The adsorption increased seven-fold between 500 and 600 °C and slightly further at 800 °C. Uptake fell to a negligible amount when the temperature was increased further to 1000 °C. At this temperature the pore mouths had closed. Diffusivity of CO$_2$ passed through its maximum at 600 °C. The study utilized commercially available Durez resin.

The difference between pyrolysis of non-cross-linking and cross-linking polymers is exemplified by comparing polyvinylchloride (PVC) and polydivinylchloride (PVDC), which differ by just one chlorine, yet respectively produce graphitizing and non-graphitizing carbon [83, 84]. Pyrolysis of PVC releases one HCl per repeat unit and the remaining fragments easily cyclize to form aromatic domains. One HCl is also liberated during the decomposition of PVDC, but an additional chlorine remains on the polymer chain. Elimination of the second HCl requires an intermolecular reaction, which leads to cross-linking.
1.5 Structure of nanoporous carbon

Multiple model structures of non-graphitizing carbons exist. Rosalind Franklin gave a simplistic model suggesting graphitizing and non-graphitizing carbons are a distribution of $sp^2$-hybridized domains, see Figure 1.9 [1]. In the case of a graphitizing carbon the domains are well aligned at low temperature. Little driving force is required to completely align the domains and form graphite. However, randomly oriented domains connected by disordered, or curved, carbon sheets characterize the non-graphitizing carbon. Misalignment gives rise to porosity [85]. Rearrangement of the domains is unfavorable due to their chaotic distribution and three-dimensional interconnectivity [86].

![Proposed structures of (a) graphitizing and (b) non-graphitizing carbons.](image)

Figure 1.9: Proposed structures of (a) graphitizing and (b) non-graphitizing carbons.

Jenkins and Kawamura suggested a three-dimensional network of curved graphitic ribbons, or microfibrils, which loop around each other with no preferred orientation [83]. The model is shown in Figure 1.10. A similar concept has also been proposed by Stoeckli [87].
Dahn et al. describes a “falling cards model,” wherein the cards are graphenes stacked in a random manner [88, 89]. Based on extensive TEM analysis, Harris envisions the carbon as a collection of multilayered fullerene-like fragments [90-93]. An example is shown in Figure 1.11. Burian and Dore offer supporting evidence [94].
In each scenario the carbon contains a structural component with curvature, which blocks the formation of a highly-ordered graphite structure even at high temperatures. It is known that curvature is forced into a sheet of six-member rings by introducing five and seven-membered rings. The effect has been demonstrated by simulation and verified experimentally by pair distribution function analysis [95-98]. Examples of a graphene containing non-hexagonal rings are shown in Figure 1.12. The image is reproduced from work by Smith, Foley and Lobo [97]. The rigorous definition of a graphene is a single carbon layer of the graphite structure [99]. In this thesis the definition is relaxed to include non-hexagonal rings and describe a single carbon sheet, not necessarily from the graphite structure. Strano et al. have published a review of attempts to model the structure of NPC \textit{in silico} [100]. Conversion of disordered carbon to graphite requires annealing of the non-hexagonal rings out of the graphenes, followed by alignment of the layers along edges and basal planes.

Figure 1.12: Graphenes with non-hexagonal rings.
NPC structure can be directed at the mesoscale by templating [101, 102]. The nanoporous structure of the NPC is maintained while introducing mesopores with controlled diameters and orientation. Zarbin and coworkers polymerized FA within the channels of Vycor glass, which had interconnected 8 nm pores [103]. After pyrolysis the template was removed by etching with HF. The walls of the 8 nm pores were comprised of nanoporous carbon with 0.5 nm pores. Alvarez and Fuertes impregnated mesoporous silica with PFA to produce carbons with controlled mesopore diameters between 2 and 14 nm [104]. Graphitizing carbon has also been templated [105].

1.6 High temperature treatment of nanoporous carbon

Extensive research has been conducted in the area of high temperature treatment (HTT) of graphitizing and non-graphitizing carbons. The process of graphitization in both materials is reviewed by relaying the results of several authors.

Catalytic graphitization occurs in the presence of a variety of transition metals [106-108]. Several authors have focused specifically on iron catalyzed graphitization of PFA derived carbon [109, 110]. Graphite formed after HTT at less than 1000 °C [111].

Oya and Marsh have written an excellent review of catalytic graphitization [112]. Four types of carbon are created by various processes, typical XRD patterns are shown in Figure 1.13, which is reproduced from Ref. [112]. The G-component (graphite) had a d$_{002}$ of 3.354 Å, and L$_c$ >50 nm. L$_c$ is the size of the graphite crystal is the c-direction, which is perpendicular to the basal plane. The T$_a$-component was considered to be turbostratic carbon, which is a term invented by Biscoe and Warren to describe a carbon
with graphene layers approximately stacked parallel and equidistant, but with random orientation [113]. Values of d_{002} are larger than graphite due to the random stacking. Oya and Marsh gave a range of 3.38-3.42 for d_{002}, although a wider range has been accepted [114]. L_c was 6-20 nm. A-type carbon was more ordered than pre-graphitization, but it remained amorphous in comparison to the G- and T-type carbons. T_n-carbon gave a composite (002) peak with three components: amorphous, turbostratic (2θ=26°), and graphitic (2θ=26.5°).

![Graphite Crystal Growth](image)

**Figure 1.13:** (002) peaks of carbon before (dotted) and after catalytic graphitization (solid).

Research related to purely thermal induced transformations is of interest in the present study. Thermally activated graphite crystal growth occurs via three processes
In-plane crystallite growth is defined as incorporation of non-graphitic carbon into existing graphene layers and occurred at all temperatures. Growth is only in the direction parallel to the layer planes, which is along the a-axis, thereby increasing the crystallite size $(L_a)$ in that dimension. Coalescence of crystallites in the c-direction occurs only above $1000 \, ^\circ C$. Differing crystallites must migrate and align. $L_c$ increases in this scenario. Finally, coalescence in the a-direction requires alignment of crystallite edges, which again increases $L_a$. The process is active above $1400 \, ^\circ C$ in graphitizing carbon, but not until $2400 \, ^\circ C$, or even much greater, in non-graphitizing carbon.

Based on detailed XRD and TEM analysis, Oberlin and coworkers have proposed a model describing HTT of anthracene, which is a graphitizing carbon [116-120]. The carbon microstructure passes through four stages during conversion to graphite. The stages are depicted in Figure 1.14, which is reproduced from Ref. [119]. Pyrolysis creates stage one, where the carbon is comprised of randomly aligned individual basic structural units (BSU). A BSU is a domain of graphene layers approximately 1 nm in diameter and 1 nm thick. Stage two is achieved by removal of labile heteroatoms, which allows alignment of the BSU along the c-axis to form distorted columns. Heteroatoms are generally oxygen and hydrogen. Inter-layer defects are annealed out of the structure during stage three, leaving turbostratic carbon with wrinkled layers. Removal of heteroatoms fixed at the defects in the layers permits the defects to heal and form highly crystalline graphite at stage four.
Figure 1.14: Stages of graphitization, as proposed by Rouzaud and Oberlin.

The authors also investigated saccharose based carbons, which are non-graphitizing. They found the heteroatoms more strongly affixed to the BSU in the case of saccharose. The H/C ratio of saccharose at 1500 °C equaled anthracene at just 900 °C. The non-graphitizing carbon passes through the same four stages as the graphitizing carbon, but the crystallization occurs on a much smaller scale. Movement of the BSU is retarded by cross-linked structures and extreme long range disorder. Therefore the number of BSU involved in the four stages is small, whereas many BSU interacted over
long ranges in the graphitizing carbon. Saxena and Bragg have given a similar model [121].

Inagaki has shown that increased pressure forces graphitization of a non-graphitizing carbon at temperatures as low as 1800 °C [122]. Franklin reported heterogeneous graphitization of non-graphitizing carbon at ambient pressure [123]. The transformation is referred to as stress graphitization. The cross-linked structures in non-graphitizing carbon are immobile at high temperature, which prevents homogeneous graphitization, but causes a buildup of great internal stress during annealing. Once the structure breaks down, small regions of highly ordered graphite are formed under high pressure imparted by the surrounding matrix. Honda et al. observed this phenomenon for a non-graphitizing carbon derived from an acetone-furfural resin [124]. Above 2400 °C a composite (002) XRD line was seen. Peaks at 26 and 26.5° were superimposed over a broad background. The lines sharpened when HTT was increased up to 2950 °C. In a short communication Reiswig et al. attributed graphitization of PFA carbon to the presence of strain [125]. Graphitization has also been promoted by HTT under a partial pressure of oxygen [126-129].

Several studies have tested the relationship between porosity and graphitization. Kawamura and Tsuzuku varied the bulk density of pellets of compacted carbon powders [130]. An optimum bulk density maximized stress graphitization by balancing stress concentration and release of strain. The strain release was more difficult in denser carbons due to greater contact between grains in the specimen. Kamiya and Suzuki prepared a continuous carbon derived from phenolformaldehyde resin with pore sizes of ~100 μm [131]. Preferential stress graphitization was observed in regions surrounding
the pores. The role of microporosity was studied by J. L. Kaae by annealing fast neutron irradiated and unirradiated carbons [132]. Densification and a slight increase in L_c occurred upon irradiation. Further growth of L_c in the irradiated carbon with HTT mirrored the unirradiated carbon. The only difference was the small offset introduced by irradiation. Kaae concluded the presence of microporosity had no effect on the tendency of the carbon to graphitize.

HTT of NPC reduces nanopore volume and surface area [133, 134]. Mariwala et al. reported a sharp drop in CO_2 diffusivity at temperatures above 800 °C [4]. Skeletal density measurements performed by Kipling et al. have indicated the formation of closed pores in non-graphitizing carbons [135, 136]. The reduction in surface area corresponded to a drop in the skeletal density. If the disordered carbon comprising the pore walls was crystallized, the density would have increased. Therefore, only the entrances of the open pores were closed, leaving an open void in the carbon matrix inaccessible to helium. Closed porosity does not exist in graphitizing carbons. Pore closure was also documented in an activated carbon by McEnaney and Dovaston [137]. At low HTT (1200 °C) closed microporosity was recoverable up re-activation. However following greater HTT, only meso- and macropores were generated by activation. The process of activation is described further in the following section.
1.7 Activation of nanoporous carbon

Additional porosity beyond the intrinsic volume can be generated by activation. Carbon activation can be accomplished by a number of methods and the field of research is vast. Gasification by reaction with CO₂ is relevant to the experiments in this thesis, and therefore the process is outlined briefly. The overall reaction is given in Eq. 1.1 [138].

\[ C_{(s)} + CO_2 \rightarrow 2CO_{(g)} \]  \hspace{1cm} (1.1)

Marsh and Rand gasified PFA derived carbons at 850 °C [139, 140]. Creation of porosity during activation generally proceeds by three mechanisms: widening of existing pores, creation of new pores by selective gasification, and opening of previously inaccessible pores. The authors provided evidence that the first and third pathways adequately described their results. A maximum in total and nanopore volumes was observed at 70% and 25% burn-off. In a separate study, the rate of gasification was found to increase with HTT [141]. Watt and Franklin reported no change in Lₐ with activation [142]. They concluded that consumption of the graphene layers is not gradual; rather the layers were either unaffected or completely eliminated. Via TEM imaging Huttepain and Oberlin observed removal of individual graphene layers and entire BSU during oxidation [143].
1.8 Summary

Polyfurfuryl alcohol derived nanoporous carbon’s unique intrinsic porosity is a product of its disordered structure. The chaotic misalignment of graphene layers in the matrix blocks graphitization at high temperature; hence the carbon is non-graphitizing. The source of disorder in the carbon is traced back to the existence of cross-linking in the polymer state. Porosity and the carbon microstructure can be further modified by activation and/or annealing at high temperatures. Applications for nanoporous carbon include gas separation membranes, molecular sieving catalyst supports, and electrical double layer capacitors. Their effectiveness strongly depends on the porosity, structure, and stability of nanoporous carbon.

Cationic polymerization of furfuryl alcohol occurs primarily by head-to-tail condensation. Acids catalyze the reaction. Several cross-linking schemes have been proposed, however conjugation of the polymer backbone is a prerequisite for cross-linking. Two mechanisms of cross-link formation from a conjugated structure are: cationic attack at a methylene bridge, and a Diels-Alder condensation between a diene (furan ring) and dienophile (conjugated ring). Cross-linking occurs more readily in higher molecular weight PFA. Thermosetting prior to pyrolysis also accelerates the reactions.

Pyrolysis of PFA decomposes the polymer structure. Fragments reassemble to form nanoporous carbon. Furan rings fracture at 300-400 °C, at the same time aromatic domains are identifiable. Fitzer and Schafer postulated that mesopores must appear in the
structure to allow evolution of gaseous by-products [6, 82]. Pyrolysis is essentially complete by at 800 °C and raising the temperature further closes pores in the carbon.

Nanoporous carbon is globally amorphous; no periodic order is detectable beyond ~10 Å. Numerous models of the structure exist. A common thread is randomly oriented layers of curved graphenes. The curvature is introduced by addition of pentagonal and heptagonal rings to an ideal hexagonal sheet. Imperfect alignment of the graphene layers leaves voids in the matrix, which are nanopores.

High temperature treatment drives structural changes in nanoporous carbon. When doped with transition metal particles, graphitization of non-graphitizing carbon is possible. Composite powder XRD profiles are found with a graphitic line superimposed over an amorphous carbon background. Stress graphitization can occur in non-graphitizing carbon when graphitization resistant features build pressure in the matrix. Release of the stress locally graphitizes small regions of the carbon. Rouzaud and Oberlin noted four stages of graphitization for graphitizing carbon: 1) pyrolysis to generate individual BSU, 2) removal of labile heteroatoms and orientation of BSU along the c-axis, 3) elimination of inter-layer defects to create turbostratic carbon, 4) healing in-plane defects to form highly crystalline graphite. Non-graphitizing carbons pass through the same four stages with HTT, however the degree of graphitization, or long range crystallinity is restricted by the extreme disorder of the original BSU. Porosity and surface area are destroyed by HTT. Activation with carbon dioxide can generate additional porosity and surface area in porous carbons.
1.9 Objectives

Resistance to graphitization and pore formation in non-graphitizing carbon is the manifestation of cross-linking in the polymer precursor. Control of the porosity and structure, or graphitic character, of nanoporous carbon is essential to engineering carbons. Methods to modify polyfurfuryl alcohol and its derived nanoporous carbon are explored further herein. The process begins at polymerization and continues up to HTT at 2000 °C. Thorough characterization is conducted at each step. The following research objectives are discussed within the thesis:

- Tuning cross-linking in PFA to direct changes in the structure and porosity of NPC.
- Tracking the autogenesis of nano- and mesoporosity during pyrolysis.
- Determining the evolution of porosity and microstructure, or graphitic character, in NPC and activated NPC during annealing.
- Demonstrating the effectiveness of activated NPC as an electrode in an EDLC.

1.9.1 Outline

Chapter 2 provides details on the experimental methods and techniques utilized in this research. Descriptions of polymerization, pyrolysis, activation, and high temperature treatment procedures are provided. Additionally characterization tools employed to collect chemical structure, physical property, and electrochemical data are described.
The influence of polymer synthesis methods on carbon properties is discussed in Chapter 3. Co-solvent, reaction time, temperature, thermosetting, and catalyst concentration are explored as potential factors. The resulting carbons are characterized at both 800 and 2000 °C in order to understand effects on porosity and resistance to graphitization.

Chapter 4 includes detailed analysis of PFA/NPC during pyrolysis. The process was halted at several temperatures between 25 and 600 °C. The structure of the material is examined in detail at each step in order to provide a clear picture of the genesis of porosity in nanoporous carbon. The first evidence for transient mesopores is provided.

The evolution of porosity with both activation and high temperature treatment is elucidated in Chapter 5. Microstructural changes in the carbon are also followed up to 2000 °C. A comparison of the non-activated and activated nanoporous carbons provides insight to the barrier to graphitization. A surprising transformation occurs in the activated carbon at high temperature. An explanation for the unexpected graphitization of non-graphitizing carbon is given.

Chapter 6 is the final discussion of experimental results. Electrical double layer capacitors are fabricated from high surface area and porosity activated nanoporous carbons. In a comparison of carbons derived from PFA/THF and PFA/Triton X-100 precursors the effect of mesoporosity on capacitance is shown. NPC is demonstrated as a viable electrode material.

An overall summary is given in Chapter 7. The complete life of the carbon is examined from polymerization to pyrolysis and finally high temperature treatment. The impact of the research is discussed. Future directions for the project are laid out.
1.10 References


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Chapter 2
Experimental

2.1 Introduction

A general synthesis method for polyfurfuryl alcohol (PFA) and nanoporous carbon (NPC) is given in this chapter. Polymer preparations specific to the carbons utilized in each chapter are described within the experimental sections of the chapters. Procedures utilized to characterize the polymers and carbons are also noted.

2.2 Synthesis

2.2.1 Polyfurfuryl alcohol

Furfuryl alcohol (FA, 99%), p-toluenesulfonic acid monohydrate (pTSA, >98.5%), tetrahydrofuran (THF, spectroscopic grade), and Triton X-100 (TRI) were purchased from Sigma-Aldrich. In general, pTSA was first dissolved in either THF or TRI. Mild heating to ~70 °C was necessary to dissolve the acid in TRI. After cooling to room temperature, the required amount of FA was added. Ratios of the reactants are given within each chapter. Polymerizations were done in batch reactors, which were 20 ml glass vials with magnetic stir bars, immersed in either an ice bath or jacketed vessel connected to a chiller. If an ice bath was used the reaction temperature was maintained at 0 °C only until the initial batch of ice melted, then the reaction proceeded at room
temperature. In the case of the jacketed vessel, the temperature was controlled throughout the entire reaction. A commercially available PFA resin (Durez, Monomer, Polymer & Dajac Laboratories Inc., Lot A-1-143) was utilized for comparison in several instances. It was pyrolyzed without modification.

2.2.2 Nanoporous carbon

After polymerization the PFA was transferred to a quartz boat (30x4x2 cm) for pyrolysis. The boat was placed at the center of a quartz tube furnace (Blue M Single Zone, Thermo Scientific, Waltham, MA) which was heated at a rate of 10 °C min\(^{-1}\) to 800 °C. The temperature was held for 1 hour and the furnace was then allowed to cool. Flowing argon blanketed the sample throughout the entire pyrolysis. Finally, samples were ground with a mortar and pestle and sieved to a particle size of <38 μm.

2.2.3 Activated nanoporous carbon

Activated NPC was also prepared in a quartz tube furnace. 0.5 gm of carbon was spread evenly in a small quartz boat (5x1x1 cm) and heated to 900 °C over 1 h in flowing argon. After 1 h of soak time the gas was switched to CO\(_2\) and soaked the sample for an additional period of time between 0.5 and 3.5 h. The sample was cooled back to room temperature under argon. The entire experiment was conducted at atmospheric pressure.
2.2.4 High temperature treatment

High temperature treatment (HTT) was carried out in a Red Devil furnace (R. D. Webb Company, Natick, MA). Carbons were loaded into cylindrical graphite crucibles (1x1 cm). After placing the samples into the hot zone, identical crucibles were utilized to partially cap the samples and prevent mixing of fine particles from differing samples during evacuation. The hot zone was evacuated to $10^{-3}$ mbar for at least 12 hours prior to annealing, then backfilled to atmospheric pressure with argon. Flowing argon was maintained throughout the HTT. A 25 °C min$^{-1}$ heating rate was employed with a 1 hour soak at temperatures between 1200 and 2000 °C. For temperatures >1500 °C, heating was paused at 1500 °C for 15 min. During this time the temperature measurement was switched from the thermocouple to the pyrometer, which prevented damage to the furnace. Heating then continued up to the final HTT temperature.

2.3 Characterization

2.3.1 Chemical structure

2.3.1.1 Infrared spectroscopy

The chemical structure of the pyrolyzed residue was studied using a Nexus 670 FTIR spectrometer in transmission mode. The carbon samples were mixed with FTIR grade potassium bromide (Sigma-Aldrich) in a 1:99 weight ratio and pressed into a pellet under 5000 psig pressure.
2.3.1.2 Nuclear magnetic resonance spectroscopy

Solid-state $^{13}$C NMR was also utilized as a structural probe. Spectra were collected using a $^1$H to $^{13}$C variable amplitude CP-MAS technique implementing TOSS (total suppression of spinning sidebands) and TPPM (two pulse phase modulation) $^1$H decoupling. PFA25 and PFA100 were analyzed on a 125-MHz Chemagnetics Varian CMX-Infinity 500 spectrometer with $^1$H $\pi/2$ pulse width = 5.3 $\mu$s, contact time = 6 ms, and spin rate = 6 kHz. The spectra of PFA200, PFA300, and PFA400 were measured on a 75-MHz Chemagnetics Varian CMX-Infinity 300 with $^1$H $\pi/2$ pulse width = 3.95 $\mu$s, contact time = 1 ms, and spin rate = 3 kHz.

2.3.1.3 X-ray photoelectron spectroscopy

XPS analyses were performed on a monochromatic Al K$\alpha$ source with a Kratos Axis Ultra (England) instrument. Spectra were collected with a photoelectron takeoff angle of 90° and 20 eV pass energy.

2.3.1.4 Elemental analysis

Elemental analyses for C and H content were performed by Exygen Research (State College, PA).
2.3.2 Physical properties

2.3.2.1 Gas sorption analysis

A methyl chloride adsorption isotherm was used to calculate the total pore volume and the average pore size of the carbons according to the Horvath-Kawazoe and the Kelvin models in the nano- and mesopore regions respectively. A slit pore shape was assumed for pores less than 0.7 nm. The diameter of the methyl chloride probe molecule was taken to be 0.418 nm. The apparatus and models have been extensively detailed by both Mariwala and Stevens [1, 2]. Nanopores are analogous to micropores, which is the IUPAC term for pores with widths less than 2 nm.

2.3.2.2 Skeletal density

The skeletal density of the carbons was measured by helium gas displacement on an AccuPyc 1330 (Micromeritics, Norcross, GA). Samples were baked out overnight in an oven at 100 °C prior to analysis. Powders were loaded into a 1 cm$^3$ sample cup. The steel ball reference was placed on top of the carbon to prevent powder blow-off and contamination of the instrument. The instrument reported an average of 5 measurements per sample loading and 5 different aliquots of carbon were measured to obtain the material’s skeletal density. The theory of helium pycnometry is given by Webb [3]. Skeletal density differs from bulk density and is defined in Eq. 2.1. $V_{\text{apparent,carbon}}$ is the apparent volume of the carbon. Closed pores inaccessible to gas do not contribute to $m_{\text{carbon}}$ but do increase $V_{\text{apparent,carbon}}$. 
2.3.2.3 Apparent surface area

The surface area of the carbons was calculated utilizing a nitrogen isotherm measured on a Micromeritics Gemini 2370 (Micromeritics, Norcross, GA) and the BET equation [4]. Samples were outgassed at 100 °C overnight before analysis.

2.3.2.4 X-ray diffraction

XRD patterns were collected on a Scintag Pad V x-ray powder diffractometer using Cu Kα radiation with a step size of 0.01° 2θ and a count time of 0.5 seconds. Acquisition conditions were 35 kV and 30 mA. A NIST SRM 640c silicon standard was used to correct the line position and broadening of the carbon patterns. Carbons were finely ground and packed into the cavity of a quartz zero-background holder (The Gem Dugout, State College, PA). The Bragg equation (Eq. 2.2) was utilized to calculate the d-spacing of the carbon (d_{002}). The x-ray wavelength was 1.5412 Å and θ_{002} is the angle of the (002) peak. Average crystallite sizes in the c-direction (L_c), which is perpendicular to the layer planes, and a-direction (L_a), which is parallel to the layer planes, were calculated by the Scherrer equation (Eq. 2.3) [4]. k is taken to be 0.9, B is the full width at half max of the peak of interest, and θ is the position of the peak. The (002) peak was utilized for L_c and (10) peaks for L_a.
\[ \lambda = 2d_{002} \sin \theta_{002} \]  

\[ L = \frac{k\lambda}{B \cos \theta} \]

### 2.3.2.5 Pair distribution function

Pair distribution measurements were performed by Dr. Mouath Shatnawi and Dr. Simon Billinge at Michigan State University, who provided the experimental procedure. Powder samples were loaded in sample holders with thickness of 2 mm and sealed with kapton tape. The data was collected using recently developed rapid acquisition pair distribution function (RA-PDF) technique [5]. The experiments were conducted using x-rays of energy 98.11 keV (\( \lambda = 0.126371 \) Å) at the 6-IDD beamline at the Advanced Photon Source (APS) at Argonne National Laboratory. Data was collected using a circular image plate camera (Mar345) 345 mm in diameter. The camera was mounted orthogonally to the beam path, with sample to detector distance determined to be 230.3385 mm. The distance was obtained from the calibration using the silicon standard. In order to avoid saturation of the detector, each measurement was carried out by multiple exposures to the x-rays. The sample was exposed for 800 seconds at a time. Data sets were further combined and integrated using the program FIT2D [6]. Data for empty container was also collected to allow for corrections. The signal from an empty container was subtracted from the raw data and various other corrections were made as described in detail by Egami and Billinge [7]. The total scattering structure function
S(Q) was obtained using the program PDFgetX2 [8]. Finally, the pair distribution function (PDF, G(r)), which gives the probability of finding an atom at a distance r away from another atom, was obtained by a Fourier transformation of S(Q) according to Eq. 2.4, where Q is the magnitude of the scattering vector. S(Q) was truncated at Q_{max} = 20 Å since beyond that value of Q the signal-to-noise ratio was unfavorable.

\[
G(r) = \frac{2}{\pi} \int_{0}^{\infty} Q[S(Q) - 1] \sin(Qr) dQ
\]  

(2.4)

2.3.2.6 Thermogravimetric analysis

The pyrolysis of PFA was monitored by a TA Instruments TGA 2050 (New Castle, DE). The sample was heated under a flowing argon atmosphere at 10 °C min^{-1} to 800 °C. Gaseous by-products were passed through a ThermoStar mass spectrometer (Pfeiffer, Nashua, NH). The same instrument was used for oxidation experiments; however 100 sccm of air was passed rather than argon. The heating rate was 10 °C min^{-1} up to 1000 °C, unless otherwise noted.

2.3.2.7 Gel permeation chromatography

Molecular weights of PFA were determined by gel permeation chromatography. Samples were prepared by dissolving 20 mg of polymer into 10 ml of THF, to give a 2 mg ml^{-1} concentration. The solution was injected at a flow rate of 1 ml min^{-1}, separated by four Waters columns, HR 0.5, 1, 3, and 4, and detected by a Waters refractive index
detector (Milford, MA). Molecular weights were calculated with respect to polystyrene standards.

### 2.3.3 Electrochemical properties

Each electrode was comprised by 85% a-NPC (100 mg), 10% Teflon binder (Electrochem, Inc., Woburn, MA), and 5% by weight acetylene black. After thorough mixing the powder was pressed into carbon film at 5000 psi for 20 minutes. The film was cut to form an electrode with an area ~1 cm$^2$ and ~0.3 mm thickness. A two-electrode electrochemical capacitor was fabricated by sandwiching a Celgard 5400 membrane (Celgard, Charlotte, NC) between two identical carbon electrodes. Stainless steel mesh was used as the current collector. The cell was immersed in 1 M H$_2$SO$_4$ for 2 day before testing began. One of the carbon electrodes acted as both the counter electrode and reference electrode. All measurements were performed on a 263A Potentiostat/Galvanostat (Princeton Applied Research, Oak Ridge, TN). EIS measurements were done by coupling a Model 5210 Lock-in Amplifier (Signal Recovery, Oak Ridge, TN).

#### 2.3.3.1 Constant current

Constant current (CC) experiments were conducted by charging and discharging the two-electrode capacitor from 0 to 0.5 V and applying a constant load current of 250 mA gm$^{-1}$. The time necessary for the charge and discharge was recorded and the
capacitance (C) was calculated by Eq. 2.5, where the constant current applied in A is \( I \) and electrode mass is \( m \). \( dV/dt \) is the slope of the voltage versus time plot. It was measured by linearly regressing data points between 0.2 and 0.4 V of the charge cycle.

\[
C = \frac{1}{(dV/dt)m}
\]  

(2.5)

2.3.3.2 Cyclic voltammetry

Cyclic voltammograms (CV) were recorded between -0.5 and 0.5 V at a scan rate of 5 mV s\(^{-1}\). Parasitic faradiac reactions on the current collector were prevented by limiting the potential to 0.5 V. The specific capacitance was determined by Eq. 2.6, wherein \( I \) is the average current in A, \( C \) is the specific capacitance in F, \( \nu \) is the scan rate in V s\(^{-1}\), and \( m \) is the electrode mass.

\[
C = \frac{I}{\nu m}
\]  

(2.6)

2.3.3.3 Electrical impedance spectroscopy

For electrochemical impedance spectroscopy (EIS) measurement, an AC perturbation of 10 mV was applied at the condition of open circuit potential. The perturbation frequency was scanned between \( 10^5 \) Hz and \( 10^{-3} \) Hz.
2.4 References


Chapter 3

Influence of furfuryl alcohol polymerization on the properties of nanoporous carbon

3.1 Introduction

Nanoporous carbon derived from pyrolysis of polyfurfuryl alcohol is a non-graphitizing carbon [1]. Its structure is comprised of disordered, misaligned graphene layers. Resistance to graphitization is attributed to the presence of extensive cross-linking in the precursor [2]. In contrast, graphitizing carbons, which are derived from linear polymer precursors, have a relatively ordered structure. A fundamental understanding of the relationship between the structure of cross-linking in the polymer and its expression in the properties of pyrolyzed carbon is lacking. If cross-linking is related to disorder and nanoporosity, then controlling the polymerization is expected to influence the properties of the carbon. This chapter focuses on tuning the polymer synthesis, rather than pyrolysis conditions, and relates PFA polymerization parameters to porosity and resistance to graphitization in NPC.

Cross-linking in PFA is predicated by formation of conjugated structures on the polymer backbone after the \( \text{CH}_2 \) bridging groups undergo a series of hydride ion abstraction and proton expulsion reactions, as shown in Figure 1.6. The number of potential sites for cross-linking is limited by the degree of conjugation. Each conjugation structure requires three repeating units of the polymer. Increasing the molecular weight
of the polymer is expected to permit a greater amount of conjugation, and therefore cross-linking, to occur.

High-polarity solvents promote the formation of free ions, rather than ion pairs, as the counter-ion to the active center is more weakly bound [3]. Free ions lead to an increased rate of propagation. Triton X-100 (TRI) and tetrahydrofuran (THF) are utilized herein. The dipole moment of THF is 1.63, while Triton X-100 is non-polar. The two reaction mediums will be compared to the case of polymerization with no solvent (NS). Chain transfer reactions in cationic polymerization are inhibited by polymerizing at lower temperature, thereby enabling propagation [3]. The reaction temperature will be varied. Reaction time and catalyst concentration also increase the conversion of FA. Finally, thermal curing prior to pyrolysis is known to enhance cross-linking in a thermosetting resin. Each of these factors is examined to determine its effect on the properties of NPC after pyrolysis and high temperature treatment (HTT). Gas sorption analysis, thermogravimetric analysis (TGA), x-ray diffraction (XRD), and pair distribution function (PDF) techniques are utilized.

Pair distribution function analysis gives the probability of finding an atom at a particular distance from another atom in a structure. The technique provides insight into the fine structural features of the carbon at angstrom resolution. It is calculated from x-ray synchrotron scattering. An ideal graphene would give peaks at the positions shown in Figure 3.1, the image is reproduced from [4]. Distance A is the carbon-carbon bond distance, B is the second neighbor distance, and C is the third. The interlayer spacing of graphite is 3.35 Å. The technique has been used previously to characterize NPC as a function of pyrolysis temperature [4]. Disappearance of the peak at 3.35 Å and a loss of
intensity and broadening in the peak at 2.85 Å, indicates the presence of non-six-member rings in the carbon, which are believed to be responsible for curvature and disorder [5].

![Graphite hexagonal ring diagram]

Figure 3.1: Carbon-carbon bond distances in an ideal graphite hexagonal ring.

3.2 Experimental

To examine each specific factor, polymerizations were carried out according to the procedures described below. High temperature treatment at 2000 °C was used to test resistance to graphitization in the carbons. Pyrolysis and HTT procedures were described in 2.2.

For comparison of solvents, 5 ml of FA was mixed with 5 ml of THF or TRI and 0.05 M pTSA. The same catalyst concentration was used with 8 ml of FA in the no solvent case. The reaction temperature was maintained at 10 °C for 2 days of polymerization.

The effect of polymerization time was studied with polymers produced by reacting 10 ml of FA with 5 ml of THF or TRI and 0.10 M pTSA. The mixture was
placed in an ice bath at the start of the reaction. Upon melting of the ice, the polymerization reaction was allowed to proceed at 25 °C for 1, 2, or 3 days.

PFA was synthesized at several temperatures between 2 and 40 °C. The FA:TRI ratio was 4:1 with 0.1 M pTSA. The reaction was carried out for 16 h.

Thermoset polymers were prepared in the same manner as the PFA for the time study. After 2 days of polymerization, the polymers were placed in an oven set at 50, 100, or 200 °C for 24 hours, and then pyrolyzed.

The acid concentration was varied between 0.01 and 0.10 M in 1:1 FA:TRI solutions. Polymerization was for 2 days at 10 °C.

3.3 Results

3.3.1 Effect of solvent

Total and differential pore volumes for NPC synthesized without solvent, with THF, and with TRI are given in Figure 3.2. Table 3.1 provides a breakdown of nano-, meso-, and total pore volumes for each sample. Nanopore volumes for the three carbons were essentially equivalent at 0.16 cm³ gm⁻¹. Polymerization with Triton X-100 induced mesopore formation in NPC. \( V_{\text{meso}} \) for TRI was 0.04 cm³ gm⁻¹, as opposed to 0.01 cm³ gm⁻¹ for NS and THF.
Table 3.1: Nano- ($V_{nano}$), meso-, ($V_{meso}$), and total pore ($V_{total}$) volumes for NS, THF, and TRI carbons. Nanopores are less than 2 nm and mesopores are 2-20 nm.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$V_{nano}$ ($cm^3 gm^{-1}$)</th>
<th>$V_{meso}$ ($cm^3 gm^{-1}$)</th>
<th>$V_{total}$ ($cm^3 gm^{-1}$)</th>
<th>Nanopore width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NS</td>
<td>0.16</td>
<td>0.01</td>
<td>0.17</td>
<td>0.54</td>
</tr>
<tr>
<td>THF</td>
<td>0.15</td>
<td>0.01</td>
<td>0.16</td>
<td>0.54</td>
</tr>
<tr>
<td>TRI</td>
<td>0.16</td>
<td>0.04</td>
<td>0.20</td>
<td>0.54</td>
</tr>
</tbody>
</table>

Figure 3.2: Total and differential pore volumes for NPC derived from PFA without solvent, with THF, and with TRI.
Carbons from THF and TRI were also oxidized in air after annealing at 2000 °C. Weight loss was monitored by TGA. Figure 3.3 and Figure 3.4 give the profiles for TRI and THF, respectively. Heating rates in the TGA were varied between 5, 10, and 15 °C min⁻¹. In Figure 3.5 the traces of THF and TRI at 5 °C min⁻¹ are overlaid. The TRI carbons all exhibited inflection points at ~60% weight loss. Oxidation temperature lowered with decreasing heating rate. The latter trend continued in the THF samples. However, only at a heating rate of 5 °C min⁻¹ did the inflection point appear. As shown in Figure 3.5, the THF and TRI carbons exhibited nearly identical oxidation behavior when burned at 5 °C min⁻¹.
Figure 3.3: Oxidation profiles of TRI carbons annealed at 2000 °C. TGA was performed in flowing air. The heating rates are given in the legend.
Figure 3.4: Oxidation profiles of TRI carbons annealed at 2000 °C. TGA was performed in flowing air. The heating rates are given in the legend.
Figure 3.5: Comparison of oxidation profiles of TRI and TRI carbons annealed at 2000 °C. TGA was performed in flowing air.
3.3.2 Effect of polymerization time

In Figure 3.6 and Figure 3.7 total and differential pore volumes are shown for carbons derived from PFA polymerized for 1, 2, and 3 days. The differential pore volumes of THF carbons were identical regardless of the polymerization time. \( V_{\text{nano}} \) for the three carbons was 0.15, 0.15, and 0.16 cm\(^3\) gm\(^{-1}\). \( V_{\text{total}} \) was 0.16, 0.16, 0.17 cm\(^3\) gm\(^{-1}\), respectively. TRI carbons were also similar with respect to differing polymerization times. The results of gas sorption on TRI carbons polymerized for 1 and 3 days are shown in Figure 3.7. Nanopore volumes were 0.16 cm\(^3\) gm\(^{-1}\) and mesopore volumes were 0.01 cm\(^3\) gm\(^{-1}\).

![Figure 3.6: Total and differential pore volumes for NPC derived from PFA polymerized for 1, 2, and 3 days with THF.](image-url)
Figure 3.7: Total and differential pore volumes for NPC derived from PFA polymerized for 1 and 3 days with TRI.
The THF and TRI carbons, which were polymerized for 1, 2, and 3 days, were annealed at 2000 °C. Powder XRD patterns for these materials are shown in Figure 3.8 and Figure 3.9. The THF/3 Day and TRI/3 Day samples are overlaid in Figure 3.10. All of the patterns were characterized by a broad (002) line, which was indicative of a high degree of disorder in the graphene layers. \( d_{002} \) for each of the six samples was calculated from the Bragg equation and was 3.49 Å for each carbon. \( L_c \) was estimated by the Scherer equation from the (002) reflection. Again, each sample gave the same value, which was 15 Å.

![Figure 3.8: XRD patterns for NPC derived from PFA polymerized with THF. 1 Day is at the bottom, 2 Day is offset in the middle, and 3 Day is on the top.](image)
Figure 3.9: XRD patterns for NPC derived from PFA polymerized with TRI. 1 Day is at the bottom, 2 Day is offset in the middle, and 3 Day is on the top.
Figure 3.10: XRD patterns for THF/3 Day and TRI/3 Day carbons overlaid.
The 1, 2, and 3 Day samples from PFA with THF were oxidized in the TGA after pyrolysis at 800 °C and HTT at 2000 °C. Oxidation profiles are given in Figure 3.11 and Figure 3.12. Irrespective of polymerization time the carbons were shown to oxidize in the same manner. HTT at 2000 °C improved the carbons’ resistance to oxidation. Without annealing the carbons were entirely consumed in air by 700 °C, whereas weight loss just began at 700 °C after HTT.

Figure 3.11: Oxidation profiles of THF carbons pyrolyzed at 800 °C. TGA was performed in flowing air at a heating rate of 10 °C min⁻¹.
Figure 3.12: Oxidation profiles of THF carbons annealed at 2000 °C. TGA was performed in flowing air at a heating rate of 10 °C min⁻¹
3.3.3 Effect of polymerization temperature

Figure 3.13 shows the total and differential pore volumes for a series of NPCs generated from PFA polymerized at temperatures between 2 and 40 °C. Table 3.2 lists molecular weights for the polymer and the carbon pore volumes in detail. The MW of the PFA increased with polymerization temperature. An order of magnitude change is realized between 2 and 40 °C. Although the adsorption isotherms were not exactly identical, no trend was observed. The average nanopore volume for the 6 samples was 0.16 cm$^3$ gm$^{-1}$ with a standard deviation of less than 0.01 cm$^3$ gm$^{-1}$. Mesopore volumes were all 0.01 cm$^3$ gm$^{-1}$ and the pore widths were consistently 0.54 nm.

Figure 3.13: Total and differential pore volumes for NPCs derived from PFA polymerized for 16 h at 2, 10, 15, 25, 35, and 40 °C.
Table 3.2: Molecular weight (MW), nano- ($V_{nano}$), meso-, ($V_{meso}$), and total pore ($V_{total}$) volumes for NPC from 2-40 °C PFA. Nanopores are less than 2 nm and mesopores are 2-20 nm.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>MW</th>
<th>$V_{nano}$ (cm$^3$ gm$^{-1}$)</th>
<th>$V_{meso}$ (cm$^3$ gm$^{-1}$)</th>
<th>$V_{total}$ (cm$^3$ gm$^{-1}$)</th>
<th>Nanopore width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>760</td>
<td>0.16</td>
<td>0.01</td>
<td>0.17</td>
<td>0.54</td>
</tr>
<tr>
<td>10</td>
<td>904</td>
<td>0.15</td>
<td>0.01</td>
<td>0.16</td>
<td>0.54</td>
</tr>
<tr>
<td>15</td>
<td>963</td>
<td>0.15</td>
<td>0.01</td>
<td>0.16</td>
<td>0.54</td>
</tr>
<tr>
<td>25</td>
<td>1644</td>
<td>0.16</td>
<td>0.01</td>
<td>0.17</td>
<td>0.54</td>
</tr>
<tr>
<td>35</td>
<td>5485</td>
<td>0.16</td>
<td>0.01</td>
<td>0.17</td>
<td>0.54</td>
</tr>
<tr>
<td>40</td>
<td>7203</td>
<td>0.16</td>
<td>0.01</td>
<td>0.17</td>
<td>0.54</td>
</tr>
</tbody>
</table>
The previous carbons were annealed at 2000 °C. Powder XRD patterns are found in Figure 3.14. The average d_{002} for the carbons was 3.49 Å with a standard deviation of less than 0.01 Å. The average crystallite size, L_c, was again found to be 15 Å.

Figure 3.14: XRD patterns for NPC derived from PFA polymerized at 2, 10, 15, 25, 35, and 40 °C and annealed at 2000 °C. The pattern for 2 °C is shown at the bottom; subsequent patterns are stacked in order of increasing polymerization temperature.
3.3.4 Effect of thermosetting temperature

Thermosetting for 24 hours at 50, 100, and 200 °C was investigated as a potential method to enhance the resistance to graphitization in NPC. TGA profiles for the carbons at 800 and 2000 °C are shown in Figure 3.15 and Figure 3.16. No relationship between thermosetting and oxidation temperature was evident at either 800 or 200 °C.

![Graph showing TGA profiles](image)

Figure 3.15: Oxidation profiles of carbons thermoset prior to pyrolysis at 800 °C. TGA was performed in flowing air at a heating rate of 10 °C min⁻¹.
Figure 3.16: Oxidation profiles of carbons thermoset, pyrolyzed at 800 °C, and annealed at 2000 °C. TGA was performed in flowing air at a heating rate of 10 °C min⁻¹.
3.3.5 Effect of catalyst concentration

Polymers were synthesized with 0.01, 0.05, and 0.10 M pTSA. Gas sorption analysis is given in Figure 3.17 and Table 3.3. \( V_{\text{nano}} \) is equal for the three carbons; however \( V_{\text{meso}} \) increases with acid concentration.

![Graph showing pore width and volume](image)

Figure 3.17: Total and differential pore volumes for NPC derived from PFA polymerized with 0.01, 0.05, and 0.1 M pTSA.

Table 3.3: Nano- (\( V_{\text{nano}} \)), meso-, (\( V_{\text{meso}} \)), and total pore (\( V_{\text{total}} \)) volumes for NPC from PFA with varying [pTSA]. Nanopores are less than 2 nm and mesopores are 2-20 nm.

<table>
<thead>
<tr>
<th>[pTSA] (M)</th>
<th>( V_{\text{nano}} ) (cm(^3) gm(^{-1}))</th>
<th>( V_{\text{meso}} ) (cm(^3) gm(^{-1}))</th>
<th>( V_{\text{total}} ) (cm(^3) gm(^{-1}))</th>
<th>Nanopore width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01 M</td>
<td>0.16</td>
<td>0.02</td>
<td>0.18</td>
<td>0.54</td>
</tr>
<tr>
<td>0.05 M</td>
<td>0.16</td>
<td>0.04</td>
<td>0.20</td>
<td>0.54</td>
</tr>
<tr>
<td>0.10 M</td>
<td>0.17</td>
<td>0.05</td>
<td>0.22</td>
<td>0.59</td>
</tr>
</tbody>
</table>
3.3.6 Pair distribution function analysis

Several carbons were submitted for PDF analysis. An example of a TRI carbon pyrolyzed at 800 and annealed at 2000 °C is shown in Figure 3.18. The difference between the two data sets is also given for comparison. Peaks labeled A, B, and C correspond to the first, second, and third carbon-carbon distances around an six-member ring. At 800 °C discernible peaks began to diminish beyond 6 Å. After annealing at 2000 °C all peaks were sharpened and additional peaks were distinguishable out to 20 Å.

Figure 3.18: Pair distribution function (G(r)) for TRI carbon at 800 and 2000 °C. A, B, and C correspond to the first, second, and third carbon-carbons distances in a six-member ring (see Figure 3.1). The difference between the 2000 and 800 °C plots is also shown.
PDF was utilized to examine differences between THF, TRI, and NS carbons at both 800 and 2000 °C. The results are shown in Figure 3.19. The difference curves for the TRI/THF and TRI/NS plots were simply noise and revealed no structural differences between the three types of carbon at either temperature.

The effect of catalyst concentration was also studied. Figure 3.20 compares TRI carbon from PFA synthesized with 0.01 and 0.05 M pTSA at both 800 and 2000 °C. Although crystallinity clearly increased with HTT, the carbons from differing polymers were indistinguishable.
Figure 3.19: Comparison of pair distribution functions ($G(r)$) for TRI, THF, and NS carbons at 800 and 2000 °C. Difference curves are also shown.
Figure 3.20: PDF of TRI carbon from PFA synthesized with 0.01 and 0.05 M acid, pyrolyzed at 800 and annealed at 2000 °C. Difference curves are also shown.
3.4 Discussion

Non-graphitizing or graphitizing carbons are derived from polymer precursors which are either cross-linked or not cross-linked. Cross-links are the driving force for generating the disordered amorphous structure of nanoporous carbon. In the present investigation a single polymer precursor, polyfurfuryl alcohol, has been synthesized under a variety of conditions expected to influence the polymer structure. The effects of the modifications are examined in the nanoporous carbon produced after pyrolysis. The influence of precursor polymerization variations on non-graphitizing carbon properties is determined.

The cumulative pore volumes of THF, TRI, and NS carbons shown in Figure 3.2 clearly demonstrate that the nanopore volume and mean pore width of NPC is independent of additives during polymerization. THF and NS carbons have just 0.01 cm$^3$ gm$^{-1}$ of mesopores compared to 0.04 cm$^3$ gm$^{-1}$ in TRI carbon. The mesopores do not have a distinct mean diameter, rather they are distributed evenly between 2 and 20 nm. The slope of the isotherm in the mesopore region is nearly zero for THF and NS, whereas it is positive throughout the region for TRI, indicating additional meso- and macroporosity may be present beyond the range of measurement in this experiment.

It has been discovered that Triton X-100 acts as a mesopore forming agent. A Triton X-100 molecule is comprised of a benzene ring connected to both an eight carbon alkyl chain and a polyethylene glycol chain approximately 10 monomeric units in length. Strano et al. reported mesopore formation during pyrolysis of blends of pure PEG and PFA [6]. The PEG completely decomposes to gaseous by-products, leaving voids spaces
(mesopores) in the NPC matrix. Here the low-molecular weight PEG portion of Triton X-100 creates mesoporosity.

Due to its polarity THF is expected to increase the rate of propagation in the polymerization of PFA, and thus the molecular weight and opportunities for cross-linking. Oxidation of carbon occurs at defects and edges of the graphene planes. Increasing the order of the carbon reduces the number of reactive sites and raises the temperature at which the maximum rate of oxidation occurs. Enhanced cross-linking in PFA should result in more edges and defects in NPC, and therefore a decrease in its oxidation temperature. Figure 3.5 indicates that the oxidation of carbons derived from THF and non-polar TRI are identical. Solvent polarity during polymerization does not influence disorder in NPC.

However, comparison of Figure 3.3 and Figure 3.4 demonstrates the effect of mesoporosity on oxidation. The TRI carbons oxidize rapidly above 700 °C at all heating rates (5, 10, and 15 °C min⁻¹). THF carbons only oxidize rapidly at the slowest heating rate. The observations are a result of diffusion limitations of air in the carbon. Oxygen is slow to reach the interior of the carbon particles, thus the temperature increases further before oxidation is complete. Mesoporosity in TRI carbons permits easy entry of the oxidant into the carbon particle; therefore oxidation is always kinetically limited. The heating rate must be slowed to 5 °C min⁻¹ to reach this regime in THF carbons. Kinetically limited oxidation of the two types of carbon is identical, as described previously.

Total and differential pore volumes are unaffected by polymerization time for THF or TRI carbons. TRI samples were prepared with a 2:1 FA:TRI ratio, which is an
insufficient amount of surfactant to create mesopores. THF derived carbons are amorphous at 2000 °C, regardless of the polymerization time. The relationship is likewise with TRI carbons. Finally, a comparison of THF and TRI carbons derived from 3 day polymerizations, shown in Figure 3.10, confirms equivalency between the two types of polymerization mediators. Oxidation of profiles of the THF carbons at both 800 and 2000 °C provide further corroborating evidence. Controlling the polymerization time is inconsequential to the ability of the carbon to resist graphitization.

The polymerization temperature is also irrelevant with respect to the porosity and graphitizabilty of NPC. Despite measured control over the molecular weight of the polymers, the volumes of nano- and mesopores are identical across the range of polymerization temperatures, as shown in Figure 3.13 and Table 3.2. The carbons’ resistance to graphitization is also invariant. No change in d_{002} or crystallite size is seen upon HTT at 2000 °C. Each NPC remains amorphous.

Thermosetting PFA drives the polymerization reaction towards completion and accelerates cross-linking [7, 8]. After curing the polymer overnight at 50, 100, or 200 °C, the polymer forms a rigid plug in the shape of the glass polymerization vial. Monomer is either completely reacted or entrapped in the polymer matrix. During pyrolysis the plug does not melt or flow, its shape is preserved, which is in contrast to non-thermoset PFA. Despite the obvious increase in cross-linking after thermosetting, no change was found in the oxidative tendencies of NPC at either 800 or 2000 °C. The TGA profiles are equivalent.

The influence of catalyst concentration on porosity is explored in Figure 3.17, which gives total pore volumes for TRI carbons synthesized with three different
concentrations of pTSA. Again the nanopore volumes are identical; no effect on the structure of the carbon matrix is found. However, over a constant polymerization time period and FA:TRI ratio the mesopore volume is 0.02, 0.04, and 0.05 for catalyst concentrations of 0.01, 0.05 and 0.1 M, respectively. Initially the TRI is mixed with FA. Upon conversion of FA to PFA, TRI is incorporated into the PFA as well. To obtain greater mesopore volumes, the uptake of TRI into the PFA must increase. Since the FA:TRI ratio is constant, the amount of PFA generated is increasing with catalyst concentration. All other examples of NPC derived from PFA have the same porosity after pyrolysis, yet TRI carbons with variations in [pTSA] are differing. At the early stages of pyrolysis, especially before decomposition begins, polymerization continues. All three carbons are subject to the same process, and thus may be expected to reach equivalent conversion, and take up the equal amounts of Triton X-100. However, mixing does not occur in the furnace, which prevents equilibration between the surfactant and PFA. The PFA begins to decompose before Triton X-100 is completely blended in. The mesopore volumes reflect the amount of surfactant incorporated into the PFA during initial polymerization, which increases with catalyst concentration.

The effect of HTT at 2000 °C on the PDF of NPC is evident in Figure 3.18. Peaks at 1.41, 2.47, and 2.85 Å, which correspond to the first, second, and third neighbor distances in a hexagonal carbon ring, increase in intensity with annealing. This indicates a reduction of defects in the graphene sheets [4]. Pentagonal rings do not have a third neighbor distance. Additional peaks are due to longer range interactions in the graphenes. HTT grows and flattens the graphenes, which increases the intensity of the long range peaks. Given the distinct differences arising with HTT, it is clear PDF is a
powerful tool to analyze the microstructure of NPC. The technique confirms there are no structural differences introduced into NPC by polymerizing with THF, TRI, or NS. At 800 °C the difference between the TRI and THF signals and TRI and NS signals plotted in Figure 3.19 is simply noise. The same relationship is also seen at 2000 °C, except for the increases in intensity, which were explained previously. An effect of solvent during polymerization on the disordered structure on NPC is non-existent. Despite the previously explained differences in porosity, Figure 3.20 indicates that the microstructure of the carbon is indifferent to catalyst concentration. At 800 and 2000 °C the PDFs are identical.

The porosity, microstructure, and ability to resist graphitization in nanoporous carbon derived from polyfurfuryl alcohol are generally indifferent to the method of polymerization. Procedures utilized to influence the polymer synthesis are able to modify properties of the PFA, but the differences are not propagated to the final carbon. Polymerization continues during pyrolysis up to the point of decomposition. It is in fact accelerated due to the increased temperature. Initial differences between the PFA samples are eliminated as the polymerization for all the samples is extended. Additional confirmation is provided by an experiment wherein a small amount of pTSA was added directly to FA and immediately pyrolyzed. The gas sorption of this carbon was identical to those prepared after elaborate polymerizations. Finally, mesoporosity is dependent on the concentration of acid catalyst. This is due to inefficient mixing between Triton X-100 and PFA.
3.5 Conclusions

Differences between non-graphitizing and graphitizing carbons are traced back to their polymeric precursors. Cross-linking in the polymer is manifested as disorder in carbon after pyrolysis. The disorder causes nanoporosity and blocks graphitization. Efforts to modify the molecular weight and degree of cross-linking in were successful; however the variations were not propagated to the carbon. The polymers were assimilated during pyrolysis due to the continued polymerization which occurred up to the point of decomposition. Thus bulk production of NPC can proceed from PFA synthesized by any method with the assurance that the properties of the product are consistent. The exceptions were carbons derived from PFA and Triton X-100 mixtures. With sufficient amount of the surfactant present, mesopores were generated in the nanoporous carbon. Also, the volume of mesopores was dependent on the concentration of acid catalyst utilized in the polymerization. The mesopores are critical to the carbon activation process, which is discussed further in Chapter 6. Pyrolysis, rather than polymerization, is the key step in the synthesis of purely nanoporous carbon. The autogenesis of porosity is elucidated in the following chapter.
3.6 References

Chapter 4

Genesis of porosity in polyfurfuryl alcohol derived nanoporous carbon

4.1 Introduction

Understanding the origins of pore formation is critical to engineering carbons to meet specific requirements of applications. This chapter follows the development of nanopores and provides the first experimental evidence of the autogenesis of mesoporosity in PFA derived NPC at temperatures between 25 and 500 °C. The development of the carbon structure has been studied by gas sorption, IR, x-ray photoelectron spectroscopy (XPS), NMR, and thermogravimetric analysis (TGA).

Fitzer and Schafer utilized infrared spectroscopy (IR) to examine the pyrolysis of PFA in detail [1, 2]. The furan ring was found to be stable up to 275 °C. Between 300 and 400 °C the furan ring ruptured and released CO, CO₂, and H₂O. Aromatic units appeared around 400 °C as the fragments began to coalesce. At temperatures greater than 450 °C a reaction of the remaining methylene bridges with water to form keto groups was proposed. In the same temperature range, formation of methane ceased due to the oxidation of methylene bridges and a significant amount of hydrogen was released. The authors speculated that in the intermediate state between the polymer and the final carbon, open pores with diameters smaller than 100 Å must be present that allowed the transport of gaseous products formed during the pyrolysis. There was no experimental evidence given to prove this hypothesis.
The origin of nanoporosity in these carbons has been addressed via a pair distribution function method [3, 4]. It was shown that in addition to six-membered rings the aromatic domains include five- and seven-membered rings, which induces curvature of the domains, unlike graphite. Curvature causes misalignment of the aromatic domains, and thereby creates nanopores between the disordered graphenes. Mariwala et al. noted cross-linking in PFA leads to nanopore formation and resistance to graphitization in NPC [5].

The mechanism of furfuryl alcohol polymerization is cationic and cross-linking occurs readily. Choura et al. extensively studied the cross-linking reaction in polyfurfuryl alcohol, with the aid of model compounds [6]. The authors suggested cross-linking requires that mobile hydrogen atoms, present on the polymer backbone in the form of CH₂ groups, undergo a series of hydride ion abstraction and proton expulsion reactions, which leaves the polymer highly conjugated. It is the conjugated structure that reacts to form a cross-link, either by condensing with the propagating center on another chain or with a furan ring (diene) in a Diels-Alder reaction.

4.2 Experimental

0.1 M p-toluenesulfonic acid monohydrate (pTSA) was dissolved in 5 ml of tetrahydrofuran (THF) and the reaction mixture was cooled in an ice bath. To this solution, 10 ml of furfuryl alcohol (FA) was slowly added by a syringe pump at a rate of 10 ml hr⁻¹. Upon melting of the ice, the polymerization reaction was allowed to proceed for 48 hours at 25 °C. The resultant polymer was pyrolyzed under flowing argon in a
quartz tube furnace, which was heated at 10 °C min⁻¹ to a final temperature between 100 and 600 °C and allowed to soak for 1 hour.

FA was also polymerized with Triton X-100, rather than THF as the solvent. 8.8 ml of FA was added to 11.5 ml of Triton X-100 with 0.1 M pTSA. For samples prepared without solvent, 8 ml of FA was combined with 0.076 gm pTSA to make a 0.05 M solution. After combination of the reactants, the polymerization and pyrolysis proceeded as described previously. Finally for comparison, a commercially available PFA resin (Durez, Monomer, Polymer & Dajac Laboratories Inc., Lot A-1-143) was pyrolyzed without modification.

4.3 Results

Sample names correspond to their maximum temperature, for example PFA300 was pyrolyzed at 300 °C. PFA25 was reacted for a time sufficient at room temperature to induce cross-linking and solidification prior to analysis.

Figure 4.1 shows weight loss as a function of pyrolysis temperature for PFA along with its derivative. A major weight loss at 100 °C corresponded to evaporation of water, which was formed as a by-product of the polymerization reaction. As the conversion of the polymer to carbon began, weight loss occurred in two distinct temperature regimes and gaseous by-products of the decomposition were determined by mass spectrometry, see Figure 4.2. In the region of 300-400 °C the by-products were primarily H₂O and CO. A second major weight loss occurred between 400 and 600 °C.
The production of CO increased, while H₂O was slightly suppressed. Generation of CH₄ and CO₂ was initiated in this region.

![Graph](image)

Figure 4.1: TGA (dashed) and DTA (solid) profiles of pyrolysis of PFA in argon at 10 °C min⁻¹.
Infrared spectra of PFA were collected as a function of pyrolysis temperature and are shown in Figure 4.3. The main characteristic peaks for PFA25 were at 3400 cm\(^{-1}\) (-OH stretch), 3100 cm\(^{-1}\) (-CH in aromatic rings), 2970 cm\(^{-1}\), 2920 cm\(^{-1}\) and 2850 cm\(^{-1}\) (aliphatic -CH\(_2\) and -CH stretch), 1600 cm\(^{-1}\) (C=C aromatic), 1550 and 1500 cm\(^{-1}\) (ring vibrations), 1460 cm\(^{-1}\) (asymmetric CH\(_2\) bending), 1350 cm\(^{-1}\) (-CH ring deformation), 1100 cm\(^{-1}\) (C-O stretch), 1010 cm\(^{-1}\) (-OH) and 760 cm\(^{-1}\) (2,5-di-substitution of furan ring). A peak at 1710 cm\(^{-1}\) indicated carbonyl groups due to acid-catalyzed ring opening of furan rings. There was also evidence for the presence of -CH\(_3\) terminated groups at 1380 cm\(^{-1}\), which signaled the formation of conjugated sequences on the polymer backbone, as
shown by Choura et al. [6]. As we increased the pyrolysis temperature to 200 °C, we found that many of the characteristic peaks of PFA were still present. The main differences were seen in the region of \(-\text{CH}_2\) and \(-\text{CH}\) stretches; 1350 cm\(^{-1}\) had shifted to 1400 cm\(^{-1}\) and 1620 cm\(^{-1}\) (C=C aromatic) appeared.

![Infrared spectra of PFA25, PFA200, PFA300, PFA400, and PFA500.](image)

**Figure 4.3**: Infrared spectra of PFA25, PFA200, PFA300, PFA400, and PFA500.

The infrared spectrum of PFA300 exhibited new signals, which were unique to carbon, along with the remnants of the polymer. The disappearance of the peaks at 1050 cm\(^{-1}\) and 1100 cm\(^{-1}\) indicated a complete rupture of the ether linkages, while polyaromatic signals appeared at 1200 cm\(^{-1}\), 1145 cm\(^{-1}\) and 1065 cm\(^{-1}\), and the peak at 1620 cm\(^{-1}\)
broadened. The -OH groups were still present at 3400 cm$^{-1}$, but peaks due to furan ring vibrations waned. A new peak arose 1750 cm$^{-1}$ suggesting the presence of additional carbonyl groups. The spectrum of PFA400 demonstrated the continuing conversion of polymer to carbon. Strong vibrations due to –CH rocking appeared at 960 cm$^{-1}$, 850 cm$^{-1}$ and 790 cm$^{-1}$ respectively. Polyaromatic signatures dominated the PFA500 spectrum.

Detailed structural information was obtained from solid state $^{13}$C NMR; the results are given in Figure 4.4. Several structural models of PFA and its carbon, with specific moieties marked, are shown in Figure 4.5. For simplicity, the polyaromatic domain is shown as consisting of only six-membered rings. In reality there would also be defects and non-six-membered rings, as shown in Figure 1.12. The characteristic chemical shifts of PFA25 are approximately 25, 110, and 155 ppm. These resonances correspond to -CH$_2$ groups linking furan rings on the polymer backbone (labeled A), carbon atoms at the 3 and 4 positions on the furan ring (labeled D), and carbon atoms at the 2 and 5 positions on the furan ring (labeled C), respectively. The assignments were in agreement with those published by Maciel et al. [7, 8]. Two additional peaks were notable in the samples. The broad peaks at ~95 and ~130 ppm were attributed to conjugated sequences in the polymer (labeled B). A by-product of the conjugation reaction is -CH$_3$ terminated PFA (labeled E), which was found in the spectrum at 15 ppm. The signature of cross-linked structures was identified as the broad peak at 45 ppm, which corresponded to -CH groups at the two possible cross-link junctions (labeled F). PFA100 was similar to PFA25, expect for a reduction in the peak at 145 ppm, which signaled the carbon at the $\alpha$-position on a terminal furan ring. This disappearance marked the extended polymerization of the PFA. Residual THF appeared at 68 ppm in both
PFA25 and PFA100. After heating to 200 °C the indicators of conjugation were intensified at ~95 and ~130 ppm. A continued presence of cross-links was indicated by the broad peak at ~45 ppm. Hydrolyzed furan rings appeared in the spectrum at ~200 ppm for samples PFA25, PFA100, and PFA200.

Figure 4.4: Solid-state $^{13}$C NMR of PFA25, PFA100, PFA200, PFA300, and PFA400.
Figure 4.5: Models of structures found in PFA: A) methylene bridge, B) backbone conjugation, C) 2, 5 carbons, D) 3, 4 carbons, E) terminal methyl group, F) cross-links, G) polyaromatic domain, H) carbonyl group. For simplicity, the polyaromatic domain is shown as consisting of only six-membered rings. In reality there would also be defects and non-six-membered rings, as shown in Figure 1.12.

The broad peak at ~130 ppm grew substantially in the sample PFA300. It now represented both conjugated species and sp² hybridized carbon in polyaromatic domains (labeled G). All peaks representing polymer moieties were maintained at 300 °C. The spectrum of PFA400 was dominated by polyaromatics. The peaks assigned to conjugation and cross-linking were absent, yet a signal for -CH₃ groups remained at 15 ppm.

The total pore volume is given in Figure 4.6. PFA200 was essentially nonporous. It is interesting to note that as the temperature was increased to 300 °C, there was spontaneous generation of both nano- and mesopores in PFA300. The porosity of PFA400 was similar. When the temperature was raised to 500 °C, many of the carbon’s mesopores collapsed, while the nanopore volume increased. At 600 °C the nanoporosity
was unchanged and the mesopores had completely disappeared. The nanopores were relatively monodisperse in width and centered at 0.4-0.5 nm.

![Graph showing pore volume vs pore width for PFA200, PFA300, PFA400, PFA500, and PFA600](image)

**Figure 4.6:** Total pore volume of PFA200, PFA300, PFA400, PFA500, and PFA600 calculated by the methyl chloride adsorption isotherm.

High-resolution C 1s spectra of each PFA are overlaid and given in Figure 4.7.

The full widths at half max (FWHM) of the main peak corresponding to C-C or C-H are shown in Table 1 and decrease with increasing temperature. The line shape for PFA200 was very broad and almost Gaussian; this is typical for polymeric materials. There was a substantial amount of oxygen moieties in this material, the O/C ratio is ~0.28. This was reflected in the C 1s line shape as shoulder peaks at higher binding energies (286-288
The O/C ratio dropped as the pyrolysis temperature increased to 300 °C (O/C ~ 0.16) and continued to decrease gradually. The shoulder peaks in the C 1s spectra also decreased with increasing temperature. The main peak FWHM decreased and the line shape became highly asymmetric with increasing temperature. This was indicative of the increasing polyaromatic nature of the material. The FWHM nearly became less than 1, when the pyrolysis temperature exceeded 500 °C.

Figure 4.7: High resolution C 1s XPS spectra of PFA200, PFA300, PFA400, PFA500, and PFA600.
Table 4.1 also summarizes the elemental composition and skeletal density of the samples pyrolyzed at different temperatures. The H/C ratio in the sample is 1.0 at room temperature. As we increased the temperature, the H/C gradually started to decrease. It is interesting to note that a significant amount of hydrogen remained in the sample pyrolyzed up to 500 °C (H/C ~ 0.42). However, the H/C ratio dropped drastically between 500 °C and 600 °C. The densities of the samples were relatively constant over the temperature range of interest.

Table 4.1: Elemental composition, C 1s full width at half max (FWHM), and skeletal density of PFA-derived carbon.

<table>
<thead>
<tr>
<th>Sample</th>
<th>H/C</th>
<th>O/C</th>
<th>C 1s FWHM</th>
<th>ρ (gm cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFA25</td>
<td>1.02</td>
<td>0.28</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PFA200</td>
<td>0.78</td>
<td>0.27</td>
<td>2.33</td>
<td>1.40</td>
</tr>
<tr>
<td>PFA300</td>
<td>0.74</td>
<td>0.16</td>
<td>1.98</td>
<td>1.36</td>
</tr>
<tr>
<td>PFA400</td>
<td>0.62</td>
<td>0.15</td>
<td>1.40</td>
<td>1.34</td>
</tr>
<tr>
<td>PFA500</td>
<td>0.42</td>
<td>0.15</td>
<td>1.36</td>
<td>1.40</td>
</tr>
<tr>
<td>PFA600</td>
<td>0.07</td>
<td>0.12</td>
<td>1.17</td>
<td>1.49</td>
</tr>
<tr>
<td>PFA800</td>
<td>-</td>
<td>-</td>
<td>0.97</td>
<td>-</td>
</tr>
<tr>
<td>PFA2000</td>
<td>-</td>
<td>-</td>
<td>0.78</td>
<td>-</td>
</tr>
</tbody>
</table>

The thermal history of the carbons was probed by continuing the pyrolysis in the TGA up to 800 °C. The results are given in Figure 4.8. PFA200 began losing weight at ~200 °C. Both PFA300 and PFA400 were stable until ~400 °C, at which point PFA300 began to lose weight more rapidly. The profiles of PFA500 and PFA600 were similar until ~500 °C and their weight loss was much less than that of PFA400. A sample was also pyrolyzed at 300 °C with a two week soak time. The continued pyrolysis of this sample is given in Figure 4.9 and is compared to PFA300, PFA400, and PFA500. The weight loss during continued pyrolysis for the two week sample was less than that
observed for PFA300 and PFA400. The two week profile is identical to PFA400 above ~500 °C. Decomposition reactions which occurred within one hour at 400 °C were induced at 300 °C by thermal soaking for extended time. Pyrolysis reactions requiring temperatures in excess of 400 °C did not occur at 300 °C.

Figure 4.8: TGA profiles of continued pyrolysis of PFA200, PFA300, PFA400, PFA500, and PFA600.
The total pore volume for carbons prepared with Triton X-100 (TRI), no solvent (NS), and Durez resin (DZ) are given in Figure 4.10, Figure 4.11, and Figure 4.12. The trends in porosity for each carbon are identical to the carbons prepared with THF (Figure 4.6). At 300 °C both nano- and mesopores appeared. When the temperature was raised to 600 °C, the carbon’s mesopores collapsed, while the nanopore volume increased. NS and DZ carbons were entirely nanoporous with the pores monodisperse in width and centered at 0.4-0.5 nm. Although the mesopore volume of the TRI carbon was reduced at 600 °C, it was not entirely eliminated.

Figure 4.9: TGA profiles of continued pyrolysis of PFA300, PFA400, PFA500, and PFA300 2 Week.
Figure 4.10: Total pore volume of carbons derived from PFA polymerized with Triton X-100 (TRI300, TRI400, TRI600) calculated by the methyl chloride adsorption isotherm.
Figure 4.11: Total pore volume of carbons derived from PFA polymerized without solvent (NS300, NS400, NS600) calculated by the methyl chloride adsorption isotherm.
Figure 4.12: Total pore volume of carbons derived commercially available Durez resin (DZ300, DZ600) calculated by the methyl chloride adsorption isotherm.

4.4 Discussion

Inherent meso- and nanoporosity make NPC derived from PFA an attractive candidate for numerous technologies, yet the processes required to generate these properties remain poorly understood at the molecular level. The pyrolysis of PFA has been extensively characterized at several temperatures during its thermal history. These
observations have provided insight to the dramatic chemical and physical changes which occur as PFA is transformed to NPC.

At 25 °C the polymer PFA is primarily comprised of furan rings linked together by methylene (-CH₂-) bridges. According to Choura et al., cross-linking in PFA is predicated upon the formation of conjugated sequences on the polymer backbone [9]. Evidence of both conjugated and cross-linked structures has been found in the IR and NMR spectra of PFA200. Conjugation creates a double bond between the β carbons of the furan ring (labeled B), which results in a shift of the 1350 cm⁻¹ -CH stretch to 1400 cm⁻¹ and the appearance of the 1620 cm⁻¹ signal in IR spectrum. The broad peaks in the NMR spectrum at ~95 and ~130 ppm, which intensify between PFA25 and PFA200, are attributed to conjugated sequences in the polymer. A second indicator of conjugation is the peak at ~15 ppm representing -CH₃ terminated PFA chains, which are a by-product of the conjugation reaction. Cross-links are signified by the broad peak at ~45 ppm, which corresponds to -CH groups at the cross-link junctions (labeled F). The cross-links are a result of either a methylene bridge or Diels-Alder condensation.

Increasing the pyrolysis temperature to 300 °C induces the spontaneous generation of nanopores. Surprisingly, a significant amount of mesoporosity is also developed in PFA300. Loss of the IR signals at 1050 cm⁻¹ and 1100 cm⁻¹ and evolution of CO and CO₂ in the mass spectrum confirm a rupture of the furan ring ether linkages. The O/C ratio drops precipitously from 0.27 to 0.16. Furan ring vibrations disappear from the IR as the fractured rings coalesce to form polyaromatics (labeled G in Figure 4.5), whose presence is shown by the IR peaks at 1200 cm⁻¹, 1145 cm⁻¹ and 1065 cm⁻¹. The broadened signal in the region of 1620 cm⁻¹ now represents both polyaromatics and the
remnants of polymer conjugation. The polyaromatics also appear in the NMR spectrum at ~130 ppm. Incomplete scission of the ether linkages leads to carbonyl groups on the residual polymer, typified by the new peaks at 1710 cm\(^{-1}\) and 1750 cm\(^{-1}\) in the IR (labeled H). A number of oxygen moieties are also expected to reside on the polyaromatic domains (labeled H), as in activated carbon samples. There is very little change in the H/C ratio between PFA200 and PFA300; therefore the carbon must also be infused with residual hydrogen from the furan rings and methylene bridges.

At 400 °C the hydrogen content is reduced, due to the release of CH\(_4\). The IR spectrum exhibits strengthened polyaromatic signatures at 1620 cm\(^{-1}\), 1200 cm\(^{-1}\), 1145 cm\(^{-1}\) and 1065 cm\(^{-1}\). The carbonyl peaks are maintained in the IR at 1710 cm\(^{-1}\) and 1750 cm\(^{-1}\). In addition, the nano- and mesoporosity of PFA400 is similar to PFA300. Figure 4.8 demonstrates that when pyrolysis is continued in the TGA; PFA300 and PFA400 behave identically until heated to greater than 400 °C. Therefore heating the sample to 400 °C has not induced significant further decomposition of the residual polymer and heteroatoms in the sample.

The second major weight loss occurs when the PFA is heated to 500 °C. The H/C and O/C ratios are further reduced by the release of CO, CO\(_2\), CH\(_4\), and H\(_2\)O. The chemical changes are accompanied by a radical change in the porosity. Surprisingly the mesopore volume is significantly reduced. The loss of mesoporosity correlates with the elimination of carbonyl groups in the IR spectrum and reduction in hydrogen content. The post-pyrolysis TGA profile of PFA500 is more similar to PFA600 than PFA400. Much of the decomposition that will happen by 600 °C has already occurred at 500 °C.
The development and disappearance of mesopores is confirmed to be independent of the type of PFA utilized to derive the carbon. Transient mesopores are also a characteristic of carbons from polymers containing Triton X-100 or no solvent and Durez resin. The elimination of mesopores in the TRI carbons is not complete, as the surfactant is known to act as an agent of mesopore formation. This phenomenon was explained further in 3.4. Mesopores native to pyrolysis of PFA appear and disappear in this sample; however mesopores generated by inclusion of Triton X-100 are preserved.

Extensive characterization of the PFA in the temperature range of 200-600 °C allows us to address the mechanism of nano- and mesopore formation in the carbon. The ether linkages in the furan rings fracture at 300 °C, leading to liberation of oxygen in the form of CO and CO\textsubscript{2} gasses. Remnants of the furan rings coalesce to form highly disordered aromatic domains within which the nanopores reside. At this temperature the pyrolysis is incomplete, leaving partially fractured ether linkages to form carbonyl groups among the aromatics. These fragments more closely resemble the original polymer, rather than the final carbon, and are the cause of mesoporosity. A large fraction of the hydrogen species present in the original polymer also remain in the material. The polymer fragments and the oxygen (hetero) atoms buffer the aromatic domains from one another, creating the void spaces, or mesopores, in the material. The TGA profile of PFA soaked at 300 °C for 2 weeks is similar to PFA400, which was soaked for 1 hour. Although decomposition continued over the two week period, the total and differential pore volumes were identical to PFA300. Very little change in porosity occurs at 400 °C; rather the existing aromatic domains are annealed, leading to stronger IR signals. A thermal barrier to continued pyrolysis exists at 400 °C. When this obstacle is defeated by
heating to 500 °C a second major weight loss is seen as the polymer remnants are decomposed and oxygen (hetero) atoms are ejected, creating increased nanoporosity. A consequence is the loss of mesopores, which now collapse without the buffering polymeric material. The few remaining mesopores are mostly eliminated by heating to 600 °C; this effect is again accompanied by a slight increase in nanopore volume.

4.5 Conclusions

Fitzer and Schafer suspected open pores with diameters smaller than 100 Å must be present to facilitate the transport of gaseous products formed during the pyrolysis PFA [1, 2]. This hypothesis has been confirmed and a clear picture of the intermediates formed during pyrolysis is now available. Upon heating to 300 °C, PFA spontaneously decomposes and begins to convert to a mesoporous solid consisting of polymer remnants and aromatic cores that form the basis for the NPC which is produced with further pyrolysis at higher temperature. Oxygen and hydrogen moieties decorate the aromatic domains and the residual polymer in the material and thereby create the transient mesopores. The heteroatoms are driven out by heating above 400 °C and the mesopores then collapse. A carbon characterized by monodisperse nanopores remains at 600 °C. The evolution of porosity due to activation and high temperature treatment is continued on the next chapter.
4.6 References

Chapter 5

Overcoming the intrinsic barrier to graphitization in nanoporous carbon

5.1 Introduction

The unique properties of nanoporous carbon have been attributed to the presence of extensive cross-linking in the precursor, which manifests as a chaotic misalignment of graphene layers in the carbon [1-3]. Over the last sixty years, a wealth of knowledge has been accumulated with respect to the structure and properties of non-graphitizing carbon, yet the intrinsic barrier to graphitization is still not entirely understood. Efforts to overcome the barrier to graphitization are reported in this chapter.

The effect of annealing on a graphitizing carbon has been studied in detail by Rouzaud and Oberlin [3]. The carbon microstructure passes through four phases during conversion to graphite. Pyrolysis creates stage one, where the carbon is comprised of aromatic domains, deemed basic structural units (BSU). Stage two is achieved by removal of labile heteroatoms, which allows alignment of the BSU along the c-axis to form distorted columns. Inter-layer defects are annealed out of the structure during stage three, leaving turbostratic graphite with wrinkled planes. Removal of heteroatoms fixed at the defects in the layers permits the defects to heal and form highly crystalline graphite. The same four transformations are also expected to occur in non-graphitizing carbon, although on a smaller scale. Movement of the BSU is restricted by cross-linked structures.
A new pathway to synthesize a carbon with both nanoporosity and pre-graphitic domains has been discovered by annealing nanoporous activated carbon. The activation process permits the carbon to overcome its intrinsic barrier to graphitization upon high temperature treatment at 2000 °C. Gas sorption analysis, skeletal density measurements, x-ray diffraction (XRD), and transmission electron microscopy (TEM) are utilized to probe the structure of both non-activated and activated carbons at 800, 1200, 1800, and 2000 °C. The influence of activation time is also examined.

5.2 Experimental

0.048 gm of p-toluenesulfonic acid monohydrate was dissolved in 5 ml of Triton X-100 by heating mildly. To this solution, 5 ml of furfuryl alcohol (FA) was added. The reaction mixture was stirred magnetically at 10 °C. After polymerization for 48 hours the product was transferred to a quartz boat and pyrolyzed under flowing argon in a quartz tube furnace. The sample was heated at a rate of 10 °C min\(^{-1}\) to 800 °C and held for 1 hour. The carbon was ground and sieved to a particle size of < 38 μm.

Activated NPC was prepared in a quartz tube furnace. 0.5 gm of carbon was heated to 900 °C over 1 hour in flowing argon. After 1 hour of soak time the gas was switched to CO\(_2\) and soaked for up to 3.5 hours. The sample was cooled back to room temperature under argon.

High temperature treatment (HTT) was carried out in a Red Devil furnace (R. D. Webb Company, Natick, MA). The hot zone was evacuated to 10\(^{-3}\) mbar for 24 hours prior to annealing, then backfilled to atmospheric pressure with argon. A 25 °C min\(^{-1}\)
heating rate was employed with a 1 hour soak at temperatures between 1200 and 2000 °C.

5.3 Results

Samples were labeled according to the maximum temperature of HTT and activation was noted. For example, NPC1200 was annealed at 1200 °C, whereas a-NPC1200 was activated at 900 °C prior to annealing at 1200 °C. If less than 3.5 h, the activation time is also noted, for example a-NPC800, 0.5 h. NPC800 was the starting material for preparation of all the activated carbons.

A plot of the total pore volume of NPC800 is given in Figure 5.1. The carbon had a pore volume of 0.20 cm³ gm⁻¹, with monodisperse nanopores at a width of ~0.5 nm. A small amount of mesoporosity was also present. Annealing at 1200 °C rendered a majority of the nanopores inaccessible to the probe gas. Just 10% of the original pore volume remained at 2000 °C. The volumes of the nano- and mesopores are summarized in Table 5.1 in addition to the apparent carbon surface areas measured by N₂ BET.
Figure 5.1: Total and differential pore volumes of NPC800, NPC1200, NPC1800, and NPC2000.

Table 5.1: Nano- ($V_{nano}$), meso- ($V_{meso}$) and total pore ($V_{total}$) volumes, and apparent surface areas (SA) of NPC and a-NPC. Burnoff was 84% for the a-NPC samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$V_{nano}$ ($cm^3 gm^{-1}$)</th>
<th>$V_{meso}$ ($cm^3 gm^{-1}$)</th>
<th>$V_{total}$ ($cm^3 gm^{-1}$)</th>
<th>Apparent SA ($m^2 gm^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPC800</td>
<td>0.16</td>
<td>0.04</td>
<td>0.20</td>
<td>317</td>
</tr>
<tr>
<td>NPC1200</td>
<td>0.04</td>
<td>0.04</td>
<td>0.08</td>
<td>23</td>
</tr>
<tr>
<td>NPC1800</td>
<td>0.01</td>
<td>0.00</td>
<td>0.01</td>
<td>27</td>
</tr>
<tr>
<td>NPC2000</td>
<td>0.01</td>
<td>0.02</td>
<td>0.03</td>
<td>22</td>
</tr>
<tr>
<td>a-NPC800</td>
<td>0.95</td>
<td>0.35</td>
<td>1.30</td>
<td>2135</td>
</tr>
<tr>
<td>a-NPC1200</td>
<td>0.84</td>
<td>0.26</td>
<td>1.10</td>
<td>1967</td>
</tr>
<tr>
<td>a-NPC1800</td>
<td>0.57</td>
<td>0.25</td>
<td>0.82</td>
<td>1698</td>
</tr>
<tr>
<td>a-NPC2000</td>
<td>0.50</td>
<td>0.22</td>
<td>0.72</td>
<td>1060</td>
</tr>
</tbody>
</table>
Figure 5.2 illustrates the changes in skeletal density occurring as NPC and a-NPC are subjected to HTT. The density of NPC800 was 1.93 gm cm\(^{-3}\). For non-activated samples the density was not significantly altered up to 1400 °C, at which point it began to decrease towards a value of 1.40 gm cm\(^{-3}\) at 2000 °C. Activation for 3.5 h increased the density to 2.35 gm cm\(^{-3}\) for a-NPC800, which is slightly higher than the maximum density of graphite. The difference is attributed to the addition of more massive oxygen atoms to the carbon matrix. When subjected to HTT, the a-NPC density decreases linearly. At 2000 °C the density of a-NPC2000 remains 0.56 gm cm\(^{-3}\) higher than NPC2000.
Figure 5.2: Skeletal densities of NPC and a-NPC versus annealing temperature.

Powder x-ray diffraction patterns were collected for each NPC sample and are depicted in Figure 5.3. NPC800 was characterized by a broad (002) line, which was indicative of a high degree of disorder in the graphene layers. As HTT continued at progressively higher temperatures the peak narrowed and shifted towards the ideal (002) 2θ value of graphite, 26.5°. The d₀₀₂ of NPC800 was calculated from the Bragg equation and was found to be 3.68 Å. No change was observed at 1200 °C and the d₀₀₂ narrowed to 3.55 and 3.50 Å with HTT at 1800 and 2000 °C. An average crystallite size was determined by the Scherrer equation using the (002) and (10) peaks for Lₖ and L₉,
respectively. $L_c$ was found to increase from 10 to 15 Å between 800 and 2000 °C. $L_a$ increased from 15 to 27 Å over the same temperature range. All values of $d_{002}$, $L_c$, and $L_a$ are summarized in Table 5.2.

Figure 5.3: XRD patterns of NPC800, NPC1200, NPC1800, and NPC2000.
Changes in microstructure were also observed via TEM. NPC800, shown in Figure 5.4 was homogeneous and clearly globally amorphous. Ordered domains appeared and the number of stacked layers increased as a function of HTT. NPC1200 and NPC1800 are shown in Figure 5.5 and Figure 5.6. NPC2000 was inhomogeneous and comprised of highly curved ribbons no more than 10 graphene layers in thickness. An image of NPC2000 is given in Figure 5.7.
Figure 5.4: TEM image of NPC800.
Figure 5.5: TEM image of NPC1200.
Figure 5.6: TEM image of NPC1800.
Figure 5.7: TEM image of NPC2000.
Activation of NPC800 with CO\textsubscript{2} yielded \textasciitilde16\% of a-NPC800 by weight. The burnoff was 84\%. The activated carbons (a-NPC800) were then subjected to HTT. Total and differential pore volumes were measured at each temperature. The results are summarized in Figure 5.8 and Table 5.1. A six-fold increase in nanopore volume to 0.95 cm\textsuperscript{3} gm\textsuperscript{-1} was realized upon activation. As HTT increased, the nanopore volume was reduced. The nanopore volume of a-NPC2000 was 0.50 cm\textsuperscript{3} gm\textsuperscript{-1}. There was relatively very little change in the pore volume between a-NPC1800 and a-NPC2000. The differential pore volume demonstrated a shift in the mean nanopore width from 0.5 to 0.82 nm after activation, which was not altered by subsequent annealing.
Figure 5.8: Total and differential pore volumes of NPC800, a-NPC800, a-NPC1200, a-NPC1800, and a-NPC2000.
X-ray diffraction patterns for the annealed a-NPC samples are given in Figure 5.9. The (002) reflection was absent from a-NPC800, which indicated the number of graphene layers in the pore wall were reduced below the level of detection. A broad (002) line reappeared in a-NPC1800, denoting coalescence of graphene planes into thicker layers. A surprising pattern was observed when the HTT was increased further to 2000 °C; a sharp (002) line appeared superimposed on the broad background. The $d_{002}$, $L_c$, and $L_a$ values were calculated and are given in Table 5.2.

![Figure 5.9: XRD patterns of a-NPC800, a-NPC1200, a-NPC1800, and a-NPC2000.](image-url)
The (002) peak of a-NPC2000 was resolved into an amorphous (A), turbostratic (T), and graphitic (G) component [4, 5]. The fit is shown in Figure 5.10. The A-component had a $d_{002}$ of 3.66 Å, with an $L_c$ size of 10 Å. A $d_{002}$ of 3.44 Å identified the T-component. Its average $L_c$ size was 276 Å. The G-component had a 3.37 Å $d_{002}$ and 145 Å $L_c$. The trend in $L_a$ was similar to the non-activated samples. $d_{002}$, $L_c$, and $L_a$ values were calculated and are given in Table 5.2.

![Figure 5.10: Fit of A-, T-, and G-components to a-NPC2000. The $d_{002}$ of the three components were 3.66, 3.44, and 3.37 Å. Crystallite sizes ($L_c$) were 10, 276, and 145 Å, respectively.](image-url)
Table 5.2: Interlayer spacing (d_{002}), and crystallite sizes (L_c and L_a) for components of NPC and a-NPC. L_a was calculated from the (10) peaks.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Component</th>
<th>d_{002} (Å)</th>
<th>L_c (Å)</th>
<th>L_a (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPC800</td>
<td>A</td>
<td>3.69</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>NPC1200</td>
<td>A</td>
<td>3.69</td>
<td>10</td>
<td>18</td>
</tr>
<tr>
<td>NPC1800</td>
<td>A</td>
<td>3.55</td>
<td>13</td>
<td>24</td>
</tr>
<tr>
<td>NPC2000</td>
<td>A</td>
<td>3.50</td>
<td>15</td>
<td>27</td>
</tr>
<tr>
<td>a-NPC800</td>
<td>A</td>
<td>-</td>
<td>-</td>
<td>17</td>
</tr>
<tr>
<td>a-NPC1200</td>
<td>A</td>
<td>-</td>
<td>-</td>
<td>18</td>
</tr>
<tr>
<td>a-NPC1800</td>
<td>A</td>
<td>3.72</td>
<td>5</td>
<td>24</td>
</tr>
<tr>
<td>a-NPC2000</td>
<td>A</td>
<td>3.66</td>
<td>10</td>
<td>25</td>
</tr>
<tr>
<td>T</td>
<td></td>
<td>3.44</td>
<td>276</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td></td>
<td>3.37</td>
<td>145</td>
<td></td>
</tr>
</tbody>
</table>

The microstructures of a-NPC800 and a-NPC2000 were observed in TEM. a-NPC800 was confirmed to be amorphous in Figure 5.11 and no changes were observed at 1200 or 1800 °C. Two distinct microstructures were found after HTT at 2000 °C. Figure 5.12 demonstrates an amorphous structure, while Figure 5.13 displays pre-graphitic textures. Figure 5.14 shows the A-, T-, and G- component microstructures in intimate contact.
Figure 5.11: TEM image of a-NPC800.
Figure 5.12: TEM image of an amorphous region in a-NPC2000.
Figure 5.13: TEM image of a pre-graphitic region in a-NPC2000.
Figure 5.14: TEM image of amorphous and pre-graphitic regions in a-NPC2000.
In order to determine the effect of activation time on the formation of pre-graphitic structures at 2000 °C, samples of NPC800 were activated for 0.5, 1.5, and 2.5 h, in addition to the standard 3.5 h described previously. The carbon burnoffs were 15%, 42%, and 69% for 0.5, 1.5, and 2.5 h, respectively. The total and differential pore volumes for the activated carbons are given in Figure 5.15. A slight increase in nanoporosity was observed after 0.5 h. A marked increase in nanoporosity was found after 1.5 and 2.5 h of activation. Between 2.5 h and 3.5 h the total porosity increased, although it was primarily in the mesopore range. Skeletal densities were also recorded as a function of activation time. The values are shown in Figure 5.16.
Figure 5.15: Total and differential pore volumes of NPC800 and a-NPC activated for 0.5, 1.5, 2.5, and 3.5 hours.
Figure 5.16: Skeletal densities of NPC800 and a-NPC activated for 0.5, 1.5, 2.5, and 3.5 hours.
Figure 5.17 shows the x-ray diffraction patterns collected for each of the carbons activated for less than 3.5 h. The broad (002) peak of NPC800 was maintained after 0.5 h of activation. The intensity was reduced at 1.5 h and the peak was indistinguishable from the baseline beyond 2.5 h. $d_{002}$, $L_c$, and $L_a$ parameters for the samples were relatively constant regardless of the activation time. The values are summarized in Table 5.3.

![XRD patterns](image)

Figure 5.17: XRD patterns of NPC800 and a-NPC800 activated for 0.5, 1.5, 2.5, and 3.5 hours.
The porosity retained by each of the activated carbons after HTT at 2000 °C is demonstrated in Figure 5.18. Pore volumes of 0.55 and 0.72 cm$^3$ gm$^{-1}$ were maintained in the 2.5 and 3.5 h samples, respectively. For the a-NPC2000, 1.5h carbon 0.14 cm$^3$ gm$^{-1}$ of pore volume was present, which was nearly equivalent to the initial pore volume of NPC800 prior to activation or HTT. Complete pore collapse occurred when the activation was just 0.5 h. The mean pore widths were all shifted to 0.82 nm.

![Graph showing pore volume and pore width](image)

Figure 5.18: Total and differential pore volumes of a-NPC2000 which was previously activated for 0, 0.5, 1.5, 2.5, and 3.5 hours, as calculated by the methyl chloride adsorption isotherm.
Powder diffraction patterns were collected after the various activated carbons were annealed at 2000 °C and they are shown in Figure 5.19. The calculated parameters $d_{002}$, $L_c$, and $L_a$ are given in Table 5.3. The (002) reflection characteristic of activated carbon subjected to HTT at 2000 °C was evident in each of the samples. A pre-graphitic peak appeared over the amorphous background after just 0.5 h of activation; however, it was not possible to fit both A- and T- peaks. The line was attributed solely to an amorphous carbon. An A- and T-component were distinguishable in the a-NPC2000, 1.5h sample. The annealed carbon initially activated for 2.5 hours also had A- and T-components, but a G-component was also found. The growth of $L_a$ was again analogous to the non-activated samples.
Figure 5.19: XRD patterns of NPC2000 and a-NPC200, which was activated for 0.5, 1.5, 2.5, and 3.5 hours prior to annealing at 2000 °C.
Table 5.3: Interlayer spacing ($d_{002}$), and crystallite sizes ($L_c$ and $L_a$) for components of NPC and a-NPC for various activation times. $L_a$ was calculated from the (10) peaks.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Component</th>
<th>$d_{002}$ (Å)</th>
<th>$L_c$ (Å)</th>
<th>$L_a$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPC800</td>
<td>A</td>
<td>3.69</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>a-NPC800, 0.5h</td>
<td>A</td>
<td>3.74</td>
<td>10</td>
<td>16</td>
</tr>
<tr>
<td>a-NPC800, 1.5h</td>
<td>A</td>
<td>3.70</td>
<td>10</td>
<td>17</td>
</tr>
<tr>
<td>a-NPC800, 2.5h</td>
<td>A</td>
<td>-</td>
<td>-</td>
<td>16</td>
</tr>
<tr>
<td>a-NPC800, 3.5h</td>
<td>A</td>
<td>-</td>
<td>-</td>
<td>17</td>
</tr>
<tr>
<td>NPC2000</td>
<td>A</td>
<td>3.50</td>
<td>15</td>
<td>27</td>
</tr>
<tr>
<td>a-NPC2000, 0.5h</td>
<td>A</td>
<td>3.49</td>
<td>14</td>
<td>26</td>
</tr>
<tr>
<td>a-NPC2000, 1.5h</td>
<td>A</td>
<td>3.54</td>
<td>12</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>T</td>
<td>3.44</td>
<td>279</td>
<td></td>
</tr>
<tr>
<td>a-NPC2000, 2.5h</td>
<td>A</td>
<td>3.60</td>
<td>10</td>
<td>26</td>
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<td>T</td>
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<tr>
<td></td>
<td>G</td>
<td>3.38</td>
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</tr>
<tr>
<td>a-NPC2000, 3.5h</td>
<td>A</td>
<td>3.66</td>
<td>10</td>
<td>25</td>
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</tr>
<tr>
<td></td>
<td>G</td>
<td>3.37</td>
<td>145</td>
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</tr>
</tbody>
</table>

5.4 Discussion

Glassy carbon derived from pyrolysis of polyfurfuryl alcohol is considered non-graphitizing. Cross-linking in the polymer phase is believed to induce the resistance to graphitization, yet the exact manifestation of the cross-link structure in the carbon material is unknown. Characterization of NPC and a-NPC subjected to HTT up to 2000 °C has elucidated a pathway to convert a non-graphitizing carbon to a graphitizing carbon.

NPC800 derived from PFA and Triton X-100 is both nano- and mesoporous. A Triton X-100 molecule is comprised of a benzene ring connected to both an eight carbon
alkyl chain and a polyethylene glycol chain approximately 10 monomeric units in length. The low-molecular weight PEG acts as a mesopore forming agent, as reported by Strano et al. for pure PEG blended with PFA [6]. After HTT the accessibility of the methyl chloride probe gas to the nanopore structure in NPC1200 is reduced. The nanopore volume falls from 0.16 to 0.04 cm$^3$ gm$^{-1}$. Further annealing at 2000 °C closes all but a small volume of mesopores, 0.02 cm$^3$ gm$^{-1}$. Correspondingly, the apparent surface area of the carbon decreases from 317 to 22 m$^2$ gm$^{-1}$ after HTT.

The skeletal density of a perfect graphite crystal is 2.25 gm cm$^{-3}$. The density of NPC800 is much lower, 1.93 gm cm$^{-3}$. This difference is attributed to both the disordered graphene layers containing five and seven-membered rings and the presence of inherent closed porosity incorporated during pyrolysis. Closed pores leave inaccessible void spaces in the carbon structure, which contribute to the apparent volume occupied by the carbon, but do not increase its mass. Despite the immediate changes in porosity observed after annealing at 1200 °C, the skeletal density of NPC is unchanged up to 1400 °C. Thus the pore structure is not completely closed, rather the pore mouths are narrowed to exclude methyl chloride, but permit entrance of the smaller helium molecule. Annealing above 1400 °C causes complete pore closure to occur and the density decreases to 1.4 gm cm$^{-3}$ for NPC2000.

Crystalline graphite is characterized by a sharp (002) diffraction peak at 2θ = 26.5°, which corresponds to a d$_{002}$ of 3.35 Å. The x-ray diffraction patterns of NPC annealed up to 2000 °C clearly indicate that polyfurfuryl alcohol derived carbon is non-graphitizing. The crystallinity of NPC1200 is unchanged, but further heating to 1800 and 2000 °C shifts the (002) line towards 26.5° and reduces peak broadening. The d$_{002}$ is
decreased to 3.51 Å for NPC2000 and the average $L_c$ size grows from 10 to just 15 Å. Significant stacking of the layer planes does not occur; neither does edge coalescence. The $L_a$ parameter roughly doubles with HTT to 2000 °C.

The microstructure of the carbons is observed in the TEM. No clear, coherent structures are found in the image of NPC800, Figure 5.4. The graphene layers are randomly oriented with respect to each other. A change in the microstructure is evident in Figure 5.5, which corresponds to NPC1200. Small groups of layer planes have coalesced into more ordered structures. The domains of higher crystallinity continue to grow at 1800 °C. NPC2000 is comprised of intertwined ribbons of graphene layers, Figure 5.7. The ribbons are at most 10 layers thick and are highly curved, which reduces coherence in the a-direction. Continuity of the crystallinity in the graphitic domains extends only a few nanometers. According to the bulk x-ray pattern, NPC2000 is still considered globally amorphous.

Activation with CO$_2$ for 3.5 h greatly increases the pore volume of the carbon. Annealing at 1200 °C causes a 15% drop in porosity. Porosity is further diminished in a-NPC1800 and the volume of a-NPC2000 is 55% of the original a-NPC800. The pore volumes are still significantly larger than those realized prior to activation, which in contrast to NPC2000, where the pore volume is essentially eliminated. An average pore width of 0.82 nm is maintained throughout the HTT for the activated samples. The carbon remains amorphous throughout activation, as shown in Figure 5.11.

If the open pores are converted to closed pores, an accompanying decrease in skeletal density is expected. The skeletal density linearly decreases with HTT from 2.35 gm cm$^{-3}$ for a-NPC800 to 1.96 gm cm$^{-3}$ for a-NPC2000. The 0.39 gm cm$^{-3}$ drop in
density is accompanied by a 0.58 gm cm\(^{-3}\) loss of pore volume. Whereas with the non-activated samples a pore volume of decrease of 0.17 gm cm\(^{-3}\) causes a 0.53 gm cm\(^{-3}\) drop in density. Pore closure is occurring in the activated samples, but not all pores leave behind inaccessible void spaces. The decrease in density is disproportionate to the loss of porosity; therefore a portion of the pores must be converted to a higher density material.

XRD patterns of the annealed activated carbons are remarkably different from their non-activated counterparts. A (002) line for a-NPC800 in Figure 5.9 is undetectable. Intensity of the (002) peak is related to the stacking of graphenes in the layers which form the pore walls. Its absence indicates the pore wall thickness is reduced during activation below the level of detection. The pore walls of the activated carbon are comprised of very few layers or even a single layer. Annealing the carbon causes the graphenes to coalesce and form thicker domains. A broad, low intensity (002) line reappears in a-NPC1800. Further HTT to 2000 °C creates a surprising carbon material. The sharp line at 26° indicates pre-graphitic carbon is present in the sample.

De-convolution of the a-NPC2000 (002), shown in Figure 5.10, reveals three components: amorphous (A), turbostratic (T), and graphitic (G) [4, 5]. The broad amorphous background peak has a \(d_{002}\) of 3.66 Å, which is reminiscent of NPC800 with a 3.68 Å \(d_{002}\). The sharp line at 26° is assigned to turbostratic carbon and the shoulder peak at 26.5° is graphitic carbon. Confirmation of the presence of the three structures is found in the TEM image. An amorphous region of a-NPC2000 is shown in Figure 5.12. Graphitic and turbostratic morphologies are evident in Figure 5.13. The three components are shown together in Figure 5.14. The ordered structures are termed pre-
graphitic as order extends in two dimensions, not three. True graphite is ordered in here dimensions.

The effect of activation time on the tendency of the carbon to graphitize at 2000 °C was studied by reducing the activation time to several points less than 3.5 h. The slight increase in nanoporosity found after 0.5 h of activation was accompanied by an increase in skeletal density. The initially closed porosity is not yet entirely opened; else the skeletal density would approach 2.25 gm cm$^{-3}$. The entire pore structure must be open before pore wall thinning becomes the dominant activation process. Therefore the (002) peak intensity has not reduced in a-NPC800, 0.5h and graphitization has not occurred after annealing at 2000 °C (a-NPC2000, 0.5h). A sharper jump in porosity occurs after 1.5 h of activation and the density reaches 2.22 gm cm$^{-3}$, which is on par with graphite. The entire pore structure is accessible to the probe gas at this point. Additional porosity is now created by pore wall thinning and removal of disordered carbon. This is evident in the reduction of the (002) line of a-NPC800, 1.5h. Oxidation of the pore walls and disordered carbon facilitates formation of pre-graphite, as a turbostratic peak is fit to the XRD pattern of a-NPC2000, 1.5h. Continued activation to 2.5 h further increases nanoporosity, while also introducing mesoporosity. The skeletal density increases to match the 3.5 h sample and the (002) peak is approaching the limit of detection in a-NPC800, 2.5h. A G-component is identified after annealing. The final hour of activation time primarily generates mesoporosity, but also further thins the nanopore walls, as a (002) line has become indistinguishable from the background. However, activation to 2.5 h sufficiently frees the graphene layers to coalesce and form the G-component. HTT at
2000 °C is unable to eliminate the whole nanoporosity for all carbons except a-NPC2000, 0.5h, which had an activated pore volume barely larger than a non-activated carbon.

NPC pyrolyzed at 800 °C is non-graphitizing even when annealed at 2000 °C. The carbon is comprised of disordered of graphene layers, which are “kinetically frozen” [2]. Although disordered, the layers are interconnected and contain non-six-membered rings which prevent realignment of the layers to form long-range graphitic structures. Although high temperature treatment between 1200 and 2000 °C is able to progressively introduce further order in the material, it must be considered amorphous. The pore structure is rendered completely inaccessible as a result of imposing the thermally forcing conditions. Activation dramatically enhances the carbon porosity and enables gas molecules access to the entire material. A side effect is the removal of a significant amount of carbon material from the original structure. This is expected to include the portions of the highly disordered carbon containing five and seven-member rings, which are more susceptible to oxidation than pristine graphene layers. A reduction in the number of graphene layers in the pore wall is also found via XRD. After removal of a part of the highly disordered carbon, the thinner layers are more mobile and able to align themselves into pre-graphitic domains with long-range two dimensional order when annealed at 2000 °C. Activation for 1.5 h is sufficient to permit turbostratic formation. However, an additional activation, 2.5 or 3.5 h in total, is necessary to adequately thin the layers to permit graphite formation. Conversion to pre-graphite is incomplete and thus nanoporous amorphous carbon remains interspersed with the pre-graphitic structures. This inhomogeneous microstructure is advantageous as the preserved molecular sieving
nanopores, with a width of 0.82 nm, create surface area which can provide ready access to the pre-graphitic regions.

5.5 Conclusions

Rouzaud and Oberlin suggested graphitizing carbons consist of basic structural units which graphitize by passing through four stages during HTT [3]. At each stage sufficient thermal energy is provided to release heteroatoms or drive out defects in the graphene layer planes. The end result is a highly crystalline graphitic carbon. In the case of non-graphitizing carbons, this process is localized. Highly disordered carbon, which is a legacy of cross-linking in the polymeric phase, restricts the freedom of the basic structural units to align and form graphite. Activation removes disordered, oxidation-susceptible carbon structures, thereby overcoming the barrier to graphitization in polyfurfuryl alcohol derived nanoporous carbon. When activated at 900 °C and then annealed at 2000 °C a portion of the once non-graphitizing carbon is now able to organize into pre-graphitic structures. Nanopores are not completely eliminated after HTT of the a-NPC, which is in contrast to NPC. The product is a heterogeneous carbon exhibiting both nanoporosity, a property of the non-graphitizing carbon, and pre-graphite, a property of the crystalline graphitic carbon. The high surface area and porosity carbons (a-NPC800) developed in this chapter are employed to fabricate electrical double layer capacitors in Chapter 6.
5.6 References


Chapter 6

Nanoporous activated carbon for electrical double layer capacitors

6.1 Introduction

Energy storage in an electrical double layer capacitor (EDLC) is based on separation of charged species in a double-layer formed at the electrode/electrolyte interface [1]. Thus an effective EDLC should be designed to maximize the area of the electrode contacting the electrolyte solution [2]. Activated carbons possess high surface areas. Nanopores which have widths less than 2 nm, strongly contribute to a carbon’s surface area. Mesopores have diameters between 2 and 20 nm, and macropores have diameters greater than 20 nm. Larger mesopores and macropores improve electrolyte transport, but do not contribute significantly to the carbon surface area. The activated nanoporous carbons with high surface area and porosity described in Chapter 5 are candidates for this application.

The synthesis and electrochemical performance of a nanoporous activated carbon derived from a polyfurfuryl alcohol (PFA) precursor is reported in this chapter. The porosity of carbons prepared by polymerizing furfuryl alcohol with Triton X-100 (TRI) and tetrahydrofuran (THF) as solvents is evaluated as a function of activation time. The carbons are utilized without subjecting them to HTT beyond 800 °C. Gravimetric and volumetric capacitances are determined after constant current galvanostatic charge/discharge measurements (CC), cyclic voltammetry (CV), and electrochemical
impedance spectroscopy (EIS). Activated NPC (a-NPC) with tunable porosity is shown to be an effective electrode for EDLC.

6.2 Experimental

6.2.1 Synthesis of polyfurfuryl alcohol and activated nanoporous carbon

0.048 gm of $p$-toluenesulfonic acid monohydrate was initially dissolved in 5 ml of either THF or Triton X-100. Mild heating was necessary when using Triton X-100. To this solution, 5 ml of furfuryl alcohol was added. The reaction mixture was stirred magnetically at 10 °C for 48 hours. The polymer was transferred to a quartz boat and pyrolyzed under flowing argon in a quartz tube furnace. The sample was heated at a rate of 10 °C min$^{-1}$ to 800 °C and held for 1 hour. Prior to activation, the carbon was ground and sieved to a particle size of < 38 μm.

Activated NPC was prepared in a quartz tube furnace. 0.5 gm of carbon was heated to 900 °C over 1 hour in flowing argon. After 1 hour of soak time the gas was switched to CO$_2$ and soaked for an additional period of 0.5, 1.5, 2.5, or 3.5 hours. The sample was cooled back to room temperature under argon.

6.2.2 Electrochemical characterization of nanoporous activated carbon

Each electrode was comprised of 85% a-NPC (100 mg), 10% Teflon binder (Electrochem, Inc., Woburn, MA), and 5% by weight acetylene black. After thorough mixing, the powder was pressed into carbon film at 10,000 psi for 20 minutes. The film
was cut to form an electrode with an area ~1 cm² and ~0.3 mm thickness. A two-electrode electrochemical capacitor was fabricated by sandwiching a Celgard 5400 membrane (Celgard, Charlotte, NC) between two identical carbon electrodes. Stainless steel mesh was used as the current collector. The cell was immersed in 1 M H₂SO₄ for 2 day before testing began. One of the carbon electrodes acted as both the counter electrode and reference electrode. All measurements were performed on a 263A Potentiostat/Galvanostat (Princeton Applied Research, Oak Ridge, TN). EIS measurements were done by coupling a Model 5210 Lock-in Amplifier (Signal Recovery, Oak Ridge, TN).

Constant current (CC) experiments were conducted by charging and discharging the two-electrode capacitor from 0 to 0.5 V and applying a constant load current of 250 mA gm⁻¹. The time necessary for the charge and discharge was recorded and the capacitance was calculated by Eq. 6.1.

\[
C = \frac{I}{(dV/\,dt)m}
\]  

The constant current applied in A is \(I\) and electrode mass is \(m\). \(dV/\,dt\) is the slope of the voltage versus time plot. It was measured by linearly regressing data points between 0.2 and 0.4 V of the charge cycle.

Cyclic voltammograms (CV) were recorded between -0.5 and 0.5 V at a scan rate of 5 mV s⁻¹. Parasitic faradiac reactions on the current collector were prevented by limiting the potential to 0.5 V. The specific capacitance was determined by Eq. 6.2, where \(I\) is the average current in A, \(C\) is the specific capacitance in F, \(\nu\) is the scan rate in V s⁻¹, and \(m\) is the electrode mass.
\[ C = \frac{I}{\nu m} \]  

(6.2)

For electrochemical impedance spectroscopy (EIS) measurement, an AC perturbation of 10 mV was applied at the condition of open circuit potential. The perturbation frequency was scanned between \(10^5\) Hz and \(10^{-3}\) Hz.

### 6.3 Results

Examples of the nomenclature for the carbon samples are described here. Carbons derived from PFA synthesized with THF and activated to 11% burn off were labeled THF11. Those polymerized in the presence of Triton X-100 and activated to 84% burn off were denoted TRI84.

The influence of activation time on the development of porosity in THF carbons is shown in Figure 6.1. Values for the nano- and mesopore volume, and nanopore width of each sample are summarized in Table 6.1, in addition to the carbon yield, and the bulk density of the electrode. Activation up to 2.5 h almost exclusively created nanopores. Burn off was 33% at this point. The nanopore volume increased from 0.15 to 0.70 cm\(^3\) gm\(^{-1}\) over that period, while the mesopore volume increased by just 0.02 cm\(^3\) gm\(^{-1}\) to a value of 0.03 cm\(^3\) gm\(^{-1}\). Extending the activation time to 3.5 h (80% burn off) promoted both nanoporosity and mesoporosity. The total pore volume of THF80 was 1.00 cm\(^3\) gm\(^{-1}\) distributed as 0.90 cm\(^3\) gm\(^{-1}\) of nanopores and 0.10 cm\(^3\) gm\(^{-1}\) of mesopores. The differential pore volume is shown in Figure 1b. In all samples, except THF80, the distribution was essentially flat greater than 2 nm. The inset plot is expanded between
0.2 and 2 nm. The mean pore width was seen to shift and broaden with activation time. Initially the pores were 0.54 nm. After 33% burn off they expanded to 0.62 nm and another slight increase to 0.67 nm was found in THF56. The final hour of activation increased the pore width markedly to 0.82 nm. The bulk density of the carbons (~1 gm cm\(^{-3}\)) was unchanged between burnoffs of 11 and 33%. Further gasification reduced it to 0.54 gm cm\(^{-3}\) at 80% burnoff.

![Graph](image.png)

**Figure 6.1**: Pore volume (a) and differential pore volume (b) of nanoporous carbon derived from PFA with THF and activated to 0, 11, 33, 56, and 80% burn off.
Table 6.1: Nano- ($V_{nano}$), meso- ($V_{meso}$) and total pore ($V_{total}$) volumes, mean nanopore width ($w_{nano}$), and bulk densities ($\rho$) of THF and TRI nanoporous carbons. Burn off with respect to activation time is also given.

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Time (h)</th>
<th>Burn off (%)</th>
<th>$V_{total}$ ($cm^3 gm^{-1}$)</th>
<th>$V_{nano}$ ($cm^3 gm^{-1}$)</th>
<th>$V_{meso}$ ($cm^3 gm^{-1}$)</th>
<th>$w_{nano}$ (nm)</th>
<th>Electrode Bulk $\rho$ (gm cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF0</td>
<td>0</td>
<td>0</td>
<td>0.16</td>
<td>0.15</td>
<td>0.01</td>
<td>0.54</td>
<td>-</td>
</tr>
<tr>
<td>THF11</td>
<td>0.5</td>
<td>11</td>
<td>0.22</td>
<td>0.21</td>
<td>0.01</td>
<td>0.54</td>
<td>1.02</td>
</tr>
<tr>
<td>THF33</td>
<td>1.5</td>
<td>33</td>
<td>0.41</td>
<td>0.39</td>
<td>0.02</td>
<td>0.62</td>
<td>0.99</td>
</tr>
<tr>
<td>THF56</td>
<td>2.5</td>
<td>56</td>
<td>0.73</td>
<td>0.70</td>
<td>0.03</td>
<td>0.67</td>
<td>0.72</td>
</tr>
<tr>
<td>THF80</td>
<td>3.5</td>
<td>80</td>
<td>1.00</td>
<td>0.90</td>
<td>0.10</td>
<td>0.82</td>
<td>0.54</td>
</tr>
<tr>
<td>TRI0</td>
<td>0</td>
<td>0</td>
<td>0.19</td>
<td>0.16</td>
<td>0.03</td>
<td>0.54</td>
<td>-</td>
</tr>
<tr>
<td>TRI15</td>
<td>0.5</td>
<td>15</td>
<td>0.28</td>
<td>0.24</td>
<td>0.04</td>
<td>0.54</td>
<td>1.02</td>
</tr>
<tr>
<td>TRI42</td>
<td>1.5</td>
<td>42</td>
<td>0.59</td>
<td>0.53</td>
<td>0.06</td>
<td>0.62</td>
<td>0.72</td>
</tr>
<tr>
<td>TRI69</td>
<td>2.5</td>
<td>69</td>
<td>0.98</td>
<td>0.85</td>
<td>0.13</td>
<td>0.67</td>
<td>0.61</td>
</tr>
<tr>
<td>TRI84</td>
<td>3.5</td>
<td>84</td>
<td>1.3</td>
<td>0.98</td>
<td>0.32</td>
<td>0.82</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Results of gas sorption experiments for TRI carbons are given in Figure 6.2 and also Table 6.1. Carbons derived from PFA with Triton X-100 were both nano- (0.16 cm$^3$ gm$^{-1}$) and mesoporous (0.03 cm$^3$ gm$^{-1}$) after pyrolysis at 800 °C without modification. Activation for 0.5 h (15% burn off) slightly increased both nano- and mesopore volumes to 0.24 and 0.04 cm$^3$ gm$^{-1}$, respectively. The nanopore volume grew two-fold to 0.53 cm$^3$ gm$^{-1}$ in TRI42, while the increase in mesoporosity was again minor. Another jump in nanoporosity occurred at 2.5 h (69% burn off), however the mesopore volume now doubled to 0.13 cm$^3$ gm$^{-1}$. Further activation to 3.5 h produced a burn off of 84% and a relatively small increase in nanoporosity, but the mesopore volume again doubled. TRI84 had a total pore volume of 1.30 cm$^3$ gm$^{-1}$, which was broken down into 0.98 cm$^3$ gm$^{-1}$ of nanopores and 0.32 cm$^3$ gm$^{-1}$ of mesopores. The differential pore volume is shown in Figure 2b. The change in mean nanopore width with activation time for TRI carbons was identical to their THF analogues. Bulk densities decreased steadily with activation from 1.02 gm cm$^{-3}$ for TRI15 to 0.50 gm cm$^{-3}$ for TRI80.
Figure 6.2: Pore volume (a) and differential pore volume (b) of nanoporous carbon derived from PFA with Triton X-100 and activated to 0, 15, 42, 69, and 84% burn off.

The constant current charge/discharge profiles for THF carbons are shown in Figure 6.3. Specific capacitances are given in Table 6.2. Capacitance was unmeasurable for the 0 or 11% burnoff materials at a loading current density of 250 mA gm⁻¹. Charging occurred at negative time, a full charge was reached at 0 s, and discharge occurred at positive time. The electrodes charged and discharged linearly, indicating there were no parasitic faradaic reactions on the carbon surface. The ohmic drop at full charge was small for all carbons, less than 0.05 V. Gravimetric and volumetric capacitances were calculated according to Eq. (1) and are given in Table 2. THF33 had a total pore volume of 0.41 cm³ gm⁻¹ with a specific capacitance of 109 F gm⁻¹. Capacitance increased non-
linearly with additional activation, reaching values of 150 and 164 F gm\(^{-1}\) for THF56 and THF80, respectively. Volumetric and gravimetric capacitances were similar for THF33, but the volumetric decreased to 88 F cm\(^{-3}\) at 80% oxidation, when the bulk density was halved.

![Figure 6.3](image-url)

**Figure 6.3**: Constant current (CC) charge/discharge measurements for a two-electrode capacitor fabricated with activated THF nanoporous carbons. A full charge occurred at 0 s.
Table 6.2: Time constant (τ), equivalent series resistance (ESR), and gravimetric and volumetric capacitances measured by CC and CV.

<table>
<thead>
<tr>
<th>Carbon</th>
<th>( w_{\text{nano}} ) (nm)</th>
<th>( V_{\text{total}} ) (cm(^3) gm(^{-1}))</th>
<th>Bulk ( \rho ) (gm cm(^{-3}))</th>
<th>( \tau ) (s)</th>
<th>ESR (Ω)</th>
<th>Capacitance (CC) (F gm(^{-1}))</th>
<th>Capacitance (CV) (F cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF33</td>
<td>0.62</td>
<td>0.41</td>
<td>0.99</td>
<td>14.84</td>
<td>1.4</td>
<td>109</td>
<td>108</td>
</tr>
<tr>
<td>THF56</td>
<td>0.67</td>
<td>0.73</td>
<td>0.72</td>
<td>25.13</td>
<td>2.5</td>
<td>150</td>
<td>107</td>
</tr>
<tr>
<td>THF80</td>
<td>0.82</td>
<td>1.00</td>
<td>0.54</td>
<td>42.55</td>
<td>1.4</td>
<td>164</td>
<td>173</td>
</tr>
<tr>
<td>TRI15</td>
<td>0.54</td>
<td>0.28</td>
<td>1.02</td>
<td>14.84</td>
<td>1.1</td>
<td>106</td>
<td>114</td>
</tr>
<tr>
<td>TRI42</td>
<td>0.62</td>
<td>0.59</td>
<td>0.72</td>
<td>25.13</td>
<td>3.8</td>
<td>116</td>
<td>132</td>
</tr>
<tr>
<td>TRI69</td>
<td>0.67</td>
<td>0.98</td>
<td>0.61</td>
<td>25.13</td>
<td>1.7</td>
<td>136</td>
<td>145</td>
</tr>
<tr>
<td>TRI84</td>
<td>0.82</td>
<td>1.3</td>
<td>0.50</td>
<td>42.55</td>
<td>1.5</td>
<td>160</td>
<td>174</td>
</tr>
</tbody>
</table>

Capacitance values obtained from CC for the TRI carbons are given in Table 6.2. Charging and discharging curves were again both linear. 106 F gm\(^{-1}\), or 109 F cm\(^{-3}\) was reached with just 15% burnoff. The nanopore width was 0.54 nm at this point. Continued activation increased the capacitance to 116, 136, and finally 160 F gm\(^{-1}\) at 84% burnoff. The carbon density decreased with gasification, lowering the volumetric capacitances from 109 F cm\(^{-3}\) for TRI15 to 80 F cm\(^{-3}\) for TRI84.

Figure 6.4 displays the CC behavior of an electrode fabricated from THF33 carbon over several cycles. The capacitive behavior is not diminished with repetition.
Figure 6.4: Constant current (CC) charge/discharge measurements for a two-electrode capacitor fabricated with THF33 carbon.
Cyclic voltammograms for THF and TRI carbon electrodes are shown in Figure 6.5 and Figure 6.6, respectively. Capacitances derived from the CV experiments are found in Table 6.2. The pore volume of THF11 was 0.22 cm$^3$ gm$^{-1}$, but the carbon exhibited very small capacitance of 5 F gm$^{-1}$. Once 33% burnoff was reached the capacitance increased to 119 F gm$^{-1}$ and continued to rise with activation. THF80 gave 173 F gm$^{-1}$. For TRI carbons, 15% burnoff resulted in 114 F gm$^{-1}$ and TRI84 gave 174 F gm$^{-1}$.

![Cyclic voltammograms for THF and TRI carbon electrodes](chart)

Figure 6.5: Cyclic voltammograms for a two-electrode capacitor fabricated with activated THF nanoporous carbons. The scan rate was 5 mV s$^{-1}$. 
Figure 6.6: Cyclic voltammograms for a two-electrode capacitor fabricated with activated TRI nanoporous carbons. The scan rate was 5 mV s$^{-1}$. 

![Cyclic voltammograms for a two-electrode capacitor fabricated with activated TRI nanoporous carbons. The scan rate was 5 mV s$^{-1}$](image-url)
The imaginary capacitance as a function of frequency was determined by EIS and is plotted in Figure 6.7 for both THF (a) and TRI (b). Time constants (τ) are given in Table 2. Values increased with activation time and total pore volume. Time constants for THF11, THF56, and THF80 were 14.84, 25.13, and 42.55 s, respectively. While the numbers for TRI15, TRI42, TRI69, and TRI84 were 14.84, 25.13, 25.13, and 42.55 s.

![Graph](image-url)

Figure 6.7: Imaginary capacitance as a function of frequency for a) THF and b) TRI activated nanoporous carbons.
The Nyquist plot for THF (a) and TRI (b) carbons is shown in Figure 6.8. Resistance due to external factors, such as the leads and current collectors, was ~ 1 Ω. The diameter of the semi-circle is equal to the equivalent series resistance (ESR) contributed by the carbon electrode. No trend in ESR was observed as a function of activation time, as shown in Table 6.2.

Figure 6.8: Nyquist plots for a) THF and b) TRI activated nanoporous carbons.
6.4 Discussion

Two nanoporous carbons, one of which was also intrinsically mesoporous, were activated by reaction with \( \text{CO}_2 \) and utilized to fabricate electrodes for EDLCs. The physical properties of THF and TRI carbons were analyzed during activation. Both carbons proved to be effective for making ELDC electrodes.

Carbons obtained from mixtures of PFA with THF or Triton X-100 have equivalent micropore volumes. However, TRI carbon is also found to be mesoporous after pyrolysis. A Triton X-100 molecule is comprised of a benzene ring connected to both an eight carbon alkyl chain and a polyethylene glycol chain approximately 10 monomeric units in length. The low-molecular weight PEG acts as a mesopore forming agent, as reported by Strano et al. for pure PEG blended with PFA [3]. The slight mesopore volume prominently influences the activation of the TRI nanoporous carbon.

Gasification of carbons is believed to occur primarily by two methods: opening of previously inaccessible pores and widening of existing pores [4]. Both mechanisms are clearly active during the oxidation of nanoporous carbon. Over the first 0.5 h of activation pores are created solely by pore opening as the pore initial pore width of 0.54 nm is maintained. Also the yields between THF and TRI carbons are nearly equal, 89\% versus 85\%. Beyond 0.5 h conversion of NPC to activated NPC is greater in the TRI samples, due to the enhanced transport of \( \text{CO}_2 \) in the carbon provided by the initial mesoporosity. The yields on TRI carbons are lower, hence greater porosity, yet the nanopore widening occurring in both carbons as activation proceeds is equivalent. The maximum nanopore volume achieved in the absence of great mesoporosity is 0.70 cm\(^3\).
Larger values of $V_{\text{nano}}$ are realized in the TRI carbons, up to 0.98 cm$^3$ gm$^{-1}$, however mesoporosity is also present. Porosity in both carbons is shown to be tunable in order to minimize inclusion of mesopores. Little surface area for double-layer formation is contributed by mesopores. Their presence lowers the material bulk density.

Electrodes fabricated from non-activated PFA derived NPC do not exhibit appreciable capacitive behavior. Despite similar nanopore volumes, 0.21 versus 0.24 cm$^3$ gm$^{-1}$, and burnoffs THF11 and TRI15 are dramatically different electrodes. 106 F gm$^{-1}$ is obtained by CC measurement for the TRI carbon, while the THF carbon had <20 F gm$^{-1}$. The difference between the two samples is the mesopore volume, which is 0.01 for THF and 0.04 for TRI. This slight amount of mesoporosity is enough to enhance the mass transfer of the solvated ions to the nanopores and thereby increase capacitance. For the TRI15 sample 106 F gm$^{-1}$ was realized with a nanopore width of 0.54 nm. The size of the pore is less than the size of the solvated ion, which is 0.8 nm. This behavior is similar to the result of Vix-Guterl et al. and Chmiola et al., who reported an anomalous increase in capacitance in nanopores of carbide derived carbons [5, 6]. The authors suggested that the solvation shell was distorted when compressed into small pores, which decreased the distance between the ion and electrode surface and increased capacitance. Since the bulk density of the carbon is 1.02 g cm$^{-3}$, the carbon can be used for high volumetric capacitance applications. It was noted that twice the amount of carbon must be oxidized for a THF sample to reach the capacitance of 109 F gm$^{-1}$ for THF33.

Continued activation increases the gravimetric capacitances of the carbons. At high burnoffs, THF80 and TRI84 have similar capacitances (~164 F gm$^{-1}$). However, the
highest volumetric capacitances are realized at low burnoffs as increasing the accessible porosity lowers the bulk density of the electrode.

Time constants for the capacitors increase with activation for both the THF and TRI carbons. Increased nanopore volume requires a longer time to complete electrolyte adsorption during charging for each carbon. However mesopores significantly improve the transport in the TRI carbons. Nanopore volumes for THF0 and TRI69 are nearly equal at 0.90 and 0.85 cm$^3$ gm$^{-1}$, respectively. Yet the time constant for the TRI carbon is 25.13 s, compared to 42.55 s for THF. A further increase in nanopore volume to 0.98 cm$^3$ gm$^{-1}$ in TRI84 raised $\tau$ to 42.55 s. However the sample appears to have a broad peak indicating a distribution of pore sizes with differing time constants (Figure 6.7). This correlates with the wide differential pore volume of TRI84.

6.5 Conclusions

Controlled gasification of polyfurfuryl alcohol derived nanoporous carbons provided materials with a range of properties for fabrication of electrical double layer capacitor electrodes. Nano- and mesopore volumes, as well as nanopore width were tunable depending on the burnoff. Two starting carbons were utilized. One derived from PFA synthesized in the presence of THF, the other with the surfactant Triton X-100, which acted a mesopore forming agent. A gravimetric capacitance of 106 F gm$^{-1}$ was reported for just 15% burnoff and a nanopore volume of 0.28 cm$^3$ gm$^{-1}$. This was for a TRI carbon with 0.04 cm$^3$ gm$^{-1}$ of mesopore volume. Double the burnoff, to 33% was required to realize the same capacitance in a THF carbon, which was not significantly
mesoporous. Volumetric capacitances for the low burnoff carbons were excellent, as the
bulk densities were 1.02 gm cm\(^{-3}\). 109 F cm\(^{-3}\) was measured for the TRI sample. The
highest gravimetric capacitance (164 F gm\(^{-1}\)) was achieved at 80% burnoff, however due
to a reduction in bulk density the volumetric value was 88 F cm\(^{-3}\). ESR values for the
electrodes are low and time constants increase with pore volume, but do not exceed 42.55
s. Polyfurfuryl alcohol has been demonstrated as an appropriate precursor for activated
nanoporous carbons for capacitor applications.
6.6 References

Chapter 7

Conclusions and future directions

7.1 Conclusions

Nanoporous carbon derived from polyfurfuryl alcohol has been thoroughly characterized at each step of its synthesis: polymerization, pyrolysis, activation, and high temperature treatment. The relationship between cross-linking during polymerization and carbon structure was investigated. The genesis and evolution of porosity and microstructure in the carbon has been observed between room temperature and 2000 °C. An electrical double layer capacitor was fabricated from nanoporous activated carbon.

Efforts to modify the molecular weight and degree of cross-linking in the polymer were successful; however the process parameters had very little effect on the carbon properties. The polymers were assimilated during pyrolysis. Polymerization continued during pyrolysis up to the point of decomposition, which allowed the polymer properties to equalize. Thus bulk NPC from PFA synthesized by any method was assured to have the same properties. The exception was carbon derived from PFA and Triton X-100 mixtures. With sufficient amount of the surfactant present, mesopores were created in the nanoporous carbon. Pyrolysis was the key step in controlling the properties of nanoporous carbon.

The pyrolysis of polyfurfuryl alcohol was studied up to 600 °C. Upon heating to 300 °C, PFA spontaneously decomposed and began to convert to a solid consisting of
polymer remnants and aromatic cores that formed the basis for the NPC which was produced with further pyrolysis at higher temperature. Surprisingly, mesopores were also detected at this temperature. Oxygen and hydrogen moieties decorated the aromatic domains and the residual polymer in the material. The heteroatoms were driven out by heating above 400 °C and the mesopores then disappeared. A carbon characterized by monodisperse nanopores remained at 600 °C. The unreacted polymer and heteroatoms induced mesoporosity by buffering the nanopores created by polyaromatic domains. Raising the pyrolysis above 400 °C released the buffering material, thereby collapsing the mesopores.

Porosity and microstructure continued to evolve as NPC was subjected to HTT between 800 and 2000 °C. Previous work showed that graphitization of PFA derived NPC was localized, as movement of graphene layers in the highly disordered carbon was restricted. HTT of NPC confirmed this behavior; the carbon remained amorphous up to 2000 °C and access to nanopores was completely eliminated by closure of the pore mouths. Prior to activation the nanopore walls were comprised of several layers of disordered graphenes. Activation eliminated the barrier to graphitization by reducing the number of layers below the limit of detection and removing carbon material highly susceptible to oxidation. Followed by annealing at 2000 °C a portion of the once non-graphitizing carbon was now able to graphitize. Unprecedented pre-graphitic domains amongst the nanoporous carbon were discovered. Additionally, nanopores were not completely eliminated after HTT of the activated carbon, which was in contrast to the non-activated counterpart. The product was a heterogeneous carbon exhibiting both
nanoporosity, a property of the non-graphitizing carbon, and a pre-graphite structure, a property of the graphitic carbon.

Activated nanoporous carbons were advantageous for the production of electrodes for electrical double layer capacitors. Nano- and mesopore volumes, as well as nanopore diameter were tunable depending on the burnoff. Two starting carbons were utilized. One derived from PFA synthesized in the presence of THF, the other with the surfactant Triton X-100, which acted a mesopore forming agent. A gravimetric capacitance of 106 F gm\(^{-1}\) was reported for just 15% burnoff and a nanopore volume of 0.28 cm\(^3\) gm\(^{-1}\). This was for a TRI carbon with 0.04 cm\(^3\) gm\(^{-1}\) of mesopore volume. Double the burnoff, to 33%, was required to realize the same capacitance in a THF carbon, which was not significantly mesoporous. Volumetric capacitances for the low burnoff carbons were excellent, as the bulk densities were 1.02 gm cm\(^{-3}\). 109 F cm\(^{-3}\) was measured for the TRI sample. The highest gravimetric capacitance achieved was 164 F gm\(^{-1}\), however due to a reduction in bulk density the volumetric value was 88 F cm\(^{-3}\). ESR values for the electrodes were low and time constants increased with pore volume, but did not exceed 42.55 s. Polyfurfuryl alcohol was demonstrated as an effective precursor for activated nanoporous carbons for capacitor applications.
7.2 Future directions

A successful research project answers questions, but also leads to new inquiries and research directions. Although the cross-linking mechanism has been reduced to two possibilities due to its reliance on conjugation, it is unknown whether one of the reactions occurs exclusively or both act in concert. The exact pathway could be elucidated by careful two-dimensional NMR experiments. The effect of catalyst concentration on mesoporosity of carbons synthesized with Triton X-100 should also be studied in more detail.

Transient mesopores provide pathways for gaseous decomposition by-products to exit the carbon matrix. The effect on the final carbon product due to increasing the autogenerated mesoporosity during pyrolysis should be studied. Blending polymers with high oxygen content or pyrolyzing in an oxygen atmosphere may serve to enhance the number of carbonyl groups in the carbon, thus increasing mesoporosity. The greater concentration of carbonyl groups may not be completely eliminated before the carbon matrix is fixed. If they were preserved at high temperatures, permanent mesopores could be formed without the aid of a pore forming agent.

The influence of activation on graphitizability of non-graphitizing carbon should be examined further. Thus far the phenomenon has been discovered only in polyfurfuryl alcohol derived carbon. Non-graphitizing carbons can also be acquired from cellulose, saccharose, polyacrylonitrile, polyvinylidine chloride, and other sources. A similar course of study involving activation and HTT should be undertaken with these precursors.
Nanoporous carbon with pre-graphitic domains could potentially improve several applications. Lithium-ion batteries with carbon electrodes depend on intercalation and de-intercalation of lithium in the carbon matrix. The process is easily reversible in graphite, but the surface area and porosity is low, thus the capacity is also low. Highly porous carbons have great capacity, but the intercalation is not completely reversible. Nanoporous carbon with pre-graphitic domains is a potential solution. Access to the graphitized regions is provided by the high surface area and porosity carbon surrounding it. Both issues of capacity and reversibility are addressed. Porous carbon electrodes are also required to support a platinum catalyst for polymer electrolyte fuel cells. The conductivity of the electrodes could be improved by utilizing nanoporous carbon with pre-graphitic domains, while also maintaining the surface area and porosity necessary to support the catalyst.
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Publications

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