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Mesoporous Carbon-based Materials for Alternative Energy Applications

A dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy in Chemical Engineering

by

Kimberly Michelle Cross

2012
ABSTRACT OF THE DISSERTATION

Mesoporous Carbon-based Materials for Alternative Energy Applications

by

Kimberly Michelle Cross

Doctor of Philosophy in Chemical Engineering

University of California, Los Angeles, 2012

Professor Yunfeng Lu, Chair

Increasing concerns for the escalating issues activated by the effect of carbon dioxide emissions on the global climate from extensive use of fossil fuels and the limited amount of fossil resources has led to an in-depth search for alternative energy systems, primarily based on nuclear or renewable energy sources. Recent innovations in the production of more efficient devices for energy harvesting, storage, and conversion are based on the incorporation of nanostructured materials into electrochemical systems. The aforementioned nano-electrochemical energy systems hold particular promise for alternative energy transportation related technologies including fuel cells, hydrogen storage, and electrochemical supercapacitors. In each of these devices, nanostructured materials can be used to increase the surface area where the critical chemical reactions occur within the same volume and mass, thereby increasing the energy density, power density, electrical efficiency, and physical robustness of the system.
Durable corrosion resistant carbon support materials for fuel cells have been designed by adding conductive low cost carbon materials with chemically robust ceramic materials. Since a strict control of the pore size is mandatory to optimize properties for improved performance, chemical activation agents have been utilized as porogens to tune surface areas, pore size distributions, and composition of carbon-based mesoporous materials. Through the use of evaporative self-assembly methods, both randomly disordered and surfactant-templated, ordered carbon-silica nanocomposites have been synthesized with controlled surface area, pore volume, and pore size ranging from 50-800 m$^2$/g, 0.025-0.75 cm$^3$/g, and 2-10 nm, respectively.

Multi-walled carbon nanotubes (MWNTs) ranging from 0.05-1.0 wt. % were added to the aforementioned carbon-silica nanocomposites, which provided an additional increase in surface area and improved conductivity. Initially, a conductivity value of 0.0667 S/cm was measured for the composite without carbon nanotubes and the conductivity value improved by over an order of magnitude to 1 S/cm with the addition of 0.5 wt.% CNTs. Triggered by dispersion issues, the agglomeration of MWNTs during the drying process prevented each nanotube from being loaded over a maximum interfacial area. In order to improve the dispersion of carbon nanotubes within the carbon-silica network, electrospinning was explored as a method to improve the alignment of the carbon nanotubes. The electrospun fibers produced with the highest concentration of MWNTs at 1.0 wt.% produced the largest surface area and electrical conductivity values of 333.36 m$^2$/g and 2.09 S/cm, respectively. Capacitance measurements were calculated to examine if improved conductivity results in higher capacitance values. The best capacitance performance was 148 F/g from a carbon-based mesoporous composite with 0.5 wt. % MWNTs in an aqueous electrolyte with a 2.0 mV/s scan rate. An 80% increase in capacitance occurs with the addition of
0.5 wt. % MWNTs. This is in the range of capacitance values produced by hierarchically ordered mesoporous-microporous carbons, reported at 180 F/g.

Fibrous carbon tubes assembled from hydrofluoric acid etched perylenetetracarboxylic diimide bridged silsesquioxane (PDBS) were capable of hydrogen adsorption on the order of 1.3-2.5 wt. % at 77K. Lastly chemically activated phenol-formaldehyde resins produced microporous carbon with 1500 m$^3$/g surface areas and pore sizes ranging from 0.3-0.5 nm, which has potential for asymmetric super-capacitor electrodes. Judicious control over the composition and pore structure of carbon-based nanocomposites can lead to improved performance of various alternative energy materials.
The dissertation of Kimberly Michelle Cross is approved.

Harold Monbouquette

Selim Senkan

Qiping Pei

Yunfeng Lu, Committee Chair

University of California, Los Angeles

2012
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To Professor Yunfeng Lu, thank you for providing me the resources and giving me the opportunity to obtain a PhD from your research group; it has been a pleasure.
**VITA**

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<tr>
<td>Spring 2003</td>
<td>B.S., Chemical Engineering University of California, Riverside</td>
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2008-2009  Teaching Assistant of the Year Award  
Department of Chemical Engineering  
University of California, Los Angeles

2008-2009  Convention Planning Chairperson  
National Society of Black Engineers 35th Annual Convention  
Las Vegas, Nevada

2009-2010  National Science Foundation (NSF) GK-12 Fellowship

2009-2010  Convention Planning Chairperson Emeritus  
National Society of Black Engineers Annual Convention Planning Advisory Board

Spring 2011- Fall 2011  Louis Stokes Alliance for Minority Participation (LSAMP) Bridge to the Doctorate Fellowship Dissertation Year Fellowship

May 2011-Present  Renewable Energy Applications Consultant  
Department of Defense: Office of Public Works  
Oceanside, CA

PUBLICATIONS AND PRESENTATIONS


CHAPTER 1: INTRODUCTION

1.1. Motivation & Applications

The reliance on the combustion of fossil fuel for energy consumption is forecasted to have a severe impact on global economies and environments in the future. This issue highlights the need to move toward more sustainable development which can be provided from a wide availability of renewable energy technologies. Renewable energy sources such as solar, wind, and hydro (rivers, waves, etc.) generate electrical energy that must be stored for use in autonomous systems such as transportation or electronics. Electrochemistry, which encompasses chemical and physical processes that involve the transfer of charge, is strongly being considered as an additional viable alternative energy and power source because it meets environmental and sustainability requirements.

Hydrogen storage, fuel cells, and electrochemical capacitors (ECs) are systems for electrochemical energy storage and conversion. The performance of these devices depends intimately on the properties of their materials. Nanostructured materials have attracted great interest because of their unusual mechanical, electrical, and optical properties enhanced by confined dimensions on the nanoscale. These unique properties are due to the combination of both bulk and surface properties to their overall performance behavior. Currently, there is a pressing need to substantially improve the performance of both electrochemical energy storage and conversion systems to meet the higher performance requirements of future systems. From portable electronics to hybrid electric vehicles, new materials must be developed by advancing the understanding of the electrochemical interfaces on the nanoscale.
Electrochemistry is the study of the interchange of chemical and electrical energy, in which two driving forces are embodied: chemical potential ($\mu_c$), the potential that a substance has to produce in order to alter a system, and the work associated with moving a charged particle.

$$(\mu_{EC}) = z F \phi + \mu_c$$ (1.1)

In Equation 1.1 $\phi$ is the electrical work associated with bringing a unit charge, $z$, into the material system and the Faraday constant, $F$, represents Avogadro’s number of an elementary charge ($e_0 = 1.602 \times 10^{-19}$ C).

A fuel cell is an electrochemical device where the reaction between the fuel and oxidant converts the chemical energy of the fuel directly into electrical energy without combustion or pollution. Whenever hydrogen is used as the fuel source, hydrogen storage is a key issue to be conquered for the successful implementation of fuel cell technology in transport applications. Technologies such as fuel cells that use hydrogen require improved approaches for high-capacity storage at temperatures ranging from near ambient to approximately 100°C and at pressures below approximately 100 bar. Various porous materials are being considered to meet these needs. In the case of electrochemical capacitors (supercapacitors), energy is stored by the accumulation of charges at the porous electrode/electrolyte interface.

The most promising future markets for fuel cells and supercapacitors reside in the same application sectors as batteries. Originally fuel cells were intended to replace combustion engines and combustion power sources due to possible higher energy conversion efficiencies and lower environmental impacts. Fuel cells are not able to compete with today’s combustion engines and gas/stream turbines because of much higher cost, inferior power and energy performance, and insufficient durability. A simplified Ragone plot (Figure 1.1) shows that fuel cells can be considered as high-energy systems, whereas electrochemical capacitors are considered to be
high-power systems (Aricò, 2005). Energy delivery systems are typically compared against the internal combustion engine, which have both high energy density and power density, thus its ability to store energy for a long distance and quickly accelerate. Both high power and high energy is best achieved when available electrochemical conversion and storage systems are combined.

![Ragone plot](image)

Figure 1.1. A simplified Ragone plot of the energy storage domains for various electrochemical energy storage and conversion systems compared to internal combustion engines, turbines, and conventional capacitors (Aricò, 2005).

1.1.1. Fuel Cell Technology

Fuel cell technologies hold great promise for energy conversion because they deliver energy densities that are orders of magnitude greater than conventional batteries and capacitors. They most closely approximate the energy densities of internal combustion engines, and they can be powered with renewable fuels such as hydrogen. The most promising commercial applications of fuel cells appear to be as stationary power sources for central and dispersed power stations (large fuel cells operating 200-300 kW), and as mobile power sources for portable
electronic devices, bus propulsion, and automobiles (smaller cells operating 50-75 kW) (Larminie, 2003; Winter, 2004). Most US vehicles operate between 60-200 hp (44.78-149.25 kW) so this would place existing fuel cells in the small-medium automobile range.

One of the attractions of the fuel cell is the high efficiency of conversion of chemical energy into electrical energy. Unlike the combustion engine, where the heat of combustion of the fuel is first converted into mechanical energy which is then converted into electrical energy, the fuel cell efficiency is not limited by the Carnot Cycle. In a fuel cell the maximum (theoretical) electrical efficiency (Equation 1.2), $\varepsilon$, at standard conditions of temperature and pressure, is given by the ratio of the Gibbs free energy change, $\Delta G$, of the reaction to the enthalpy change, $\Delta H$:

$$\varepsilon = \frac{\Delta G}{\Delta H} = -\frac{2FE^o}{\Delta H^o}$$

(1.2)

The standard theoretical cell potential for the hydrogen fuel cell is approximately 1.23 V, based on the basic reaction of a H$_2$ fuel cell.

(anode rxn.) $\text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \quad E^o = 0.00V$  \hspace{1cm} (1.3)

(cathode rxn.) $\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O} \quad E^o = 1.229V$ \hspace{1cm} (1.4)

For these half reactions (Equations 1.3 and 1.4) $\Delta G^o = -235.76$ kJ/mol and $\Delta H^o = -285.15$ kJ/mol. For a fuel cell at low temperature, where the product is liquid water, the efficiency is approximately 83% (in comparison to 40% efficiency for the internal combustion engine). In most fuel cells, the theoretical efficiency is not achieved due to irreversible voltage losses associated with the flow of current and the actual construction of the cell.

Two key issues preventing widespread commercialization of fuel cells are cost and durability (He, 2005). The fuel cell costs must be dramatically reduced to meet the US
Department of Energy (DOE) target of $30/kW by 2015 to be competitive with virtually every type of power application (He, 2005). The other major technical barrier for the acceptance of fuel cells as a practical power source is durability under a wide range of operational conditions. Durability is defined as the ability of a fuel cell stack to resist permanent change in performance over time. Durability decay does not lead to catastrophic failure, but a decrease in performance that is not recoverable or reversible (i.e., due to loss of electrochemical surface area, carbon corrosion, etc.) (Wilkinson, 2003). For different applications, the requirements for fuel cell lifetime vary significantly, ranging from 5,000 hours for cars to 20,000 hours for buses and 40,000 hours of continuous operation for stationary applications (Wilkinson, 2003). The durability issue is due to the continuous exposure of fuel cells to highly oxidizing environments, which leads to significant performance deterioration and future device failure (He, 2005). Mass transport properties degrade as a result of the accumulation of excess water in the gas diffusion pores within the fuel cell.

A fuel cell is a device that uses hydrogen or a hydrogen-rich fuel and oxygen to create electricity and water by an electrochemical process (Scott, 2004). A single hydrogen fuel cell consists of an electrolyte and two catalyst-coated porous electrodes (Scott, 2004). Platinum, a costly precious metal element is commonly coated on carbon based substrates of fuel cell electrodes to facilitate the split of the hydrogen atom, which enables the membrane within a proton-exchanged membrane (PEM) fuel cell to generate charge (Larminie, 2003). Nafion®, a proton conducting media is used to bind carbon supported catalyst particles (Larminie, 2003). Within the fuel cell oxidation occurs in the anode, reduction occurs in the cathode, and ions carry the current between the electrodes within the electrolyte. A polymer electrolyte membrane (PEM) also known as the proton-exchanged membrane fuel cell is based on a polymer membrane
sandwiched between the anode and cathode electrodes as seen in Figure 1.2. Since the membrane is not electrically conductive, the electrons released from the hydrogen travel along the electrical detour provided and an electrical current is generated. The chemical energy present in the combination of hydrogen and oxygen is converted into electrical energy by controlled electrochemical reactions at each of the electrodes in the cell. The first \( \frac{1}{2} \) reaction (Equation 1.3) involving hydrogen oxidation is facile amongst the presence of a platinum based catalyst, characterized by exchange-current densities \( (i_0) \) on the order of \( 10^{-3} \) A/cm\(^2\)PT (Marković, 1997). The oxygen reduction reaction (ORR) (Equation 1.4) at the cathode is known to be a rate determining step for the overall PEM fuel cell reactions, so it is critical to develop a low platinum loaded catalyst which can catalyze the ORR. The ORR kinetics on Pt is approximately six orders of magnitude slower than the \( \text{H}_2 \) oxidation kinetics \( (i_0 \) of the order \( 10^{-9} \) A/cm\(^2\)PT) (Gasteiger, 2003). The difficulty in oxygen reduction stems from the exceptionally strong O=O bond (498 kJ/mol) making activation of this bond kinetically slow.

![Figure 1.2. A schematic displaying the details of a single stack polymer electrolyte membrane fuel cell electrode, including details of the transport of gasses, protons, and electrons within the fuel cell stack (Lister, 2004; Michel, 2008)](image-url)
The PEM fuel cell electrodes are susceptible to corrosive conditions which include high water content, low pH (<1), temperature conditions (50-90°C), high operating voltage potential (0.6-1.2V), and high oxygen concentration (Kinoshita, 1988). An operating PEM fuel cell continuously produces water at the air cathode and water enables ion transport in the membrane that in turn enables the electrochemical reactions at each electrode (Scott, 2004). The driving force for oxidative degradation of the catalyst support is due to the air electrode being constantly exposed to oxygen during operation, creating a wet, acidic, and highly oxidative environment (Reiser, 2005). Therefore, carbon corrosion induces porosity changes which can significantly contribute to fuel cell performance loss, in which the corrosion of the carbon support may lead to particle detachment and changes of the catalyst layer porosity (Wu, 2008). This concept is represented in Equation 1.5.

\[
C(s) + 2H_2O(l) \rightarrow CO_2(g) + 4H^+ + 4e^{-}
\]  

(1.5)

The primary mechanism of catalyst support degradation is “reverse current. Reverse current takes place when the air, introduced to the anode from the outside or through the membrane, replaces the hydrogen (Reiser, 2005; Patterson, 2006). This is likely to occur during startup after a long period of time from shut down, or if hydrogen is locally starved. Start/stop induced degradation leads to a cathode catalyst layer morphology that hinders the transport of oxygen to active sites and removal of water (Patterson, 2006). The carbon support pore structure collapses from an interconnected network to a dense carbon layer with mainly isolated pores. The resulting decrease in porosity and pore size of the carbon support hinders mass transport, leading to severe fuel cell performance loss (Patterson, 2006).

A good catalyst must have optimal mass transport characteristics. During cell operation the reactant gases, hydrogen and oxygen, traverse the porous electrode layer to reach active
platinum sites. Resistance to the transport of gases must be minimized. Water, formed at the cathode and essential to the efficient fuel cell operation, can be a hindrance to the free flow of the gases (Wu, 2008). Water is a great conductor of protons through the cell, but accumulation of water in the electrode layer may lead to cell flooding that blocks access of the gases to platinum (Wu, 2008). The water that is produced must be appropriately eliminated from the cell. The catalyst layer must allow for an optimal balance of water to maintain an efficient operation. The physical and chemical properties of the carbon substrate can alter the nature of water-catalyst interaction (Wu, 2008). Porous supports typically exhibit higher water sorption (Wu, 2008). Depending on the pore size distribution in the carbon, water may or may not accumulate within the catalyst layer (Wu, 2008).

Nanostructured materials are having an impact on processing methods in the development of low-temperature fuel cells (T < 200 °C), through the dispersion of precious metal catalysts, and the development of catalysts supports within the fabrication of the membrane-electrode assembly (MEA) (Larminie, 2003). The main requirements of suitable supports for fuel cell catalysts are: high surface area, good electrical conductivity, suitable porosity to allow good reactant flux, and high stability in fuel cell environment. The specific activity of the platinum or platinum alloy catalyst nanoparticles can decrease with decreasing particle size (particle-size effect), so the catalysts are supported on a porous high surface area substrate leading to a higher number of active sites for platinum deposition (Watanabe, 1989; Kinoshita, 1990; Yahikozawa, 1991; Kabbabi, 1994). The support material for a fuel cells catalyst must also have sufficient electrical conductivity in order to act as a path for the flow of electrons. During cell operation, electrons and protons generated or consumed at the platinum sites migrate through the electrode layer (Schulenburg, 2011). The electrode layer must exhibit
good electronic and protonic conductivities to minimize resistive losses in the cell (Schulenburg, 2011). Moreover, carbon supports should have a high percentage of mesopores to provide accessibility to catalyst and to monomeric units of the Nafion® ionomer (He, 2005). In addition to high surface area, porosity, and electrical conductivity, corrosion resistance is also an important factor in the choice of a good catalyst support. If the catalyst particles cannot maintain their structure over the lifetime of the fuel cell, change in the morphology of the catalyst layer from the initial state will result in a loss of electrochemical activity (He, 2005). For these catalysts more severe requirements have to be met to achieve the required long-term stability of 40,000–60,000 hours (He, 2005). Due to the presence of oxygen, carbon is lost from the system through oxidation leading to significant losses of carbon over a short period of time.

Current efforts towards corrosion-resisted catalyst supports have been focused on engineering existing carbon materials to improve their durability or seeking alternative catalyst supports. The most common used catalyst support is high purity carbon black (Conductex® 975 or Vulcan® XC72): a low cost, easily available, particulate amorphous carbon material which has high porosity, high surface area (250-1200 m²/g), and adequate conductivity (~ 1 S/cm) (He, 2005). Carbon blacks have high specific surface area, but are contributed mostly by micropores less than 1 nm (He, 2005). This results as a disadvantage for catalyst support materials in which the pores of the amorphous material are more difficult to access, in addition to poor connectivity. When the average diameter of the pores is less than 2 nm, supply of the fuel may not occur smoothly and the activity of the catalyst may be limited (Wu, 2008).

Additional alternative support materials have been explored which are different from carbon black at the nanoscopic level in terms of their structural conformation and pore texture, and at the macroscopic level in terms of their form. The materials include various nanostructured
carbon materials such as mesoporous carbons (Joo, 2001), carbon aerogels (Anderson, 2002; Ye, 2003), carbide derived carbons, and carbon-nanotubes (Li, 2003; Wang, 2004). Compared with carbon blacks, overall mesoporous carbons contain higher surface areas and lower amounts or the absence of micropores. However, all the previously mentioned carbon based materials face the same corrosion issue similar to that of carbon black.

Appropriate choice and modification of reagents for carbon support can influence catalyst properties. These features can be controlled by the design of the catalyst synthesis process. Ceramic materials are highly stable in corrosive environments, however making low cost, conductive ceramic materials with adequate electronic conductivity, and controlled pore structure remains challenging. A new generation of mesoporous corrosion resisted fuel cell catalyst supports can be designed by incorporating the conductivity and low cost of carbon based materials with the chemical robustness of ceramic materials. Precise control over the composition and pore structure of the nanocomposites balances the conductivity, transport efficiency, and corrosion resistance, providing novel robust materials for catalyst support applications. Since porosity of the catalyst layer is an important feature which determines catalytic behavior, chemical activation methods will be employed to tune the surface area, pore volume, and pore-size distribution of the fabricated carbon ceramic materials.

1.1.2. Electrochemical Capacitor Technology

Capacitance is a measure of the charge stored for a given electrical potential between the electrodes (Dorf, 2001).

$$C = \varepsilon_0 \varepsilon_r \frac{A}{d}$$  \hspace{1cm} (1.6)
Within Equation 1.6 the variables include: $\varepsilon_0 = \text{free space permittivity (dielectric constant at vacuum)}$, $\varepsilon_r = \text{dielectric constant of material between the electrodes}$, $A = \text{specific surface area of the electrodes}$, $d = \text{distance between the plates (charge separation distance)}$. The energy stored (Equation 1.7) is related to the charge at the interface, $q$, and the potential difference between the electrodes, $V$ (Dorf, 2001).

$$E = \frac{1}{2} qV = \frac{1}{2} CV^2 \quad (1.7)$$

Capacitors can be generally classified as electrostatic, electrolytic, and electrochemical. Electrostatic capacitors are typically made of two metal electrodes (parallel plates) separated by a dielectric, a non-conducting material that can be polarized by an applied electric field (Sharma, 2010). Conventional dielectric capacitors can accumulate and deliver electric charge vary rapidly, for example, they operate in pulse mode with pulse widths in the nanosecond scale (Sarangapani, 1996). However, their charge storage capability is rather poor (pico- to nanofarads per cm$^2$) compared to electrochemical capacitors (Sarangapani, 1996). Electrolytic capacitors are similar in construction to electrostatic capacitors but they have a conductive electrolyte salt in direct contact with the metal electrodes (Sharma, 2010). For example, an aluminum electrolytic capacitor consists of two aluminum conducting foils coated with an insulating oxide layer and a paper spacer soaked in an electrolyte. Electrochemical capacitors (ECs) also use electrolyte solutions, yet have a greater capacitance per unit volume due to their porous solid electrode structure (Sharma, 2010).

ECs exhibit 20 to 200 times greater capacitance than conventional capacitors and are known by different names such as ultra-capacitor, electrical double layer capacitor (EDLC), or supercapacitor based on different manufacture trade names (Sarangapani, 1996). Supercapacitors
occupy a region between batteries and conventional solid state electrostatic capacitors on the Ragone plot (Figure 1.1) that describes the relation between energy and power (Aricò, 2005). A supercapacitor is an energy storage device where the charge is stored in the electrical double layer (EDL) of high surface area electrodes in an aqueous or organic electrolyte (Sharma, 2010). While batteries store the electrical energy in chemical bonds, supercapacitors store it directly in the double layer (Su, 2010). The specific energy of the supercapacitor is low, 5-15 Wh/kg, which is well below the 30-40 Wh/kg minimum figure for batteries (Conway, 1999). The supercapacitor is ideal for energy storage that undergoes frequent charge and discharge cycles at high current and short duration such as rechargeable power sources for various applications. Various parameters of both conventional electrostatic capacitors and batteries have been compared to supercapacitors in Table 1.1 (Zhao, 2011).

Table 1.1. Comparison of electrostatic capacitor and battery performance to supercapacitors (Zhao, 2011)

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<td>1–15</td>
</tr>
<tr>
<td>Power Density (W/kg)</td>
<td>$&gt;$10 000</td>
<td>50–200</td>
<td>1000–2000</td>
</tr>
<tr>
<td>Cycle Life</td>
<td>$&gt;$500 000</td>
<td>500–2000</td>
<td>$&gt;$100 000</td>
</tr>
<tr>
<td>Charge/Discharge Efficiency</td>
<td>~1.0</td>
<td>0.7–0.85</td>
<td>0.90–0.95</td>
</tr>
</tbody>
</table>

Supercapacitors have been extensively studied in response to the increasing demand for a new kind of electrical energy accumulator of long durability (over $10^6$ cycles) and high specific power (more than 10 kW/kg) achieved within shorter times (a few seconds) (Conway, 1999). The main advantage of this storage system is a high dynamic of charge propagation that can be utilized for short-term pulses in hybrid electrical vehicles, cold-start vehicle assistance,
digital telecommunications systems, uninterruptible power supply (UPS) for computers and pulse lasers, and memory back up (Vix-Guterl, 2005).

All capacitors have voltage limits based on the breakdown voltage of the electrolyte used, which is due to the thermodynamic stability of the electrolyte solution. Aqueous electrolytes (1 M H₂SO₄) working voltage per unit cell is limited to 1.5-1.6 V and organic electrolytes (1.4 M tetraethyl ammonium tetrafluroro borate in CH₃CN) confine the supercapacitor voltage to 2.5-2.7 V per unit cell (Vix-Guterl, 2005). Commercial supercapacitor modules with working voltage as high as 300 V are available at this time (Obreja, 2008). To achieve higher voltages, several supercapacitors cells are connected in series. Note, this has a disadvantage since several connections reduce the total capacitance, and strings of more than three capacitors require voltage balancing to prevent any cell from going into over voltage (Obreja, 2008). It is also noteworthy to mention organic electrolytes have a lower conductance (0.04 S/cm vs. 0.8 S/cm for 3M H₂SO₄) and a significantly higher specific resistance (a factor of at least 20) which affects the equivalent distributed resistance of the porous layer and consequently reduces the maximum usable power which is calculated according to Equation 1.8, where R represents the total effective series resistance (ESR) (Kötz, 2000). ESR comes from various types of resistance associated with the intrinsic electronic properties of the electrode matrix and electrolyte solution, mass transfer, resistance of the ions in the matrix, and contact resistance between the current collector and the electrode. For a supercapacitor to have a good performance, it must simultaneously satisfy the requirements of having a large capacitance value, high operating cell voltage, and minimum ESR.

\[ P = \frac{V^2}{4R} \]  

(1.8)
The performance of electrochemical capacitors is predominantly dependent on the device construction and its functional components, including the electrodes, electrolyte, and separator, as shown in Figure 1.3. When a biased voltage is applied between two electrodes, a layer of positive charge formed at the internal surface of one electrode causes attraction of negative ions from the electrolyte, while the layer of negative charge at the internal surface of the other electrode causes attraction of positive ions from the electrolyte. An EDL is formed at the internal electrode surface, causing a high capacitance value in comparison to other types of conventional capacitors designed with dielectric materials. This is due to the small separation distance, d, between electrolyte ions and the carbon electrode, and the high specific surface area of the carbon electrodes according to Equation 1.6, where A is now the electrode’s specific surface area accessible to electrolyte ions. Improvements within the supercapacitor arrangement have been made in cell packaging and electrolytes, however the electrode material is considered to be one of the key barriers preventing the commercialization of capacitors with both high energy and high power density.
Several types of electrochemical capacitors can be distinguished depending on the charge storage mechanism as well as the electrode active materials in use. Symmetric supercapacitors are the most common devices present which have both electrodes with high surface area carbon-based active materials (Simon, 2008). Great interest has been focused on the application of carbons as electrode materials because of their unique properties that include high surface area, the existence of different allotropes (graphite, diamond, fullerenes/nanotubes) in different forms (powders to fibers, foams, fabrics, and composites), availability, low cost, environmental friendliness, and established electrode production technologies (Frackowiak, 2001). Targeting the energy and power limitations of the device require immense efforts on discovering multifunctional electrode materials that can circumvent the shortcomings of traditional active-carbon-based electrode materials. The preparation of activated carbons does not allow the porous structure to be perfectly controlled which makes it difficult to adapt the pore size to that of
solvated anions and cations in order to achieve an optimized performance of the supercapacitor. The double layer capacitance of active carbon reaches 100-120 F/g in organic electrolytes, and this value can exceed 150-300 F/g in aqueous electrolytes (Sharma, 2010).

The second group of electrochemical capacitors, known as pseudo-capacitors or redox supercapacitors, use fast and reversible surface or near-surface reactions for charge storage with transition metal oxides (Ru, Co, Ni, Mn oxides/hydroxides) or electrically conductive polymers as active materials (Simon, 2008). The highest reported capacitance, 800-1000 F/g, has been achieved with pseudocapacitors where RuO$_2$ is used as active material loaded on vapor grown carbon fibers in 1.0 M H$_2$SO$_4$ aqueous electrolytes, retaining 97% capacitance with long-term cycle-life tests of $10^4$ cycles (Lee, 2007). This is the highest value reported to date for RuO$_2$.xH$_2$O-based electrodes with a thickness of $\sim$325 nm (Lee, 2007). Such a high-rate of performance is believed to be due to the highly open morphology of the composite nanomaterial, and to the highly electronically conducting fibrous carbon support that provides favor to optimization of proton and electron transportation through the RuO$_2$.xH$_2$O solid matrix (Rolison, 2009). A rutile-like nanocrystalline network interpenetrated by a disordered hydrous domain has been shown to achieve both high ionic conductivity and metallic electrical conductivity, which exemplifies the necessity of nanoscopic architectures to balance the electronic and ionic transportation inside supercapacitors (Rolison, 2009).

A critical aspect in nanotechnology for supercapacitors is to reach a compromise between large specific surface area values (to ensure high capacitance) for effective charge accumulation, and an appropriate pore structure and size distribution for good electrolyte wetting and rapid ionic motion. Well defined porous electrodes are required to have large surface areas, $\sim$1500 m$^2$/g, in order to have a high charge storage capability (Sharma, 2010). Pore structure is a
significant factor in determining electrochemical capacitor performance. Good pore connectivity is required for ions to penetrate into deeper regions of the carbon to prevent surface exposure that may not be utilized for charge storage (Fernandez, 2009). Pore connectivity is also related to an important characteristic of electrical energy storage, the capacitors ability for energy to be retrievable in discharge over the same potential range as that required to store the energy while charging is critical (Fernandez, 2009). The ideal pores should be slightly larger than the size of the de-solvated ions (Wei, 2011). Smaller pores prevent efficient ion electro-adsorption, whereas significantly larger pores reduce the capacitance (Wei, 2011). In 2006, systematic studies by Chmiola et al. and by Raymundo-Pinero et al. clearly showed significant enhancement of the specific capacitance in small micropores (~0.7nm), where the ion solvation shell becomes highly distorted and partially removed (Chmiola, 2008). The resulting smaller charge separation distance between the ion centers and the pore walls leads to greatly increased capacitance. In this case ions form a monolayer or a wire inside a carbon pore for slit or cylindrical shaped pores respectively (Huang, 2008; Huang, 2008). The co-existence of mesopores with small micropores and good 3D-interconnectivity is required for rapid ion transport and high power characteristics of supercapacitors (Shi, 1996). Reduced dimensions of the electrode materials can enlarge the electrode/electrolyte contact area per unit mass significantly, providing more ion adsorption sites for double-layer formation and charge-transfer reactions.

The pore size distribution of porous carbons influences to a large degree the fundamental performance criteria of carbon-based supercapacitors (Su, 2010). Microporous activated carbon is the current material of choice for commercial supercapacitors with a specific surface area of up to 2000 m²/g providing capacitance in excess of 200 F/g in an aqueous electrolyte, operating at up to 1.2 V (Zhao, 2011). It is quite difficult to adapt the pore size to that of solvated anions
and cations in order to get an optimized performance of the supercapacitor. The poor control of the internal structure in activated carbons has three intrinsic property shortcomings: short shelf-life and degraded cycling stability, limited (< 10 Wh/kg) energy density, and poor rate capability (Lee, 1999). In contrast, templated carbons exhibit uniform pore geometry and larger pore size, however they did not show any exciting improvement in either energy or power performance (Fernandez, 2009). The impressive increase in performance that has been demonstrated in the past couple of years is due to the discovery of new electrode materials and improved understanding of ion behavior in small pores (Lee, 2007). Thus, significant advancement will depend on the discovery of novel charge storage concepts and material design of nanoporous carbon or carbon hybrid materials resulting in improved specific energy and power delivery. The optimal porous characteristics required for carbon-based materials must be better determined; therefore it is of great interest to synthesize carbon materials with a well-tailored porous structure.

1.1.3. Hydrogen Storage

Hydrogen has been recognized as an ideal fuel for many energy converters because of its high efficiency and non-polluting nature. However, a major drawback for the practical usage of hydrogen is the difficulty to store it safely and economically. Neither hydrogen storage as a compressed gas (high pressure 700 bar) nor as a cryogenic liquid (20K) appears to be suitable for wide-scale applications of technologies that uses hydrogen as an energy carrier (Vajo, 2009). Hydrogen physisorption on porous materials is one of the main methods being considered for hydrogen storage for vehicle applications. The objective is to store large amounts of hydrogen at near-ambient temperatures and ‘safe’ pressures. These materials would also need to satisfy the requirements of reasonable volume, weight, and realistic kinetics for charging and discharging
hydrogen. Table 1.2 lists the values of current DOE targets for onboard hydrogen storage systems ("DOE Hydrogen and Fuel Cells Program-Hydrogen Storage, 2011 Interim Update," 2011).

<table>
<thead>
<tr>
<th>Storage parameter (units)</th>
<th>2017</th>
<th>Ultimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>System gravimetric capacity (kWh/kg)</td>
<td>1.8</td>
<td>2.5</td>
</tr>
<tr>
<td>System gravimetric capacity (wt.% H₂)</td>
<td>5.5</td>
<td>7.5</td>
</tr>
<tr>
<td>System volumetric capacity (kWh/L)</td>
<td>1.3</td>
<td>2.3</td>
</tr>
<tr>
<td>System volumetric capacity (g H₂/L)</td>
<td>40</td>
<td>70</td>
</tr>
<tr>
<td>H₂ delivery temp (Min/Max °C)</td>
<td>-40 / 85</td>
<td>-40 / 85</td>
</tr>
<tr>
<td>Operating pressure (min/max) (MPa)</td>
<td>0.5/1.2</td>
<td>0.3/1.2</td>
</tr>
<tr>
<td>Kinetics (g H₂/s)/kW</td>
<td>0.2</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Various hydrogen storage systems (Figure 1.4 (a)) such as hydrides: metal, complex, and chemical; nanomaterial adsorbents: nanotubes, nanofibers, nanohorns, nanospheres, and nanoparticles; clathrate hydrates; polymer nanocomposites; and metal organic frameworks (MOFs) have been explored for onboard hydrogen storage applications (Seayad, 2004; Fichtner, 2005). However, none of these materials qualifies and fulfill all hydrogen storage criteria such as (1) high hydrogen content (>6.0 wt.%), (2) favorable or tuning thermodynamics (30–55 kJ/mol H₂), (3) operate below 100°C for H₂ delivery, (4) onboard refueling option for a hydrogen-based infrastructure, and (5) cyclic reversibility (~1000 cycles) at moderate temperatures. Carbonaceous materials are attractive candidates for hydrogen storage because of a combination of adsorption ability, high specific surface area, pore microstructure, and low-mass density. Among the various hydrogen storage systems, carbon-based nanomaterials and their wide applications for energy storage are being further explored.
Nanostructured materials have potential promise in hydrogen storage because of their unique features such as adsorption on the surface, inter- and intra-grain boundaries, and bulk absorption (Schulz, 1995). Nanostructured and nanoscale materials strongly influence the thermodynamics and kinetics of hydrogen dissociation and adsorption by increasing the diffusion rate as well as decreasing the required diffusion length (Niemann, 2008). They also lead to the design of light weight hydrogen storage systems with better hydrogen storage characteristics.

The weak interaction of hydrogen physisorbed within pores needs to be understood in order to optimize porous materials for hydrogen adsorption. The important measurements for this application are (1) amount adsorbed as a function of pressure, (2) temperature dependence of adsorption, (3) the enthalpies of adsorption, and (4) the adsorption/desorption characteristics.
Carbon materials have been studied extensively as potential hydrogen storage materials because of their low density, wide variety of structural forms, extensive pore structure, good chemical stability, and the ability to modify the structures using a wide range of preparation, carbonization, and activation conditions (Thomas, 2006). Recent literature indicates that hydrogen adsorption of approximately 5 wt. % at 77 K and 1-2 wt. % at room temperature can be achieved under high pressure conditions for a wide variety of nanoporous carbon materials (Vajo, 2009). High surface area porous materials with very narrow pores or pore size distributions are required for enhanced hydrogen capacity at low pressures (Thomas, 2006). Techniques to synthesize high surface area porous carbon include template methods and chemical activation processes, both which can create porosity characterized by micropores (pores less than 2 nm) and mesopores (pore size between 2 and 50 nm). These techniques will be further discussed and are suitable to enhance surface area and the nature of porosity of carbon for hydrogen storage.

In response to the durability issues faced by carbon support materials for fuel cells and the need to enhance porosity and conductivity for the fabrication of nanoporous carbons for supercapacitors and hydrogen storage, mesoporous carbon and carbon/ceramic materials have been synthesized and characterized with controlled composition and pore structure. Detailed background information on the development of mesoporous silica, mesoporous carbon, and carbon-silica nanocomposites are provided in the next section. Important topics such as sol-gel chemistry, evaporation induced self-assembly, and chemical activation are also discussed to provide a complete overview on the fabrication of mesoporous silica-carbon nanocomposites.
1.2. Mesoporous Materials Overview

The ability to judiciously control and design materials on the nanoscale has drawn a lot of attention towards the synthesis of nanocomposites. Two or more phases can be combined together that historically have been viewed as incompatible, creating domain sizes below 100 nm. The resulting materials are more homogenous than conventional hybrid materials and obtain complementary properties which cannot be obtained within the single components. Molecular self-assembly provides routes to create a variety of materials with diverse multicomponent structure of atoms, ions, and/or molecules held together by weak non-covalent interactions such as hydrogen bonds, van der Waals forces, π-π interactions, and/or electrostatic effects. The weak interactions can drive inorganic-organic assembly and organic-organic assembly to form inorganic and organic frameworks, respectively.

Porous materials contain voids as the majority phase, either with random character (disordered pore systems) or with high regularity (ordered pore systems) from the viewpoint of pore or channel packing regularity (Figure 1.5 (a-b)) (Mastai, 2002). Pores in solids are classified: intraparticle and interparticle on the basis of their origin; micro-, meso-, or macropores on the basis of their size; open and closed on the basis of their state; and rigid and flexible on the basis of their strength (Inagaki, 2009).
Ordered porous materials are of great scientific and technological interest due to their ability to interact with atoms, ions, and molecules not only at their surfaces, but also throughout their bulk (Davis, 2002). The backbone of the construction of ordered porous materials is the self-assembly process in which molecules or parts of molecules spontaneously organize into stable structurally well-defined nanometer length aggregates. Porosity can be present on different lengths ranging
from sub-nanometer to micrometers, and possess different features such as inter-particle porosity (pores open to the surface) and intra-particle porosity (pores close to the surface) (Greggs, 1982).

The pore system of any porous material may be classified, according to IUPAC (International Union of Pure and Applied Chemistry), based on the pore diameter (Rouquerol, 1994). Pores below 2 nm are classified as micropores and the typical representative materials are zeolites or activated carbons (Rouquerol, 1994). Ultramicropores are pores less than 0.7 nm and pore sizes ranging from 0.7-2.0 nm are categorized as supermicropores (Inagaki, 2009). The movement through micropores is described by surface migration or surface diffusion which is the creeping of adsorbed molecules along the surface of the pores (Bird, 2002). Pores that fall in the size range between 2 and 50 nm are called mesopores, and the mesoporous M41S family and SBA series of materials are prominent examples of this class (Rouquerol, 1994). As seen in the illustration in Figure 1.5c, mesoporous flow is classified by Knudsen diffusion which describes the diffusion through pores with narrow diameters in which molecules frequently collide with the pore’s walls (Bird, 2002). Pores above 50 nm are called macropores, and amorphous aluminosilicates and porous glass are typical representatives of macroporous materials (Rouquerol, 1994). Molecular diffusion is the mechanism of transport through macropores (Bird, 2002). The focus of this literature review will primarily be on materials with mesoporous pore structure.

In the early 1990s, the announcement by Kato and co-workers in Japan and Kresge and colleagues at Mobil Research and Development Corporation of a new class of materials called FSM and M41S respectively, led to a new synthetic strategy for preparing mesoporous materials (Yanagisawa, 1990; Beck, 1992). These mesoporous materials are derived from the self-
assembly of surfactants and inorganic precursors in a dilute aqueous solution (Figure 1.6) (Beck, 1992; Kresge, 1992; Hou, 1994; Zhao, 1998; Zhao, 1998).

Figure 1.6. A schematic displaying the general formation of FSM or M41S materials from inorganic precursors and surfactants (Ying, 1999)

Liquid crystal templating was used to form mesoporous uniform channels (1.6-10 nm) from the calcination of aluminosilicate or silicate gels in the presence of quaternary ammonium surfactants (Kresge, 1992). The silicate materials formed inorganic walls between ordered surfactant micelles (Kresge, 1992). The FSM and M41S materials ushered a new approach in materials synthesis, where instead of using single molecules as templating agents (as in the case of zeolites) self-assembled molecular aggregates or supramolecular assemblies are employed as structure-directing agents, resulting in materials with high surface areas and nanometer pore diameters (Ying, 1999). Synthesized in a basic solution, the M41S family contains three well defined mesostructures: MCM-41 (hexagonal), MCM-48 (cubic), and MCM-50 (lamellar) (Figure 1.7) (Beck, 1992; Kresge, 1992). Mesoporous silicates with diverse pore structures, narrow and uniform pore size distributions (2-50 nm), and high surface areas (800-2000 m²/g)
have applications in the separation of large molecules, drug delivery, sensors, devices, sorption agents, and catalyst supports.

![Illustrations of mesoporous M41S materials](image)

Figure 1.7. Illustrations of mesoporous M41S materials (a) MCM-41, (b) MCM-48, and (c) MCM-50 (Vartuli, 1996)

Over the next few years, extensive research was carried out to make silicate materials more stable, expand pore size, extend the framework composition, and examine new supramolecular templates. Stucky, G. and coworkers established a generalized approach to synthesize periodic mesophases of metal oxides based on the assembly process being controlled by electrostatic complementarity between the inorganic ions in solution, the charged surfactant head groups and inorganic counterions (in the case when these charges have the same sign) (Hou, 1994). Triblock copolymers in non-aqueous media have been used to prepare mesoporous oxides such as titanium oxide (TiO₂), zirconium oxide (ZrO₂), aluminum oxide (Al₂O₃), niobium oxide (Nb₂O₅), tantalum oxide (Ta₂O₅), tungsten trioxide (WO₃), hafnium oxide (HfO₂), tin dioxide (SnO₂), and a variety of mixed oxides. As a result of these efforts, mesoporous materials with pores sizes ranging from 2 to 50 nm have been produced to synthesize transition metal oxides, metal sulfides, metals, carbon, and hybrid silica/organic frameworks.

1.2.1. Mechanism of Mesostructure Formation

In the past, numerous models were proposed to explain the formation of mesoporous materials. Common to all these models is the usage of surfactants in a solution to guide the formation of inorganic mesostructure from the solubilized inorganic precursors (Ying, 1999).
Surfactants contain a hydrophilic head group and a long hydrophobic tail group within the same molecule and will self-organize in such a way to minimize contact between incompatible ends. The means in which the inorganic precursors interact with the surfactant is the issue whereby the models diverge; the differences in the type of interaction between the surfactant and the inorganic precursor vary amongst synthetic routes (Ying, 1999).

Lyotropic liquid crystal templating (LCT) is an approach for nanostructure and nanocomposite formation that utilizes the self-assembled structure of a liquid crystal to regulate the structure of a growing inorganic material (Tiddy, 1980). Within the LCT mechanism the inorganic phase condenses around a stabilized surfactant mesophase. The structure and pore dimensions are intimately linked to the properties of the surfactant, including chain length and solution chemistry. The structure of the inorganic phase directly replicates the structure of the liquid crystal; thus the liquid crystal is a ‘template’ for the inorganic phase (Tiddy, 1980). Lyotropic liquid crystals are composed of at least two covalently linked components, one of which is usually an amphiphile, and the other a solvent. The dual properties of an amphiphile lead to the interesting self-assembly of these molecules in solution by means of surface segregation, formation of micelles, and vesicles (Tiddy, 1980).

Self-assembly, defined by Brinker as “spontaneous organization of materials though non-covalent interactions such as hydrogen bonding, van der Waals forces, electrostatic forces, π-π interactions, etc. with no external intervention”, is governed by the delicate hydrophilic-hydrophobic balance among non-volatile components (Brinker, 1999). These include surfactants, silicates, additives, and volatile solvents such as water and ethanol (Brinker, 1999). The inorganic and organic arrays of the selected materials meet at the surface interface. The interface curvature is energetically defined to optimize charge repulsion and van der Waals interactions.
Phase transitions are associated with changes in the curvature of the interface; and competitions between the elastic energy of bending the interfaces and energies resulting from the constraints of charge separation (Gruner, 1989). Hence size, charge, and shape of surfactants are important structure determining parameters. The mesostructures can be predicted by a classical micellar packing parameter, $P = \frac{v}{a_0 l_c}$, where $a_0$ is the cross sectional hydrophilic head group area, $v$ is the surfactant volume, and $l_c$ is the length of the hydrophobic tail (Israelachvili, 1976; Zhang, 2005). Mesostructures of assembled inorganic materials can be tuned reflecting a decrease in surface curvature from hexagonal to cubic to lamellar phases by tuning the packing parameter $P$ (Israelachvilli, 1976). In classical micelle chemistry, as the $P$ value is increased above critical values, mesophase transitions occur. The expected mesophase phase sequence as a function of the packing parameter is provided in Table 1.3 (Hou, 1996).

<table>
<thead>
<tr>
<th>$P$</th>
<th>Mesophase</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1/3$</td>
<td>Cubic ($Pm\overline{3}n$)</td>
</tr>
<tr>
<td>$1/2$</td>
<td>Hexagonal ($p6mm$)</td>
</tr>
<tr>
<td>$1/2 - 2/3$</td>
<td>Cubic ($Ia3d$)</td>
</tr>
<tr>
<td>$1$</td>
<td>Lamellar</td>
</tr>
</tbody>
</table>

The formation of mesopores depends on numerous other parameters, in addition to phase transformation criteria. The interaction between the inorganic and organic precursors is an essential parameter in controlling the formation of mesoporous materials, but the mechanisms depend on the experimental conditions of the synthesis (Palmqvist, 2003). From the literature it is clear that the mechanism involved in the formation of ordered mesoporous materials depends largely on parameters related to the specific chemistry and chemical interactions involved not only for any given system studied, but also on the physical conditions employed (Patarin, 2002).
The following factors are of general importance: (i) type of inorganic material (metal, metal oxide, or other) and its tendency to crystallize in the walls; (ii) type of precursors used (alkoxides or salts) and the kinetics of their hydrolysis and condensation; (iii) type of surface-active molecules (cationic, anionic, or non-ionic); (iv) the respective and relative concentrations of surfactant (micellar or liquid crystal) and inorganic species; (v) pH (acidic or alkaline); (vi) temperature (low temperature or hydrothermal) and synthesis time; (vii) additives (inorganic salts and organic molecules); (viii) order of mixing; (ix) type of solvent (aqueous or non-aqueous) and solvent composition; (x) types of synthesis (evaporation induced self-assembly or precipitation); and (xi) physical shape of product formed (monolith, film, fiber or powder) (Patarin, 2002).

1.3. Mesoporous Silica

Mesoporous silica represents a family of novel materials prepared by surfactant directed assembly of silicate building clusters. These materials contain tunable pore structures, chemistries, and functionalities. Research on mesoporous materials was initially motivated by the desire for ordered silica/alumina materials with larger pore dimensions than those present in microporous zeolites for use in petrochemical catalysis (Palmqvist, 2003). Silica containing ordered mesopores can be prepared by templating surfactants and block copolymer liquid crystalline mesophases, resulting in mesoporous particles, fibers and films (Kresge, 1992; Schacht, 1996; Hou, 1997; Yang, 1997; Zhao, 1998). Typically, these materials are synthesized under conditions where silica-surfactant self-assembly occurs simultaneously with condensation of the inorganic species, yielding mesoscopically ordered composites.
Initially mesoporous silica materials such as MCM-41 (of the M41S family) were prepared using hydrothermal processes with a silica source (i.e. tetraethyl orthosilicate (TEOS), Ludox, fumed silica, or sodium silicate) and cationic cetyltrimethylammonium (CTA+) surfactants, which after calcination yielded a hexagonally ordered porous solid with uniform pore sizes of 2-3 nm (Kresge, 1992). The pore size of MCM-41 was expanded up to 10 nm through the use of an additional organic source such as 1,3,5 trimethylbenzene (TMB) (Schmidt-Winkel, 2000). However, less resolved x-ray diffraction (XRD) patterns with only a single broad diffraction peak was observed (Schmidt-Winkel, 2000). Extended thermal treatment during synthesis resulted in expanded pore sizes up to 5 nm (Schmidt-Winkel, 2000). Pinnavaia and co-workers used nonionic surfactants in neutral aqueous media to synthesize worm-like disordered mesoporous silica with uniform pore sizes 2-6 nm (Bagshaw, 1995; Prouzet, 1997). The results of Pinnavaia and co-workers established that amphiphilic polymers of large molecular weight should be used to increase the dimensions of pore structures produced in inorganic-organic composite synthesis (Zhao, 1998). Considerable interest was given to a report by Voegtlin et al. of the synthesis of ordered mesoporous silica with improved X-ray diffraction through the use of non-ionic surfactants in the presence of fluoride anions under near neutral conditions (Voegtlin, 1997). This work suggested that the fluoride anions are coordinated to silica intermediates, which provide electrostatic shielding and effective hydrogen bonding to form mesoporous silica structures that yield narrow (100) Bragg diffraction peaks (Voegtlin, 1997).

Well ordered (2D) hexagonal (p6mm) mesoporous silica SBA-15 with tunable large uniform pore sizes up to 30 nm was obtained through the use of amphiphilic block copolymers as organic structure-directing agents in aqueous acidic environments (Kruk, 2000). Unlike conventional ionic surfactants, non-ionic block copolymer surfactants have the advantage that
their properties can be continuously tuned during synthesis by adjusting composition, molecular weight, and architecture (Hou, 1996). The hydrophilic groups are made up of water-soluble moieties (polymer chains) such as poly(ethylene oxide) (PEO) rather than charged head groups. Poly(alkylene oxide) triblock copolymers such as poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) PEO-PPO-PEO (with the commercial name of Pluronic) were used because of their meso-structural ordering properties, amphiphilic character, low cost, commercial availability, low toxicity, and biodegradability (Hou, 1996). The PEO moieties interact more strongly with the silica species and are closely associated with the inorganic wall than the more hydrophobic PPO block (Hou, 1996). However, at higher temperatures the PEO block becomes more hydrophobic, resulting in increased hydrophobic domain values, smaller lengths of PEO segments associated with silica walls, and increased pore sizes (Hou, 1996). Pore sizes were increased to 30 nm by increasing the hydrophobic volume of the self-assembled aggregates (Zana, 1997). SBA-15 contained thicker silica walls and greater thermal stability in comparison to MCM-41 (made with cationic surfactants). The pore size and thickness of the silica walls of SBA-15 can be adjusted by varying the reaction solution heating temperature and time (Kruk, 2000). The concentration of block copolymer greater than 0.5 wt. % (less than 0.5 wt. % produces only amorphous silica) and less than 6 wt. % (above 6 wt. % produces only silica gel) is ideal with reaction temperatures between 35°C and 80°C (Kruk, 2000).

Consistent with the results for Voegtlin, balanced Coulombic, hydrogen bonding, and van der Waals interactions with charge matching in aqueous media provide an effective means of enhancing long range periodic order (Voegtlin, 1997). These interactions are critical at the inorganic-organic interface. The pH value needs to be below the aqueous isoelectric point of silica (pH ~ 2) (Hou, 1994; Hou, 1996). Above the isoelectric point no precipitation or the
formation of silica gel occurs due to the absence of sufficient electrostatic or hydrogen bonding at pH values 2-7. At pH ~ 1 positively protonated silicate species interact preferentially with the more hydrophilic PEO block and promotes cooperative self-assembly of the silica block copolymer rich mesophase from a dilute water rich phase (Hou, 1994; Hou, 1996). Solubilization of PEO-PPO-PEO in hydrochloric acid (HCl) where hydronium ions are associated with alkylene oxygen atoms, provides long range Coulombic interaction to the co-assembly process. The matching of charge density at the surfactant/inorganic interfaces governs the assembly process. The protonated Si-OH moiety, i.e., [SiO\textsubscript{H}\textsuperscript{+}OH\textsuperscript{+}], designated as I\textsuperscript{+} assembles as a (S\textsuperscript{0}H\textsuperscript{+})(X\textsuperscript{-}I\textsuperscript{+}) double layer hydrogen bonding interaction in which S\textsuperscript{0} is the non-ionic surfactant and X\textsuperscript{-} is the halide ion (counter-anions) (Hou, 1994; Hou, 1996). Under these conditions, the structure of ordered mesoporous silica is controlled by the surfactant species selected, in which each type of surfactant favors a specific mesostructured silica phase. When considering the (S\textsuperscript{0}H\textsuperscript{+})(X\textsuperscript{-}I\textsuperscript{+}) assembly, the rate of assembly (r) increases with increasing concentration H\textsuperscript{+} and Cl\textsuperscript{-} and follows the rate law \[ r = k[H^+]^{0.31}[Cl^-]^{0.31} \] (Zhao, 1998). In addition to the charge density matching between the surfactant head-groups and hydrolyzed inorganic oligomers, the minimization of free surface energy (F) during the coalescence and condensation of liquid crystal-like phase made up of the block copolymer/inorganic hybrid species should be taken into account. Although the free energy of the mesophase formation (\(\Delta G\)) is responsible for the final mesostructure, the competition between \(\Delta G\) and the surface free energy (F) of this liquid crystal-like phase determines the morphologies of the final mesoporous materials (Wan, 2007). Non-ionic block copolymers are an interesting class of structure directing agents whose self-assembly characteristics lead to kinetically quenched structures (Zhao, 1998). Mesostructural control is established by tuning the co-assembly of surfactant and silicate.
The effect of counter-anions for four different acids on the formation of mesostructured silica was studied by Che et al. (Che, 2002). Three-dimensional bicontinuous mesoporous silica with \( \text{Ia3d} \) symmetry was prepared using TEOS at a low temperature with cetyl-triethyl ammonium bromide (CTEABr) surfactant and \( \text{HNO}_3 \) as an acid (Che, 2002). An additional synthesis containing hydrobromic acid (HBr) instead developed a material with 2D-hexagonal \( \text{p6mm} \) structure, and the use of \( \text{HCl} \) resulted in the cubic \( \text{Pm3n} \) mesostructure (Che, 2002). Using \( \text{H}_2\text{SO}_4 \) acid, on the other hand, resulted in the formation of facetted single crystals with the 3D-hexagonal \( \text{P6}_3\text{mmc} \) mesophase (Che, 2002). The difference between the acids was explained by the difference in the contribution of their counter-anions to the partial reduction of the repulsion between the surfactant head-groups, and thus resulting in increasing surfactant packing parameter values (Che, 2002).

Aside from using different types of surfactants and the interaction between surfactants and inorganic species in acidic media, the pore sizes and structures of mesoporous silica materials have been controlled by changing the hydrophobic volumes of the templates, which may be achieved by changing the reaction temperature or by adding organic co-solvents as swelling agents. Liu et al. developed large pore 3D bicontinuous mesoporous silica (FDU-5) in acidic media at room temperature using \( \text{PEO}_{20}-\text{PPO}_{70}-\text{PEO}_{20} \) (P123) triblock copolymer as a surfactant directing template, TEOS as an inorganic source, and small amounts of 3-mercaptopropyltrimethoxysilane (MPTS), benzene, or benzene derivatives (methyl-, ethyl-, dimethyl-, or trimethyl- benzene) as additives (Liu, 2002). The addition of organosiloxanes or small organic molecules increases the hydrophobic/hydrophilic ratio and results in a transition of the assembled inorganic-organic mesostructure from high-curvature hexagonal \( \text{p6mm} \) to low-curvature bicontinuous cubic \( \text{Ia3d} \) (Liu, 2002).
Sol gel based dip coating methods were developed for the rapid synthesis of mesoporous thin silica films on solid substrates (Lu, 1997). This process produced films with hexagonally packed one dimensional channels or cubic phase at the solid-liquid and liquid-vapor interfaces above the critical micelle concentration (CMC) of bulk silica-surfactant solutions through interfacial self-assembly (Manne, 1995; Aksay, 1996; Yang, 1996; Yang, 1996; Lu, 1997). Grosso et al. reported on the detailed characterization of the formation of two-dimensional hexagonal silica films prepared by dip-coating an alcoholic acidic solution of TEOS and Pluronic F127 (Grosso, 2001). They found that a phase with randomly oriented domains of organized pore channels formed at the center of the film, while the channels were well aligned with the surface at both film interfaces (Grosso, 2001). By increasing the ethanol content the well-aligned phase was preferentially formed, whereas by increasing the water content the disoriented phase was formed (Grosso, 2001). The final mesostructure did not form until the ethanol and excess water used for pre-hydrolysis had been evaporated and the film was dry (Grosso, 2001).

Well-ordered silica spherical particles of hexagonal and cubic topology have been prepared using aerosol based self-assembly, in which evaporation induced self-assembly (EISA) was confined into spherical aerosol droplets (Lu, 1999). The method of aerosol assisted self-assembly is a highly efficient approach that can continuously synthesize spherical mesostructured silica particles within a time scale of several of seconds (Brinker, 1999). Well defined large mesopores (30-50 nm) have been prepared through the use of oil-in-water microemulsions as colloidal templates to prepare mesostructured cellular foam materials (Schmidt-Winkel, 2000). Functionality to the pore surface or pore walls of mesoporous silica have been established to covert inert silica into various functional materials (Stein, 2000; Wang, 2004). The co-assembly of surfactants with organosilane precursors that contain non-
hydrolyzable pendant or bridged organic ligands provided a direct synthesis method of mesoporous silica with functionalities (Fowler, 1997; Lim, 1997; Asefa, 1999; Hall, 1999; Inagaki, 1999; Corriu, 2002; Hamoudi, 2002; Inagaki, 2002; Wang, 2003). Other silica sources other than TEOS have been reported for mesoporous silica materials. Kim et al. found blends of non-ionic amphiphilic block copolymers as structure-directing agents and sodium silicate as silica source under acidic conditions to give lamellar, hexagonal, and cubic mesostructures (Kim, 2002). The structural transformations were suggested to be caused by changes in the hydrophobic surface curvatures, which can be controlled by using polymer blends with different hydrophilic head-group sizes of the individual components (Kim, 2002).

After the discovery of mesoporous silica materials, organic-inorganic assembly combined with sol gel processes by using surfactants as structure directing agents had been considered to be the major pathway for creating mesoscaled periodic materials. However, many mesostructured materials cannot be prepared using sol gel processes. Nanocasting of highly ordered mesoporous silica as hard templates (Figure 1.8) has led to (a) nanowire arrays with diameters smaller than 10 nm; (b) high surface areas and narrow pore size distributions; (c) tunable 2-D or 3-D mesostructures; (d) controlled morphologies such as spheres, rods, films, and monoliths; and (e) different components including carbon, metals, metal oxides, and metal sulfides (Hampsey, 2005; Yang, 2005; Wan, 2008).
However there are numerous issues and drawbacks using the nanocasting processes. For example, the driving force for promoting the movement of precursors into the mesopores is the capillary effect, and a weak interaction between the silica walls and the precursors may decrease the capillary function and cause the precursors to remain outside the mesopores and/or stick inside the mesopore channels and/or block the channels (Scott, 2001). In this case nanocasting can fail and the periodic replica mesostructures are not generated after removing the silica templates.

When preparing mesoporous composites a great number of parameters can influence the self-assembly process. They can be divided into two classes. The first case involves the chemical factors that govern the quantities of surfactant and inorganic precursor and the sol-gel hydrolysis/condensation reactions. The second involves the processing conditions that dictate the diffusion and evaporation of volatile ethanol (EtOH), H₂O, and HCl molecules to form the composite, fixing the composition of the dry composite, and its final thickness. It is thus
noteworthy to provide an overview of common non-ionic surfactants, sol gel processing, and evaporation induced self-assembly.

1.3.1. Parameters for Non-Ionic Surfactants

The main classes of non-ionic surfactants for synthesizing ordered mesostructures are oligomeric alkyl ethylene oxides, oligomeric alkylphenol ethylene oxides, sorbitan ester surfactants, and amphiphilic block copolymers (Figure 1.9) (Wan, 2007).

![Figure 1.9](image)

**Figure 1.9.** A list of examples of common commercial non-ionic surfactants utilized as detergents, emulsifiers, foamers, wetters, and gel forming agents (Wan, 2007).

To select a surfactant various parameters based on their fundamental features should be considered such as the hydrophilic/hydrophobic ratio, critical micelle concentration (CMC),
hydrophile–lipophile balance (HLB), critical micelle temperature (CMT), cloud-point (CP) value, etc. (Wan, 2007).

Block copolymers with certain hydrophilic/hydrophobic ratios are extremely suitable for assembling ordered mesoporous silicates. In general, if surfactants have CMC values less than 20 mg/L ordered mesostructures are always obtained (Yu, 2003). Surfactants with larger CMC values within this range generally give cubic mesostructures. In the case of values 20-300 mg/L, strategies can be used to decrease the CMC values in order to yield ordered mesostructures (Yu, 2003). It is difficult to make ordered mesostructures when CMC values of surfactants are higher than 300 mg/L (Yu, 2003).

Based on emulsification data, semi-empirical HLB numbers, ranging from 0 to 40, can be assigned to surfactants which have a hydrophilic–lipophilic balance (Zhao, 1998). Surfactants with HLB values ranging from 4 to 12 favor the formation of ordered mesostructures. In the case when HLB values of surfactants are higher than 12, cubic and disordered mesostructures are the possible products (Zhao, 1998). Lyophilic surfactants with HLB values lower than 4 always direct the formation of lamellar mesostructures (Zhao, 1998). As hydrophobicity increases HLB values decrease.

The hydrophilic/hydrophobic volume ratio \( V_H/V_L \) is a guide for nonionic-surfactant-templating to account for the formation of different mesophases (Kipkemboi, 2001). Nonionic surfactants with high \( V_H/V_L \) ratios (such as F108 (EO\(_{132}\)PO\(_{50}\)EO\(_{132}\)), F98 (EO\(_{123}\)PO\(_{47}\)EO\(_{123}\)), F127 (EO\(_{106}\)PO\(_{70}\)EO\(_{106}\)) and Brij700 (C\(_{18}\)H\(_{37}\)EO\(_{100}\)) opt for the formation of caged-like cubic mesoporous materials, whose topological curvatures are rather high, while block copolymers with medium hydrophilic/hydrophobic ratios (e.g. P123 (EO\(_{20}\)PO\(_{70}\)EO\(_{20}\)) and B50-1500 (BO\(_{10}\)EO\(_{16}\), BO = butylene oxide)) usually direct the synthesis of mesostructures with medium
curvatures (e.g. 2D hexagonal structure with space group of \( \text{p6m} \) or 3D bicontinuous cubic \( \text{Ia}\tilde{3}\text{d} \)) (Zhao, 1998). The concentration of block copolymers which affect the \( V_H/V_L \) ratios can also alter mesostructures, typically higher concentrations lead to mesostructures with lower mesophase curvature (Zhao, 1998; Tian, 2002).

The synthesis temperature for mesoporous materials is relatively low, ranging from −10 to 130 °C, but it is normally higher than room temperature owing to the high CMT values. For most Pluronic copolymers the CMT values range from 25-40°C. Many nonionic surfactants become insoluble in warm water (Wan, 2007). The temperature in which the solution becomes cloudy due to phase separation and the surfactant begins to precipitate is referred to as the cloud point (CP). The synthesis temperature must be lower than the CP values of surfactants. In the synthesis of SBA-15 templated by triblock copolymer P123, the optimal synthetic temperature is 35–40 °C (Zhao, 1998); either lower or higher temperature may prevent the formation of micelles due to the solubility limit and the CMT value (Zhao, 1998; Zhao, 1998; Martines, 2004). The CP values are influenced by many factors, such as solvents, co-surfactants, inorganic salts and organic agents.

1.3.2. Sol Gel Process

It is well known that a sol-gel process is a useful technique to prepare a nanocomposite of organic and inorganic materials. This section provides a summary detailing the sol gel processing of silicate materials as described by C. J. Brinker in “Sol-Gel Sciences: The Physics and Chemistry of Sol Gel Processing” (Brinker, 1990). The sol-gel process involves the development of inorganic networks through the formation of a colloidal suspension, the sol, and gelation of the sol to form a continuous network containing both liquid and solid phases, the gel. The precursors for synthesizing these colloids consist of a metal or metalloid elements surrounded by
various reactive ligands. Metal alkoxides are the most popular precursors because they readily react with water. The most extensively used metal alkoxides are the alkoxy silanes, such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS).

The sol gel process utilizes alkoxides which are hydrolyzed and condensed to form polymeric species composed of M-O-M bonds. Three reactions are generally used to describe the sol-gel process as shown below for silica:

\[
\begin{align*}
\text{Hydrolysis} & : & \text{Si}-\text{OR} + \text{HOH} & \underset{\text{Reesterification}}{\longrightarrow} & \text{Si}-\text{OH} + \text{ROH} \\
\text{Alcohol Condensation} & : & \text{Si}-\text{OH} + \text{Si}-\text{OR} & \underset{\text{Alcoholysis}}{\longrightarrow} & \text{Si}-\text{O}-\text{Si} + \text{ROH} \\
\text{Water Condensation} & : & \text{Si}-\text{OH} + \text{Si}-\text{OH} & \underset{\text{Hydrolysis}}{\longrightarrow} & \text{Si}-\text{O}-\text{Si} + \text{HOH}
\end{align*}
\]

(1.9)  
(1.10)  
(1.11)

Based on Equations 1.9-1.11 it is evident that the structure of silica is the product of successive hydrolysis and condensation reactions. The characteristics and properties of a particular sol-gel inorganic network are related to a number of factors that affect the rate of hydrolysis and condensation reactions such as pH, solvent, temperature and time of reaction, water to alkoxide molar ratio, nature and concentration of catalyst reagent concentrations, aging temperature and time, and drying. By controlling these factors, it is possible to vary the structure and properties of the sol-gel-derived inorganic network over a vast range.

Hydrolysis is a chemical process in which a certain molecule is split into two parts by the addition of a molecule of water. One fragment of the parent molecule gains a hydrogen ion (H⁺)
from the water molecule, and the other group obtains the remaining hydroxyl group (OH\(^{-}\)). The hydrolysis reaction takes place when a nucleophilic attack occurs using the electronegative oxygen contained in water on the silicon atom of the silica source like TEOS. Hydrolysis is facilitated in the presence of homogenizing agents (alcohols, dioxane, THF, acetone etc.) which are especially beneficial in promoting the hydrolysis of silanes containing bulky organic or alkoxy ligands (Vorankov, 1978). However, it is noteworthy to mention that the addition of solvents may promote esterification or depolymerization reactions according to the reverse of Equations 1.9-1.11 (Vorankov, 1978). Figure 1.10 shows how pH affects the rate of hydrolysis (Pohl, 1985).

![Figure 1.10](image)

**Figure 1.10.** (a) The pH rate profile for hydrolysis of γ-glycidoxypropyltrialkoxyisilane in aqueous solution (Pohl, 1985) and (b) Rate of H\(^{+}\) catalyzed TEOS hydrolysis (gel time) as a function of pH (Pohl, 1985)

Hydrolysis is most rapid and complete in the presence of a catalyst. Generally, ammonia or mineral acids are used in sol-gel processing. The rate and extent of the hydrolysis reaction is most influenced by the strength and concentration of the acid or base catalyst employed in the reaction. Aelion et al. determined that the acid catalyzed reactions were first order in respect to
acid concentration in which weaker acids required longer reaction times to achieve the same extent of reaction in comparison to strong acids (Aelion, 1950). Under acidic conditions, it is likely that an alkoxide group is protonated in a rapid first step, as shown in Figure 1.11. Electron density is withdrawn from the silicon atom, making it more electrophilic and thus more susceptible to attack from water (Pohl, 1985). This results in the formation of a penta-coordinate transition state with significant S_N2-type character (Pohl, 1985). The transition state decays by displacement of an alcohol and inversion of the silicon tetrahedron.

\[
\begin{align*}
\text{Si-OR} + \text{H}^+ & \rightarrow \text{Si-O-OR} \\
\text{Si-OH} + \text{ROH} + \text{H}^+ & \rightarrow \text{Si-OR} + \text{HOH}
\end{align*}
\]

Figure 1.11. The acid-catalyzed mechanism for sol gel hydrolysis

Base-catalyzed hydrolysis of silicon alkoxides proceeds much more slowly than acid-catalyzed hydrolysis at an equivalent catalyst concentration. Under basic conditions, the hydrolysis reaction was found to be first-order in respect to base concentration. However, as the TEOS concentration was increased the reaction deviated from a simple first-order to a more complicated second-order reaction. Previous findings have shown that acid-catalyzed hydrolysis with low H_2O/Si ratios produces linear or weakly branched “polymeric” networks, whereas base-catalyzed hydrolysis with large H_2O/Si ratios produces highly branched “colloidal” particles.
Depending on the amount of water and catalyst present, hydrolysis may proceed to completion, so that all of the OR groups attached to silica are replaced by OH groups. Any intermediate species \([(OR)_2\text{-Si-(OH)}_2]\) or \([(OR)_3\text{-Si-(OH)}]\) would be considered the result of partial hydrolysis. In addition, two partially hydrolyzed molecules can link together in a condensation reaction to form a siloxane \([\text{Si-O-Si}]\) bond. Thus, polymerization is associated with the formation of a 1, 2, or 3-dimensional network of siloxane \([\text{Si-O-Si}]\) bonds accompanied by the production of H-O-H and R-O-H species.

Condensation reactions involve two molecules or moieties combining to form one single molecule with the loss of another small molecule. When this small molecule is water, it is known as a dehydration reaction. Further examination of Equations 1.10 and 1.11 suggest that polymerization to form siloxane bonds occurs by either an alcohol producing condensation reaction (Equation 1.10) or a water producing condensation reaction (Equation 1.11). Under most conditions, condensation commences before hydrolysis is complete. A mutual solvent such as alcohol is needed to facilitate the process because water and alkoxides are immiscible. As the number of siloxane bonds increase, the individual molecules are bridged and jointly aggregate in the sol. A gel is formed when the sol particles aggregate or inter-knit into a network. Upon drying, trapped volatiles (water, alcohol, etc.) are driven off and the network shrinks as further condensation occurs.

When the pH value is below 2, the condensation rates are proportional to the \([\text{H}^+]\) concentration. Because the solubility of silica is quite low below pH 2, formation and aggregation of the primary silica particles occur together and ripening (i.e., growth of a network) contributes little to growth after particles exceed 2 nm in diameter. Thus, developing gel networks are composed of exceedingly small primary silica particles. Between pH 2 and pH 6
condensation rates are proportional to [-OH] concentrations. Above pH 7, polymerization occurs similar to the pH 2 to pH 6 ranges, however, in this pH range, condensed species are ionized and therefore, mutually repulsive. Growth occurs primarily through the addition of monomers to the more highly condensed particles rather than by particle aggregation. Due to the greater solubility of silica and the greater size dependence of solubility above pH 7, particles grow in size and decrease in number as highly soluble small particles dissolve and re-precipitate on larger less soluble particles. Growth stops when the difference in solubility between the smallest and largest particles becomes indistinguishable. This process is referred to as Ostwald ripening. Particle size is temperature dependent, in that higher temperatures produce larger particles.

Similar to hydrolysis, condensation reactions are improved by incorporating acid or base catalyst. Condensation reactions are acid and base specific. The acid-catalyzed condensation mechanism involves a protonated silanol species. Protonation of the silanol makes the silicon more electrophilic and thus susceptible to nucleophilic attack. Sol-gel polymerization occurs in three stages: (a) polymerization of monomers to form particles; (b) growth of particles; and (c) linking of particles into chains, then networks that extend throughout the liquid medium, then thickening into a gel.

Mesoporosity and mesoporous structure (pore size and distribution) strongly depend on the sol-gel reaction conditions. It is of paramount importance for the successful synthesis of mesoporous materials such as silica and titania that the rates of precursor hydrolysis and inorganic condensation are properly adjusted to the rate of the surfactant self-organization. Klotz et al. showed that the two main synthesis parameters of importance in the preparation of hexagonal mesoporous silica were the aging of the sol before deposition and the surfactant volume fraction in the medium after removal of the volatile components (Koltz, 2000). They
used alcoholic acidic mixtures of cetyltrimethylammonium bromide (CTAB) and TEOS and found that it is important that the alkoxide be adequately hydrolyzed (Koltz, 2000). However, a prerequisite for ordered structures is that the \( Q_3 \) silicate species not form during the aging time of the deposited solution (Koltz, 2000). Here, \( Q_n \) denotes silicate species with a central Si atom connected to \( n \) \((n = 0–4)\) other Si atoms by Si-O-Si bonds and more condensed Si is reflected by higher \( n \) values (Koltz, 2000). Thus, there is an optimal aging time for the solution before deposition. After the sol-gel formation is complete a supercritical drying processes relives the large capillary forces generated during the drying process, and makes it possible to reserve the highly cross-linked and porous structure generated during sol-gel polymerization.

1.3.3. Evaporation Induced Self-Assembly (EISA)

The corporative self-assembly process involves the combination of surfactant and inorganic molecules to form a hybrid intermediate that behaves as an independent surfactant species and building block for mesoporous structure (Boissiere, 2001; Grosso, 2002). Amphiphilic surfactant molecules are commonly used due to their preprogrammed ability to organize into well-defined supramolecular assemblies (Grosso, 2002). Surfactants assemble into micelles and these micelles result in the formation of spherical or cylindrical structures that maintain the hydrophilic parts in contact with water while shielding the hydrophobic parts within the micellar interior. Increasing the surfactant concentration results in the organization of micelles into periodic hexagonal, cubic, or lamellar mesophases, as seen in the phase diagram in Figure 1.12 (a) (Yang, 1996).
Figure 1.12. (a) Illustrations of (a) a phase diagram of micelle formation which leads to the formation of various phases and (b) EISA driven pathway during dip coating and the aerosol processes (Brinker, 1999).

Despite excellent control of pore size, early mesoporous materials were made in the form of powders, making their use impossible in thin film applications like membranes, low dielectric constant inter-layer and optical sensors. Mesoporous films were initially fabricated through the use of homogenous silica/surfactant/solvent mixtures onto substrates with initial surfactant concentration, \( (C_0) \), greater than the critical micelle concentration (Brinker, 1999). Frequently diluted synthesis mixtures are used in film formation, and the solvent is typically a mixture of ethanol and water. The reason for this is to avoid the condensation of the inorganic precursors, which disturbs the organization of the amphiphilic molecules. Sol gel dip-coating suggest an alternative route to form thin films. Starting with a homogenous solution of soluble silica and surfactant prepared in an ethanol/water solvent with \( C_0 \ll \text{CMC} \), the preferential evaporation of ethanol concentrates the depositing film in water and nonvolatile surfactant and silica species (Lu, 1997). As seen in Figure 1.12 (b), the increasing surfactant concentration drives the self-assembly of silica-surfactant micelles and their further organization into liquid crystalline
mesophases (Brinker, 1999). Initial silica-surfactant structures, which exist at the solid-liquid and liquid-vapor interfaces at $C < \text{CMC}$, serve to nucleate and orient mesophase development, resulting in the rapid formation of thin film mesophases oriented in the direction of the substrate surface (Lu, 1997). The alignment of the mesostructure is also assisted by the presence of the air/film and substrate/film interfaces within the film formation (Palmqvist, 2003).

Evaporation induced self-assembly of liquid droplets is a means to create nanostructured particles. Solvent evaporation can create a radial gradient of surfactant concentration within each droplet that steepens with time and maintains a maximum concentration at the droplet surface (Lu, 1999). The radial concentration gradient and the liquid vapor interface causes ordered silica-surfactant liquid crystalline domains to grow radially inward (Lu, 1999). In this case the surfactant CMC is first exceeded at the surface of the droplet and as evaporation continues the CMC is progressively exceeded throughout the droplet (Lu, 1999). This surfactant enrichment induces silica self-assembly into micelles and further organization into liquid crystalline mesophases.

1.4. Mesoporous Carbon

Elemental carbon materials exhibit unique electronic, mechanical, and chemical properties that make them attractive for electronic devices, electrode materials, strength enhancing materials, separation media, catalyst supports, energy storage/conversion systems, and optical components (Zhao, 1998; Ying, 1999). Well ordered nanoporous carbon materials are essential for a number of these applications. Carbon can bond with itself principally via \( sp^3 \) (diamond-like) and \( sp^2 \) (graphite-like) covalence linkages. This unique ability leads to diversified molecular structures such as nanotubes and fullerenes which have garnered considerable interest (Baughman, 2002).
Porous carbon materials have attracted much attention because of their high surface areas, large pore volumes, chemical inertness, and high mechanical stability. Several different synthetic approaches have been used to develop porous carbon materials with various pore sizes and structures. Disordered microporous activated carbons have been synthesized through both chemical and physical activation processes. Ordered microporous carbon materials have been synthesized using zeolites as templates. Mesoporous carbons with a disordered pore structure have been synthesized using various methods, including catalytic activation using metal species, carbonization of polymer/polymer blends, carbonization of organic aerogels, and template synthesis using silica nanoparticles. Ordered mesoporous carbons with various pore structures have been synthesized using mesoporous silica materials such as MCM-48, HMS, SBA-15, MCF, and MSU-X as templates. Ordered mesoporous carbons with graphitic pore walls have been synthesized using soft-carbon sources that can be converted to highly ordered graphite at high temperature. Hierarchically ordered mesoporous carbon materials have been synthesized using various designed silica templates and various organic precursors.

In comparison to inorganic-organic self-assembly, the preparation of mesoporous carbon materials with ordered open pore structure is difficult in solution and was initially challenging due to the high formation energy of C-C bonds (Lee, 1999; Yu, 2001). Ordered porous carbon materials have previously been replicated by using colloidal crystals and pre-synthesized mesoporous silicas as scaffolds (Joo, 2001). These methods are difficult to adapt to the fabrication of large-scale ordered nanoporous films with controlled pore orientations. Although numerous methods such as chemical vapor deposition, ultrasonic deposition, silica template synthesis, hydrothermal decomposition of carbide compounds, and polymer coating and
pyrolysis have been developed for the fabrication of carbon films, it was initially very difficult to develop ordered porous structure (Cai, 2004).

Numerous porous carbon materials have been fabricated by controlled foaming, ion track etching, molecular imprinting, phase separation and inorganic templates including zeolites, alumina membranes, opal, and silica sol gels (Cai, 2004). Initially, carbon molecular sieves were synthesized using mesostructured silica (or aluminosilicate) materials as inorganic templates creating cubic, disordered, hexagonal, and foam-like mesostructured carbon materials. Phase separation can occur from organic-organic phases, while the pore structures can be formed after etching, or by dissolving one block (A) from the assembled block copolymer (A-B) (Zalusky, 2002). Most of the resulting porous polymer structures are disordered with wide pore size distributions because of the concentration and swelling from changes in volume, as well as the structure defects from changes in volume, and structured defects formed during template removal (Zhu, 1997). The lack of covalent bonds makes the resistance of pore structure to heat and solvents low due to the materials being formed by weak van der Waals forces and physical twists between polymer chains (Meng, 2006). In this case the carbonization process which has been used for active carbons and related materials can only generate porosity with a tunable pore size, but not regular pore structures (Meng, 2006).

By employing the mesoporous silica structures such as MCM-48 with \textit{Ia3d} symmetry as a hard template, ordered mesoporous carbon replicas were synthesized by Ryoo et.al. from a nanocasting strategy (Lee, 1999; Ryoo, 1999; Jun, 2000; Joo, 2001; Lee, 2002; Tian, 2003). The resulting carbon designated as CMK-1 was prepared by carbonizing sucrose inside the pores of MCM-48 mesoporous silica (Kresge, 1992; Ryoo, 1999). However, the CMK-1 XRD pattern indicated that the carbon underwent a systematic transformation into a different structural
symmetry from that of the silica template. Later reports indicate that the structural symmetry of the silica template was retained through the use of ordered mesoporous silica molecular sieve SBA-15 as the template, sucrose as the carbon source, and sulfuric acid as the carbonization catalyst, resulting in the creation of CMK-3 (Zhao, 1998; Jun, 2000).

A class of mesoporous carbons were synthesized through the carbonization of preformed polymers filled into the void mesopores of calcined cubic and hexagonal mesostructured templates (Ryoo, 1999; Jun, 2000; Yoon, 2001). The general synthetic procedure for these mesoporous carbons using mesoporous silica templates is the following order: (i) silica/surfactant self-assembly nanocomposite materials are synthesized from the co-assembly of surfactant and silicates, (ii) the surfactants are removed by extraction or calcination, (iii) incorporation of carbon precursor into the pore of the mesoporous silica material, (iv) carbonization, and lastly (v) removal of the silica template. This general nanocasting approach is long, complicated, costly, and therefore is an industrial unfeasible method. Shorter and simpler synthetic approaches are required in order to achieve widespread usage. Direct one-step methods that can eliminate the preformed template and infiltration steps have been the focus of numerous studies.

A direct synthesis method to produce mesoporous carbon was reported by Moriguchi, I. et al. by the in situ polymerization of divinylbenzene in the hydrophobic region of a hexagonally arrayed micelle/silica nanocomposite, followed by carbonization and HF treatment (Moriguchi, 2002). However the final result was wormhole-like disordered mesopores of ~2 nm (Moriguchi, 2002). Yu and coworkers reported the direct preparation of highly ordered nanoporous carbon with high mechanical and thermal stability using as-synthesized MCM-48 silica/surfactant nanocomposite, with an additional carbon precursor of divinylbenzene (DVB) with a free radical
initiator of azobisisobutyronitrile (AIBN) synthesized inside the empty space of the silica/surfactant composite (Yoon, 2002). Kawashima et al. used sol gel processing to prepare uniformed mesoporous carbon on the order of 4 nm in diameter using TEOS in the presence of furfural alcohol (FA) as a carbon precursor (Kawashima, 2000).

Uniform porous carbons were also synthesized through colloidal templates of monodispersed silica spheres 30-100 nm in diameter by carbonization of sugars such as sucrose or glucose as carbon precursors in the presence of sulfuric acid (Yu, 2001). Sulfuric acid was used as a dehydrating agent to turn sugar into carbon (Yu, 2001). An aerosol based one-step approach was reported by Hampsey, J. E. and collaborators in which both microporous and mesoporous spherical carbon particles were synthesized from aqueous sucrose solutions containing colloidal silica particles and/or silicate cluster templates resulting in highly porous foam like structures (Hampsey, 2005).

Ordered mesoporous carbon materials were successfully synthesized directly by the carbonization of sulfuric acid treated silica/triblock copolymer/sucrose composites (Li, 2006). The combination of P123 and sucrose were used both as structure directing agents and carbon precursors. Both carbon precursors were cross-linked together by sulfuric acid in order to improve carbon yield. Kim, J. et al. synthesized mesocellular carbon foams and mesoporous carbons with hexagonally ordered carbon nanorod structures from the direct carbonization of as-synthesized silica/triblock copolymer nanocomposites by performing acid catalyzed sol-gel polymerization using sulfuric acid (Kim, 2004).

Dai and co-workers successfully prepared ordered mesoporous carbon films with open pore structures by employing resorcinol and formaldehyde as carbon sources and the diblock copolymer poly(styrene)-b-poly(4-vinylpyridine) (PS-b-P4VP) as a template (Liang, 2004). The
additional resorcinol and formaldehyde carbon source was needed because the direct pyrolysis of the self-assembled block copolymers alone did not result in ordered nanoporous carbon films due to the linearly structured block copolymers having very poor carbon yields during carbonization. Tanaka et al. used resorcinol/formaldehyde and triethyl-orthoacetate (EOA) as the carbon co-precursors and triblock copolymer F127 as a surfactant under highly acidic conditions to prepare mesoporous carbons with channel structure and reported similar results (Tanaka, 2005). TEOS was also added to decrease the polymerization rate of resorcinol and formaldehyde under strong acid conditions and enhance the interaction between the carbon precursors and the surfactant templates. In this case organic-organic interaction between a thermosetting polymer and a thermally decomposable surfactant formed periodic ordered carbon nanocomposites. Lee, J. and coworkers developed uniform sized mesoporous carbons with three-dimensional interconnected covalently bonded zeolite-like mesopores having various hierarchical structures synthesized by the carbonization of sol-gel polymerized silica, P123 triblock copolymer surfactant, and phenol resin as a structure directing agent, followed by silica removal (Lee, 2004). High surface area wormhole-like mesoporous carbons, meso-cellular carbon foams with bimodal pore structures, and nanofiber-type mesoporous carbons were the result of the these studies (Lee, 2004).

Organic-organic self-assembly has been applied to synthesizing organic nanostructures and carbon materials via carbonization. The carbonization of polymer blends composed of a carbon precursor polymer and a decomposable polymer which is pyrolyzed to generate pores, produced mesoporous carbon materials. Meng, Y. et al. reported the fabrication of highly ordered mesoporous polymers by solvent evaporation induced self-assembly (EISA), by using amphiphilic triblock copolymers (PEO-PPO-PEO) as structure directing templates, and a soluble
low molecular weight polymer of phenol and formaldehyde (resol) (Figure 1.13) as the carbon precursors followed by a thermopolymerization process (Meng, 2005).

![Chemical structure of resol](image)

Figure 1.13. A schematic representing the preparation of resol, a phenolic resin, from phenol and formaldehyde synthesized under alkaline conditions

The preferential evaporation of ethanol progressively enriches the concentration of the triblock copolymer and drives the organization of resol-copolymer composites into an ordered liquid crystalline mesophase. The hydroxyl groups within resol interact strongly with the triblock copolymers through the formation of hydrogen bonds. Phenol is cheaper and has fewer reactive sites than resorcinol, which was used in previous studies. The polymerization rate of resols is more easily controlled, and thus the assembly of phenolic resins and copolymer templates takes place more readily to form ordered mesostructures without macrophase separation (Tanaka, 2005).

The thermopolymerization at a low temperature range (80°C-120°C) of the triblock copolymer can yield a rigid zeolite-like hydrocarbon network with four-connected benzene rings through the formation of covalent bonds allowing the polymers to become stable enough to permit direct transformation to a carbon network by carbonization (Meng, 2005). The resulting ordered mesoporous carbon structures FDU-15 and FDU-16 hexagonal and cubic
mesostructures, respectively had frameworks with uniform pores (~3 nm) and large surface areas (up to 1150 m^2/g). In addition, the mesostructures can be readily tuned from 2D hexagonal (p6mm), to 3D caged cubic (Im 3m), and lamellar frameworks by simply adjusting the mass ratio of the polymer precursors and amphiphilic surfactant (Meng, 2005). The only drawback is that polymerization takes place within an extremely narrow pH of 8.5 (Meng, 2005; Zhang, 2005). Ozaki et al. synthesized mesoporous carbons with a pore diameter of 4 nm from the carbonization of a polymer blend composed of a phenolic resin, and poly(vinyl butyral), and carbon fibers from a polymer blend composed of phenol-formaldehyde (PF) embedded in a polyethylene (PE) matrix (Ozaki, 1997; Oya, 2000).

The overall procedure to synthesize mesoporous carbons using resols include the following major steps: resol precursor preparation, the formation of an ordered hybrid mesophase by organic-organic self-assembly with a surfactant template along with solvent evaporation, thermopolymerization of the resols around the template to solidify the ordered mesophase, template removal, and carbonization (Meng, 2006).

Liang, C. and Dai, S. provided a general and robust method to synthesize mesoporous carbon under a wide pH range of reaction conditions using phloroglucinol, instead of a phenol-resin, in the presence of commercially available triblock copolymers as structure directing agents (Liang, 2006). However, the resulting pores had a wormy structure (Liang, 2006). The wormy mesostructures can be assembled to more ordered hexagonal mesostructures through controlled solvent evaporation or shear force through spin coating or fiber extrusion before curing.

1.4.1. Details of How Phenol Works

Phenolic resins can be produced from a wide variety of phenols (e.g. phenol, cresol, xylenols, etc.) and aldehydes (e.g. formaldehyde, acetaldehyde, glyoxal, furfural, etc.), however
the most common is the simple resin produced by phenol and formaldehyde (Tennison, 1998). Resols with molecular weights in the range of 200-500 atomic mass units are suitable precursors for the synthesis of ordered mesostructures (Meng, 2006). Three reaction sequences occur during the polymerization process: formaldehyde addition to phenol, chain growth or pre-polymer formation, and finally the cross-linking or curing reaction (Tennison, 1998). Condensation polymerization of phenol and formaldehyde produces polymethylenephenol in a weak basic solution. The base catalyzed process results in phenolic resins with a 3-D network structure with benzene rings as three or four cross-linking sites (Knop, 1985). In an ideal network of phenolic resin, one benzene ring links via covalent bonds with three other benzene rings through an aliphatic or an ether bridge (Meng, 2006). The four-connected benzene rings exist in the framework of the mesoporous polymer products, evidenced by FT-IR, elemental analysis, and NMR results (Knop, 1985). The resols interact with the hydrophilic PEO blocks of P123 or F127 by hydrogen bond interactions, in which cooperative assembly results in a resol-block-copolymer mesophase in a dilute solution (Chu, 2000). Further polymerization of the resols, lead to the formation of the polymer framework of the mesostructure.

An advantage of using resols as a carbon precursor is that it is difficult to evaporate during the EISA process, which results in a constant resin composition with high yield. The final mesostructure depends on the ratio of phenol to surfactant template. A sequence of mesostructures from lamellar to bicontinuous cubic to hexagonal to then body-centered cubic is derived with increasing phenol/P123 or F127 ratio as the hydrophilic-hydrophobic balance grows (Meng, 2006).
1.4.2. Chemical Activation

Adsorbent materials with high surface areas have porosity created by various techniques including (1) templated methods, (2) physical or chemical activation methods that develop pores by selective etching or removal of adsorbent atoms or molecules, and (3) adsorbent formation by crystallization of framework structure that has intrinsic porosity by virtue of their open crystal lattice (Molina-Sabio, 2004). Activated carbons produced through physical or chemical activation processes are the most widely known high surface area porous carbons. Physical activation consist of a pyrolysis (or carbonization) step followed by a stage of controlled oxidation to activate the carbon in the presence of a physical activating agent such as steam, carbon dioxide, etc. (Molina-Sabio, 2004). Chemical activation involves the impregnation (soaking the precursor material within the activation reagent solution) of the carbon precursor (raw material) with a given chemical reagent for a given period (Molina-Sabio, 2004). Typically, activated carbons produced with chemical activation have higher specific surface areas and more mesopores than those synthesized by physical activation (Hu, 1995). In addition, chemical activation takes place at lower temperatures and shorter times than those used in physical activation (Hu, 1995). The three main chemical reagents commonly in use are zinc chloride (ZnCl₂), phosphoric acid (H₃PO₄), and potassium hydroxide (KOH) (Caturla, 1999). These chemical reagents may promote the formation of cross-linking, leading to the formation of a rigid matrix less prone to volatile loss and volume contraction upon heating to high temperatures (Molina-Sabio, 2004). Carbonization at high temperature in an inert gas followed by washing and drying completes the process to produce porous materials.

Previous work in which granular activated carbons were prepared by the chemical activation of peach stones by zinc chloride provided useful information about the development of
porosity. Small amounts of zinc chloride induced the development of porosity, initially micropores (Hu, 1995). At $X_{Zn} > 0.4$ (g of Zn/g of carbon precursor) more porosity is evident with a heterogeneous size distribution corresponding to the development of mesopores until $X_{Zn} = 1$, which is equivalent to an impregnation ratio of 2:1 weight of zinc chloride: weight of carbon precursor (Hu, 1995). The increase in porosity with $X_{Zn}$ suggests that the porosity created by the reactant is due to spaces left by zinc chloride after washing. Zinc chloride is a dehydration agent that promotes the formation of pores during carbonization (Hu, 1995). The activation reagent inhibits the contraction of the particles during the high temperature activation process and remains inside the material to act as a template for the creation of porosity (Hu, 1995). Dehydration is favored due to the chemical being a liquid at the temperature of the process, thus facilitating the bonding to the precursor being thermally degraded. Zinc chloride causes hydrogen and oxygen atoms in the source carbon materials to be stripped away as water rather than as hydrocarbons or as oxygenated organic compounds to form a carbon skeleton. As a result, the carbon yield is much higher than that from physical activation. Zinc chloride content almost remains constant for samples treated below 700°C, but decreases with increasing temperatures above 700°C, which is explained by the boiling point of ZnCl$_2$ being 732°C (Hu, 1995). Zinc chloride melts at temperatures higher than 283°C to form a mobile liquid, and at temperatures between 283-732°C decomposition takes place as shown in Equation 1.12 (Hu, 1995).

$$\text{ZnCl}_2 \cdot \text{H}_2\text{O} \rightarrow \text{Zn(OH)Cl} + \text{HCl} \quad (1.12)$$

However, temperatures higher than 732°C are favorable for ZnCl$_2$ evaporation (Hu, 1995). At temperatures above zinc chloride’s boiling point, an interaction between the zinc compounds and
carbon atoms occur, resulting in widening of the atomic layers of carbon and pores forming in the carbon matrix (Hu, 1995).

Potassium hydroxide is known to be more effective in microporosity development, and also results in carbons with high surface areas. KOH does not act like a dehydration agent on carbon precursors, but instead causes carbon gasification, due to redox reactions between carbon and the oxygen contained in the alkali (Tseng, 2005). For example the carbon is oxidized to CO or CO$_2$ (Tseng, 2005). KOH or any of its transformation products such as K$_2$CO$_3$ is reduced to metallic potassium (Tseng, 2005). This method has been considered an “etching” of carbon atoms which opens pores creating porosity (Tseng, 2005). At higher concentrations KOH only produces widening of the microporosity making more heterogeneous micropores, in comparison to ZnCl$_2$ which develops both wide micropores and small mesopores (Tseng, 2005). The oxygen of the alkali can remove cross-linking within the carbon framework. The potassium metals liberated once the reaction temperature is met may insert and force apart the carbon atoms (Tseng, 2005). Removal of potassium salts and carbon atoms from the internal volume of the carbon creates microporosity.

1.4.3. Additional Pore Sizes: Microporous, Macroporous, and Hierarchical Carbons

Modern science, engineering, and technology demand distinct pore structure and/or pore structures for specific applications. Most porous carbons are primarily microporous, and the microporous nature is well-suited to many applications involving small molecules such as molecular sieving, adsorption, and catalysis. However, there are numerous potential uses in which the presence of mesopores or even macropores would be preferable, for instance adsorption of large hydrophobic molecules such as vitamins and polymers, chromatographic separations, or electrochemical double layer capacitor applications. Therefore, the synthesis of
mesoporous and macroporous as well as microporous carbon materials is of great importance not only from a rudimentary research perspective, but also from a practical viewpoint. For applications in electrodes, catalysis, and photovoltaic cells, hierarchically porous carbons can provide better accessibility and chemical activities. The further development of new hierarchical materials that possess not only mesopores and macropores, but also micropores is of interest for new applications involving smaller molecules.

1.4.3.1. Microporous Carbon

Microporous carbons can be prepared by the pyrolysis of a wide assortment of materials; when ‘activated’ through mild oxidation with a gas or by chemical processing, carbons with enormously high internal surface areas are generated (Jankowska, 1991). Activated carbons can be produced from a variety of carbonaceous sources such as fossil fuels, agricultural wastes, sugars, and synthetic polymers like phenol and polyimide resins (Nishiyama, 2005; Lee, 2006). Recently, high surface area (3100 m²/g) and large pore volume (1.68 cm³/g) microporous carbons with pore size distribution in the range of 0.77–0.91 nm were obtained via carbonization and activation of waste-derived biomass (Cheng, 2008). Electrostatic organic-organic interactions have been the driving force for the formation of randomly ordered microporous carbons with a narrow pore size distribution estimated at 0.53 nm synthesized from the carbonization of surfactant thermosetting polymer composites (cationic surfactant–resorcinol/formaldehyde) (Nishiyama, 2005). To make microporous carbon materials not only with uniform pores, but also with ordered regular pore arrays, rigid inorganic templates are required. Zeolites, aluminosilicate materials, have been used as inorganic templates for the synthesis of microporous carbons with uniform pore sizes because the walls of zeolites have a uniform thickness of < 1 nm (Corma, 1997). The Kyotani group was able to successfully
synthesize uniformly sized and ordered microporous carbon materials with 3600 m$^2$/g surface area and 1.5 cm$^3$/g pore volume using zeolite Y as a template via a two-step carbonization method (Ma, 2000). In order to prevent the partial collapse of the carbon framework, the additional incorporation of carbon was added by a CVD process using propylene gas after the initial carbonization of the zeolite/furfuryl alcohol (FA) composite at 900°C (Ma, 2000). Apart from zeolites, activated carbons, and polymeric resins other materials such as clays and metal-organic frameworks (MOFs) have been explored as templates to produce microporous carbon materials.

1.4.3.2. Macroporous Carbons

Spherical submicrometer-sized particles such as polystyrene and silica can self-organize to form colloidal crystals, known as opals, which have been used as templates for the synthesis of three-dimensional macroporous carbon materials with core/shell and hollow structures (Xia, 2010). The pore size of the resulting macroporous carbon materials are easily controlled by varying the particle size of the silica spheres or polymer particles. Yu and co-workers reported the successful synthesis of 3D ordered uniform porous carbon with different morphologies and pore size in the range of 10–1000 nm using crystalline silica spheres with various particle sizes as templates via carbonization of phenol with formaldehyde (Chai, 2004). Recently, Antonietti and co-workers reported a soft-template-based method for the synthesis of carbon with meso- and macroporosity in a one-step process, taking advantage of the phase separation (spinodal decomposition) of the mesophase pitch, which acted as the carbon precursor, and the commercially available organic polymer polystyrene, which acted as a soft template (Adelhelm, 2007).
1.4.3.3. Hierarchically Ordered Porous Carbons

In the past few years hierarchically ordered porous carbons, especially those possessing well-defined macropores and interconnected meso- and/or micropores, have attracted much attention because they combine the excellent performance of mass transport from macropores and the advantages of high surface areas from micro-/mesopores (Chai, 2004). In this case hierarchical carbon features a local graphitic structure (Su, 2010). The macropores serve as ion buffering reservoirs, the mesoporous walls guarantee a smaller ion-transport resistance, while the micropores accommodate charges, and the localized graphitic structure enhances electrical conductivity (Su, 2010). This multi-hierarchical material demonstrated a super-capacitance of 180 F/g when compared to hard templated ordered mesoporous carbons (Su, 2010). Hierarchically ordered macro-/mesoporous carbons were synthesized via a facile dual-templating approach using colloidal silica crystals and Pluronic triblock copolymers PEO–PPO–PEO as templates and soluble resols as the carbon source (Xia, 2010). The obtained porous carbons have a highly ordered face centered cubic (fcc) macrostructure with tunable pore sizes of 230–430 nm and three-dimensional interconnected windows with sizes of 30–65 nm (Xia, 2010). Chai et al. developed a dual-templated method for the fabrication of macro-structurally patterned, highly ordered, three-dimensionally interconnected porous carbon with uniform mesoporous walls (Chai, 2004). They used both monodispersed polystyrene spheres and silica particles as templates and divinylbenzene as the carbon precursor. Both macroporosity and mesoporosity could be adjusted in the resulting carbon by controlling the sphere size of polystyrene and silica particles. 1.5. Mesoporous Carbon-Silica

Nanostructured organic-inorganic hybrid materials have been the subject of extensive research because they are able to combine in a single solid both the attractive properties of a
mechanically and thermally stable inorganic backbone, and the specific chemical reactivity and flexibility of organo-functional groups. Most of the properties of these new materials are dependent on their structural and chemical composition as well as the dynamic properties inside the hybrid. In addition, removal of the silica from the carbon silica composites results in mesoporous carbon that replicate the mesostructure of the silica template. Compared with the two-step synthesis of mesoporous carbon in which mesoporous carbon (an inverse replica of silica) is prepared by the infiltration of carbon precursors into mesoporous silica followed by carbonization and silica removal, carbon-silica composites provide a direct method to synthesize mesoporous carbons (Ryoo, 2001). Ordered mesoporous organic-silica nanocomposites have been achieved by surface functionalization, encapsulation of organic moieties in the channels of mesoporous silica materials, and direct synthesis of periodic mesoporous organosilicas (Scott, 2001).

Many types of organic-inorganic molecular composites or hybrid materials have been prepared by incorporating organic moieties and polymer chains, by physical entrapment, or by chemical bonding into inorganic sol-gel networks (Scott, 2001). Within the hybrid materials, the existence of primary bonding forces between the organic and inorganic components results in a reduced tendency of macroscopic phase separation caused by thermodynamic incompatibility of the components (Wei, 1998). Wei et al. synthesized several transparent and monolithic polymethacrylate-silica covalent hybrid materials, for example poly [methyl methacrylate-co-3-(trimethoxyxysilyl)propyl methacrylate]-silica (PMCM-SiO₂) and poly(2-hydroxyethyl methacrylate)-silica (PHEMA-SiO₂), using sol gel methods in which the bulk density and hardness of the materials were controlled by varying the organic-inorganic compositions between pure silica and polymers (Wei, 1998).
Functional groups were added to hybrid poly(vinyl alcohol) (PVA)-SiO$_2$ membranes by the oxidation of –SH group within mercaptopropylmethyldimethoxysilane (MPDMS) in the presence of H$_2$O$_2$ and lead to the formation of a homogenous type of cation-exchange membrane. The hybrid membranes prepared under acidic conditions in which linear polymeric clusters were formed had high ion exchange capacity, permselectivity, and conductivity values (Nagarale, 2004). Raspberry-like poly methyl methacrylate (PMMA)-silica hybrid microspheres on the order of 180-600 nm were prepared by Wu, L. et al. using a cationic monomer 2-(methacyroyl) ethyltrimethylammonium chloride (MTC) and 10-20 nm nano-silica particles (Chen, 2005). The nano-silica particles were adsorbed onto the surface of the organic particles via electrostatic interactions to form nanocomposite particles in which neither surface treatments nor surfactant or stabilizer was required (Chen, 2005).

Silica-carbon nanocomposites have been developed for solar absorber usage in which silica is used as a transparent binder and carbon nanoparticles are used as light-absorbing components (Mastai, 2002). In this case sugars were used as the carbon precursor, due to sugars being easily dehydrated by heating to form carbon. Worm-type, randomly disordered pores were formed using sugars and an additional route was used with phenol-formaldehyde resin as an alternate carbon precursor (Mastai, 2002). As compared to a bare mixture of carbon and silica, the nanocomposite has some advantages due to the nanostructure, such as low internal scattering, high mechanical performance, and optimized heat transfer between the carbon and silica sub-phase (Mastai, 2002).

Yang, Y. et al. reported the synthesis of a hybrid organic/inorganic self-assembly process in which polymerizable amphiphilic polydiacetylene (PDA) molecules serve as both structure directing agents and monomers (Yang, 2003). The PDA/silica composites with hexagonal, cubic,
or lamellar meso-scopic order exhibited unique thermal, mechanical, and solvatochromic properties (Yang, 2003). In contrast to the hydrolysis and condensation process when monomeric alkoxy silanes are used as a silica sources, silica-carbon hybrids were formed from the cross-linking of tetrasiloxane rings of oligosiloxane units generated by the rearrangement of siloxane linkage of the precursors during the reaction without the use of any structure directing agents (Shimojima, 2005).

The work by Bein and co-workers was considered a significant step toward the design of nanoscale electronic devices in which polyaniline was polymerized inside the mesoporous system of MCM-41, creating conjugated polymers with mobile charge carriers within nanometer-size domains (Wu, 1994). Later research by Moller et al. reported the polymerization of methyl methacrylate inside microporous and mesoporous silicas, and the resulting polymer had distinct physical properties in comparison to the bulk polymer (Moller, 1998). Tolbert and co-workers demonstrated that semiconducting polymers aligned inside mesopores exhibited unique energy transfer and photophysical properties. In all these cases, the polymers filled the entire volume of the silica mesopores, resulting in nonporous materials. Polymer-silica composite materials with uniform mesoporosity were obtained by free-radical polymerization, after vinyl monomers adsorbed as a thin layer on the pore walls of mesoporous silicas (Choi, 2005). The polymer layer exhibited enhanced catalytic activity and selectivity for esterification of benzyl alcohol compared with bulk polymer resins or polymers randomly filled inside the mesopores of silica (Choi, 2005). In addition, the polymer layer can also be functionalized to modify adsorption behavior toward proteins (Choi, 2005).

Bridgend silsesquioxane precursors, termed periodic mesoporous organosilicas (PMOs), where the bridging organic group is covalently bonded within the polysiloxane network were self
assembled into a mesoporous 2D-hexagonal framework with pore diameters of 2-3 nm and surface areas of 700-1200 m²/g (Hunks, 2004). Organic groups including methylene, ethane, ethylene, and benzene were incorporated into the inorganic solid pore walls within one step and the accessibility of the functional sites was improved (Hunks, 2004). Sayari and Wang reported an example of a PMO using a single precursor containing aromatic and olefinic functional groups with long range molecular order (Sayari, 2005). The carbon-carbon double bonds and phenylene groups allow for additional chemical transformations within the hybrids pore walls. Ordered mesoporous carbon/silica nanocomposites have been synthesized through the usage of phenyl-bridged organosilanes, which create pore walls with molecularly integrated carbon and silica (Pang, 2005). The carbonization of the mesoporous phenylene/silica/surfactant hybrid decomposes the surfactant and converts the phenylene moieties into carbon, resulting in mesoporous carbon/silica nanocomposites containing hydrophilic silica and hydrophobic carbon components in the pore walls (Pang, 2005).

Highly ordered mesoporous polymers and carbons synthesized by block copolymer self-assembly with resols used as an additional carbon precursor produced mesostructures with covalent-bonded polymer frameworks obtained from organic-organic assembly (Liang, 2004; Meng, 2005; Tanaka, 2005; Zhang, 2005; Liang, 2006). Serious skeleton shrinkage occurs during high temperature carbonization resulting in low surface areas, small pore sizes, and low pore volumes for mesoporous carbon products. The incorporation of a rigid constituent of silica in polymer-silica nanocomposites is an effective method to reduce framework shrinkage (Wei, 1996). Zhao et al. demonstrated a triconstituent co-assembly approach to prepare well ordered mesoporous polymer-silica and carbon-silica nanocomposites using resols as a polymer precursor, silicate oligomers as an inorganic precursor, and triblock copolymer F-127 as a
template (Figure 1.13) (Liu, 2006). The final nanocomposites have an interpenetrating framework with “reinforced-concrete” structure in which both “reinforcing-steel-bar” silicate and “concrete” polymer resins (carbons) can form mesostructured frameworks with nanoscaled phase separation. As previously discussed the silicate oligomer reacts with the hydroxyl group of the phenolic resins. However since Si-O-C bonds are unstable in comparison to Si-O-Si and C-C bonds formed during the polymerization process of resols and silicate oligomers; the silicates and carbons are two separated coexisting entities (Brinker, 1990). A weak bonding interaction occurs between the silicate surface and carbon components, but no Si-C bonds are formed within the nanocomposite (Liu, 2006). Continuous ethanol evaporation promotes co-assembly of the reactant species and drives the organization of surfactant-resols-silica composites into ordered liquid crystalline mesophases as illustrated in Figure 1.14. In addition to the primary uniform large pores, plenty of complementary small pores exist in the carbon-silica pore walls which can be simply adjusted by altering hydrolysis and condensation conditions of the silicates before the co-assembly.

Figure 1.14. A schematic displaying the co-assembly to ordered mesoporous polymer-silica and carbon-silica nanocomposites, and the resulting corresponding mesoporous silica and carbon frameworks (Liu, 2006)
From this approach ordered mesoporous carbons can be obtained with large pore sizes of ~6.7 nm, pore volumes of ~ 2.0 cm$^3$/g, and high surface areas of ~2470 m$^2$/g (Liu, 2006). The pore structure and textures are adjusted by varying the sizes and polymerization rates of the two carbon precursors, in addition by finely adjusting the aging time of TEOS ordered mesoporous carbons with bimodal pores can by synthesized.

Electrochemical energy conversion and storage are of paramount technological importance to provide a sustainable future in spite of the current energy crisis. Enhancing active materials in both fuel cells and supercapacitors with nanostructuring (decreased dimensions) and nano-architecturing (assembling nanometer scale building blocks) will lead to the development of high performance electrodes with long life cycles and stability. This chapter provided a detailed literature review of the history and development of mesoporous silica leading to the understanding of the various methodologies established on how to synthesize mesoporous materials, specifically carbon. Sol-gel processing with EISA will be utilized and discussed in future chapters to fabricate mesoporous hybrid carbon silica nanocomposites and hierarchically structured mesoporous and microporous carbon with both ordered and randomly disordered pore structure. The effects of porosity development due to the types of surfactant directing agents, carbon precursors, silica hydrolysis and condensation, and activation agents will be thoroughly examined in this research.
CHAPTER 2: METHOD OF APPROACH

The goal of this research is to synthesize tunable hierarchical mesoporous and microporous carbon-based nanocomposites for alternative energy conversion and storage systems. Incorporating ceramics into carbon at the molecular level allows for the formation of robust nanocomposites with enhanced corrosion resistance. In addition the carbon network provides adequate conductivity to normally non-conductive ceramic materials. Pore structure and composition of the materials were systematically studied to optimize conditions in order to achieve high surface area and varied pore sizes and pore volumes. Porogens through the means of chemical activation are being employed to tune pore structure (pore sizes and volumes) and provide enhanced pathways for mass transport efficiency.

Nanocomposite supports containing molecularly mixed carbon/ceramic frameworks with both ordered and randomly disordered pore channels have been designed and fabricated with enhanced porosity through the usage of zinc chloride as a porogen. Randomly disorder porous nanocomposites have been synthesized using a simple self-assembly process with a ceramic silicate species, tetraethyl orthosilicate (TEOS) and a carbon precursor, sucrose. Carbon-ceramic nanocomposites with ordered crystalline pore structures were constructed from a sol gel route using a surfactant directing agent (Pluronic F127 (PEO_{106}-PPO_{70}-PEO_{106})), an inorganic cluster (hydrolyzed TEOS), and an oligomeric assembling blocks (phenol with formaldehyde). Subsequent carbonization at high temperature produces both disordered and ordered mesoporous nanocomposites with controlled composition and pore structure. Conductivity enhancement was explored by incorporating multi-walled carbon nanotubes into both approaches. Electrospinning has also been examined as an additional fabrication technique to determine if carbon nanotubes can be better aligned within a fibrous carbon silica network.
Characterizations of these materials were administered using the following techniques: nitrogen sorption, scanning electron microscopy (SEM), transmission electron microscopy (TEM), x-ray diffraction (XRD), energy dispersive x-ray (EDX) analysis, and thermal gravitational analysis (TGA). SEM and TEM were used to analyze surface morphologies and internal pore structures, respectively. Brunauer, Emmett, and Teller (BET) analysis evaluate the nitrogen isotherms which results in surface area, pore size, and pore volume information. XRD is used to identify crystalline structure for the samples with ordered pores structure. Weight lost measurements from the combustion of carbon provided compositional information by TGA. The conductivity of the nanocomposites was determined by four-point probe measurements.

Large surface area carbon-based materials including both meso and micropores have been fabricated and undergone hydrogen storage testing and electrochemical testing. Electrochemical testing provides insight for improved corrosion resistance for fuel cell catalyst supports and enhanced capacitance measurements for supercapacitor electrodes. This is to determine if these materials have the potential to be further developed to provide performance advancement within renewable energy materials.
CHAPTER 3: MATERIAL PROPERTIES, ADD’L FABRICATION APPROACH AND CHARACTERIZATION TECHNIQUES

Sol-Gel chemistry and evaporation induced self-assembly have been used to synthesize both mesoporous and microporous carbon as well as mesoporous carbon-silica composites. Before discussing the details of the various synthetic approaches of each material that has been fabricated, it is important to have an understanding of the physical properties of carbon and silica, in particular the various bonding structures. Within the discussion about carbon, its various allotropes are also discussed and compared. The carbon materials synthesized in the various processes within this work (with the exception of carbon nanotubes) are amorphous. However, carbon nanotubes have been incorporated into some samples to improve conductivity within the sample, and thus a section has been dedicated to provide an overview exclusively to the properties of carbon nanotubes. Proceeding sections will include the core physical properties of all reactants used in this work; a complete description of an additional synthetic approach; electrospinning; the various characterization techniques; and electrochemical application based measurements used in this work.

3.1. Carbon Allotropes

Carbon is the element in the periodic table that provides the basis for life on Earth. It is also important for many technological applications, ranging from drugs to synthetic materials. This role is due to carbon's ability to bind itself to nearly all elements in limitless varieties. The resulting structural diversity of carbon based compounds and molecules are accompanied by a broad range of chemical and physical properties. Through extensive research, scientists attribute many intriguing properties to carbon substances, such as super strength, low weight, stability, flexibility, good heat conductance, large surface area, and a wide range of interesting electronic
properties. Carbon is found naturally in different forms (allotropes): graphite, diamonds, buckminsterfullerenes, nanotubes, and amorphous carbon (like coke and soot) (Johnson, 1989). Carbon has 6 electrons, 4 of which are in the outer shell. The s-orbital and p-orbitals of carbon's outer electronic shell have similar energies (Johnson, 1989). As a result, carbon can adapt to form chemical bonds with different geometries (Johnson, 1989).

![Image of bond structures of carbon allotropes]

Figure 3.1. The bond structure of 4 allotropes of carbon (a) diamond, (b) graphite, (c) amorphous, and (d) fullerene (Ströck, 2006)

3.1.1. Diamond

Diamond is the hardest material on earth. Diamonds are valuable because of their extraordinary physical and chemical properties such as hardness and light dispersion abilities (Barnard, 2000). Within diamond, one s-orbital and three p-orbitals undergo sp$^3$ hybridization to form a tetrahedral lattice, which is seen in Figure 3.1(a). A three-dimensional network of sigma bonds connect the carbon atoms in diamond (Selli, 2011). Since there are no delocalized pi bonds, the diamond structure has very poor electrical conductivity (Selli, 2011). The electrons within diamond are tightly held within the bonds between the carbon atoms. The electrons absorb light in the ultraviolet region but not in the visible region, so pure diamond appears clear to the human eye (Selli, 2011). Each carbon atom in diamond is surrounded by four nearest neighbors. They are connected together by covalent sigma bonds that separate them by a
distance of 1.5445 Å at angles of 109° (Emsley, 2002). The interlocking network of covalent bonds makes the diamond structure very rigid.

3.1.2. Graphite

The electrical conductivity and softness of graphite can be related to graphite's crystalline structure. Crystalline graphite consists of parallel sheets of carbon atoms, each sheet containing hexagonal arrays of carbon atoms. The bonds between the carbons within the layer are stronger than those in diamond with a bond length of 1.4210 Å at an angle of 120° (Pierson, 1993). Within graphite, one s-orbital and two p-orbitals undergo a sp² hybridization forming a trigonal planar lattice. Each carbon atom within graphite has three nearest neighbors in which one of the p-orbitals is left unaffected (Pierson, 1993). This last p-orbital overlaps in a sideways manner with those from neighboring carbon atoms to form the distributed π-bonds that reside above and below each graphite sheet separated by 3.35 Å (Pierson, 1993). This distributed π-bonding gives rise to delocalized electrons that makes graphite electrically conductive (Pierson, 1993). The interaction of the loosely held electrons in the π-bonds with light is responsible for its black color (Pierson, 1993). The softness and lubricating nature of graphite arises from carbon sheets bound by weak van der Waals forces. The layers within the graphite sheets can slide over each other easily, which account for graphite’s lubricating properties.

3.1.3. Amorphous Carbon

The term amorphous is used to classify carbon that does not have any crystalline structure ("Amorphous Carbon," 1997). As with all glassy materials some short-range order can be observed, but there is no long-range pattern of atomic positions ("Amorphous Carbon," 1997). While entirely amorphous carbon can be made, most of the material described as "amorphous"
actually contains crystallites of graphite or diamond with varying amounts of amorphous carbon holding them together, technically making them polycrystalline or nanocrystalline materials ("Amorphous Carbon," 1997). Amorphous carbon is obtained by heating any carbon-rich material to 650-980 °C in a limited amount of air so that complete combustion does not occur (Dannenberg, 1983). For example, coal is heated to give coke; natural gas or petroleum to give carbon black; wood to give charcoal; or bone to give char (Dannenberg, 1983). The amorphous forms of carbon, like other non-crystalline materials, do not have clear cut melting and boiling points (Dannenberg, 1983). Their densities vary depending on where they originate (Dannenberg, 1983).

3.1.4. Fullerenes

Carbon with sp² hybridization also form buckminsterfullerene (60 carbon atoms forming a sphere) also called buckyballs (Kroto, 1992). Fullerenes are similar in structure to graphite, which is composed of a sheet of linked hexagonal rings, but they contain pentagonal (or sometimes heptagonal) rings that prevent the sheet from being planar. The C60 molecules are arranged in a face-centered cubic unit cell, with the sides of this cubic cell measuring 14 Å and each C60 molecule having a 10 Å diameter (Kroto, 1992). The C60 molecule is the roundest molecule formed in nature. The molecules are held together in the crystal by weak van der Waals forces. They can trap other atoms within their framework, appear to be capable of withstanding great pressures, and have magnetic and superconductive properties (Kroto, 1992).

3.1.5. Physical Properties of Carbon Allotropes

Density is an intensive physical property that measures how efficiently a substance is spatially packed. This drastic change in density between the various forms of carbon is a consequence of the crystalline structure that each substance adopted (Johnson, 1989). The
Macroscopically measured density is usually slightly different than that measured using X-ray diffraction because of defects and/or impurities within the sample (Johnson, 1989). The hardness of a material measures how tightly the atoms are held together within it. This test is done either by scratching one substance with another or using Moh’s scale (Johnson, 1989). The electrical resistivity measures the ability of a substance to conduct electricity. The resistivity of the various carbon allotropes span that between semiconducting to insulating (Johnson, 1989). This behavior is a consequence of the bonding nature between the carbon atoms within the substance (Johnson, 1989). The melting point and boiling point are intensive physical properties that are measures of the strength and nature of the bonds that are formed within a substance. The heat capacity of a substance measures the ability of a substance to retain heat. The more loosely the components of a solid are held, the higher the substance's specific heat (Johnson, 1989). The thermal energy within a crystalline solid is conducted by electrons and/or discrete vibrational energy packets (phonons). A material’s ability to conduct heat is known as its thermal conductivity. The thermal conductivity of a substance gives a rough indication for how rigidly components within a crystalline solid are held together and how much imperfections are incorporated within a crystal (Johnson, 1989). Moving components within a substance tend to scatter the heat carrying electrons and phonons, effectively reducing the thermal conductivity of that material.
Table 3.1. A comparison of the physical properties of the four allotropes of carbon: amorphous, fullerene, graphite, and diamond (Dannenberg, 1983)

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>Amorphous</th>
<th>Fullerene</th>
<th>Graphite</th>
<th>Diamond</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>1.8 - 2.1</td>
<td>1.69</td>
<td>1.9 - 2.3</td>
<td>3.51</td>
</tr>
<tr>
<td>Refractive index</td>
<td></td>
<td></td>
<td></td>
<td>2.42</td>
</tr>
<tr>
<td>Resistivity (µΩ·cm)</td>
<td></td>
<td>1375</td>
<td></td>
<td>2.7 x 10⁹</td>
</tr>
<tr>
<td>Melting Point</td>
<td>3652 - 3697 (sublimes)</td>
<td>&gt; 800 (sublimes)</td>
<td>3652 - 3697 (sublimes)</td>
<td>3550</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>4200</td>
<td></td>
<td>4200</td>
<td>4827</td>
</tr>
<tr>
<td>Specific Heat (cal/gram K)</td>
<td>0.17</td>
<td></td>
<td>0.17</td>
<td>0.124</td>
</tr>
<tr>
<td>Hardness (Moh’s scale)</td>
<td>1 – 2</td>
<td>2 - 2.5</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>0.0159</td>
<td>0.4</td>
<td>19.6 parallel/ 0.0573 perpendicular to sheets</td>
<td>23.2</td>
</tr>
<tr>
<td>Space Group</td>
<td>Fm3m body-centered cubic</td>
<td>C6/mmc C-centered hexagonal</td>
<td>Fd3m face-centered cubic</td>
<td></td>
</tr>
<tr>
<td>Lattice Parameters (Å)</td>
<td>a = 14.14</td>
<td>a = 2.4612 c = 6.7079</td>
<td>a = 3.5670</td>
<td></td>
</tr>
<tr>
<td>Atoms/unit cell</td>
<td>240 (4 molecules)</td>
<td>4</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Cell Volume (cm³)</td>
<td>2.827 x 10⁻²¹</td>
<td>35.189 x 10⁻²⁴</td>
<td>45.385 x 10⁻²⁴</td>
<td></td>
</tr>
<tr>
<td>Bond length (Å)</td>
<td>10</td>
<td>1.415</td>
<td>1.5445</td>
<td></td>
</tr>
</tbody>
</table>

3.2. Carbon Nanotubes

Carbon nanotubes are structurally perfect materials, and this property gives rise to a whole host of unique properties, including a variety of electrical properties and high thermal conductivity. CNTs range from 1 to 12 nanometers in diameter (the diameter of 1 atom is approximately 0.1 nanometers) and are currently under intense investigation in the field of nanotechnology (Tomànek, 2000). Carbon nanotubes can be thought of as a one atom thick sheet of graphite (a hexagonal lattice of carbon) rolled into a cylinder (Pierson, 1993). Among the many physical properties of carbon nanotubes one key feature is the fact that the macromolecule is anisotropic, (directionally dependent) (Tomànek, 2000). This property is how carbon nanotubes are able to fulfill the needs of many different physical properties without being deficient in any one area (Tomànek, 2000). Functionalization of a CNT wall leads to serious
modification of the atomic structure. The functionalization may enhance the performance of carbon nanotubes in hydrogen storage, batteries, and supercapacitors (Bandaru, 2007).

The bonding in carbon nanotubes is sp² similar to graphite (Dresselhaus, 1996). The bonding structure is stronger than the sp³ bonds found in diamond resulting in CNTs having extremely high mechanical properties. Carbon nanotubes have a very broad range of electronic, thermal, and structural properties that change depending on the different kinds of nanotube (defined by its diameter, length, and chirality) (Dresselhaus, 1996). Carbon nanotubes can have a single cylindrical wall (SWNTs) or multiple walls (MWNTs) with cylinders inside the other cylinders separated by 0.34 nm as displayed in Figure 3.2 (a) (Dresselhaus, 1996). Each atom in a single layer has three nearest neighboring atoms and they are bonded by covalent bonds. Atoms on layers between MWNTs are not connected by covalent bonds and the only interaction between them is through van der Waals forces. When viewed with a transmission electron microscope these tubes appear as planes (Dresselhaus, 1996). Whereas single walled nanotubes appear as two planes, in multi walled nanotubes more than two planes are observed, and can be seen as a series of parallel lines (Dresselhaus, 1996).
Figure 3.2. Illustration of (a) single walled and multi walled carbon nanotubes and (b) the types of carbon nanotubes based on chirality (Bandaru, 2007)

The different types of CNTs are due to the fact that the graphitic sheets can be rolled in different ways and characterized by the diameter and chiral angle $\theta$, or by chirality of the tube. Chirality is defined by chiral vector, $\vec{c}_h$ (Brčić, 2009).

$$\vec{c}_h = m\vec{a}_1 + n\vec{a}_2$$ (3.1)

In the chirality equation $n$ and $m$ are integers, which represent the number of steps along the carbon bond of the hexagonal lattice. The chiral vector is in the direction along which the graphite sheet is rolled up to form a nanotube and it defines a carbon nanotube through three basic patterns: zig-zag with chiral angle $\theta = 0^\circ$, armchair with chiral angle $\theta = 30^\circ$, and chiral with chiral angle in the range of $0^\circ < \theta < 30^\circ$ (Figure 3.2(b)) (Brčić, 2009). It is possible to recognize the types based on following the pattern across the diameter of the tubes and analyzing their cross-sectional structure. Armchair and zig-zag have a high degree of symmetry and refer to the arrangement of hexagons around the circumference (Brčić, 2009). Chiral, the most common form indicates the structure can exist in two mirror-related forms (Brčić, 2009). The carbon
nanotube type has a great deal to do with determining the electronic properties of the carbon nanotube. The chirality or twist, determines whether the carbon nanotube is a metal, semimetal, or semiconductor. For a given \((n, m)\), if \((2n+m)\) is a multiple of 3, then the nanotube is metallic, otherwise the nanotube is a semiconductor (Brčić, 2009). Since the layers of MWNTs are structurally independent of one another, the chirality of the layers may be different.

Multi walled nanotubes can come in a complex array of forms because each concentric single walled nanotube can have different structures, leading to a variety of sequential arrangements (Harris, 1999). The simplest sequence is when concentric layers are identical but different in diameter (Harris, 1999). However, mixed variants are possible, consisting of two or more types of concentric CNTs arranged in different orders (Harris, 1999). These can have either regular layering or random layering (Harris, 1999).

The strength of the sp\(^2\) carbon-carbon bonds gives carbon nanotubes amazing mechanical properties (Harris, 1999). The stiffness of a material is measured in terms of its Young's modulus, the rate of change of stress with applied strain. The Young's modulus of the best nanotubes can be as high as 1000 GPa, which is approximately 5 times higher than steel (Harris, 1999). The tensile strength, or breaking strain of nanotubes can be up to 63 GPa, around 50 times higher than steel (Harris, 1999). The average diameter of a SWNT is 12Å (Dresselhaus, 1996). The carbon bond length of 1.42 Å was measured by Spires and Brown in 1996 and later confirmed by Wilder et al. in 1998 (Dresselhaus, 1996; Wilder, 1998). The C-C tight bonding overlap energy is on the order of 2.5 eV (Dresselhaus, 1996).

The best way to determine the conductivity mechanism of MWNTs and SWNTs is direct 4-point probe (or 2-probe) measurements on individual crystalline tubes limiting contact problems (Wilder, 1998). MWNT conductivity measurements demonstrated that each MWNT
exhibits unique conductivity properties that can lead to both metallic and semiconducting behavior (resistance at 300 K of $1.2 \times 10^{-4} - 5.1 \times 10^{-6}$ ohm cm; activation energies <300 meV for semiconducting tubes) (Wilder, 1998). These results were the first to suggest that the geometric differences (e.g., defects, chirality, diameter, etc.) and degree of crystallinity (hexagonal lattice perfection) of the tubular structures play a key role in the electronic response (Wilder, 1998). Bundles of SWNTs have been shown to behave as metals with resistance in the range $0.34 \times 10^{-4} - 1.0 \times 10^{-4}$ ohm-cm (Wilder, 1998).

Table 3.2. Comparisons of the various properties of single and multi-walled carbon nanotubes (Moisala, 2006)

<table>
<thead>
<tr>
<th>Properties</th>
<th>SWNTs</th>
<th>MWNTs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength (GPa)</td>
<td>23-63</td>
<td>23-63</td>
</tr>
<tr>
<td>Young’s Modulus (GPa)</td>
<td>640</td>
<td>1060</td>
</tr>
<tr>
<td>Elongation break at (%)</td>
<td>5.8</td>
<td></td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>0.8</td>
<td>1.8-2.0</td>
</tr>
<tr>
<td>Electrical Conductivity (S/m)</td>
<td>$10^2$-$10^6$</td>
<td>~$10^6$</td>
</tr>
<tr>
<td>Thermal Conductivity (W/m K)</td>
<td>6000</td>
<td>2000</td>
</tr>
<tr>
<td>Electron mobility (cm$^2$/V s)</td>
<td>~$10^5$</td>
<td>$10^4$-$10^5$</td>
</tr>
<tr>
<td>Typical diameter (nm)</td>
<td>1</td>
<td>10 – 30</td>
</tr>
<tr>
<td>Length (mm)</td>
<td></td>
<td>1 – 2</td>
</tr>
<tr>
<td>Surface area (m$^2$/g)</td>
<td>400</td>
<td>500</td>
</tr>
</tbody>
</table>
3.3. Silica

Silicon dioxide (SiO$_2$), also known as silica, is silicon's most common compound and the most abundant compound in the earth’s crust (Schweigert, 2002). It is interesting to note that the element Silicon (Si) is not found in its original form; it is always dependent on a second element for its existence. Silica commonly takes the form of ordinary sand, but also exists as quartz, rock crystal, amethyst, agate, flint, jasper, pyrogenic silica, and opal (Schweigert, 2002). Silicon dioxide is extensively used in the manufacture of glass and bricks, and as an insulator between semiconductor devices (Schweigert, 2002). Silica gel, a colloidal form of silicon dioxide, easily absorbs moisture and is used to sustain a state of dryness (O'Mara, 1990). The best-known form of silica is amorphous silicon dioxide in which the atoms are held apart at equilibrium spacing.
but with no long-range periodicity in its structure (Tan, 2003). Thermally grown and the as-deposited silicon dioxide are amorphous, the average length of a silicon oxide bond is 1.62 Å, and the distance between the oxygen ions is 2.27 Å (Tan, 2003).

Silica has a high melting point around 1700°C, in which values vary depending on the particular structure, (Schweigert, 2002). Very strong silicon-oxygen covalent bonds have to be broken throughout the structure before melting occurs. Silica does not conduct electricity because there are not any delocalized electrons. All the electrons are held tightly between the atoms, and are not free to move. Silica is insoluble in water and organic solvents (Schweigert, 2002). There are no possible attractions which could occur between solvent molecules and the silicon or oxygen atoms which could overcome the covalent bonds in the giant structure.
Table 3.4. Physical properties of amorphous Silicon Dioxide (SiO$_2$) at 300K (O’Mara, 1990)

<table>
<thead>
<tr>
<th>Properties</th>
<th>SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td>Amorphous</td>
</tr>
<tr>
<td>Melting Point (°C)</td>
<td>approx. 1710</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>2.2</td>
</tr>
<tr>
<td>Molecular density (cm$^3$)</td>
<td>2.3 x 10$^{22}$</td>
</tr>
<tr>
<td>Boiling Point (°C)</td>
<td>2300</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>1.46</td>
</tr>
<tr>
<td>Dielectric Constant</td>
<td>3.9</td>
</tr>
<tr>
<td>Dielectric Strength (V/cm)</td>
<td>10$^7$</td>
</tr>
<tr>
<td>Infrared Absorption Band (µm)</td>
<td>9.3</td>
</tr>
<tr>
<td>Energy Gap at 300K (eV)</td>
<td>9</td>
</tr>
<tr>
<td>Linear Coefficient of Thermal Expansion, $\Delta L/L/\Delta T$ (1/°C)</td>
<td>5 x 10$^{-7}$</td>
</tr>
<tr>
<td>Thermal Conductivity at 300 K (W/cm-K)</td>
<td>0.014</td>
</tr>
<tr>
<td>DC Resistivity at 25° C (Ω-cm)</td>
<td>$10^{14}$ - $10^{16}$</td>
</tr>
<tr>
<td>Etch Rate in Buffered HF (Å/min)</td>
<td>1000</td>
</tr>
</tbody>
</table>

SiO$_2$ occurs in no less than 13 different structural modifications (Holleman, 2001). With the exception of stishohovite, which is a rare form of SiO$_2$, the fundamental structural unit in all forms of SiO$_2$ is the same, a SiO$_4$ tetrahedron (Holleman, 2001). Silica bonds with oxygen in such a way that only single covalent bonds are formed with a 1:2 ratio between Si and O atoms (Holleman, 2001). Silica doesn’t react with water because of the difficulty of breaking up the giant covalent structure. In comparison to carbon, silica atoms are bigger leading to silicon-oxygen bonds being longer than carbon-oxygen bonds. The various forms of SiO$_2$ are obtained by linking the tetrahedra together in different ways (Holleman, 2001). The two forms that are the most common and the most studied are crystalline-quartz and amorphous SiO$_2$ (Holleman,
The Si-O bond is highly polar, with electrons being more attracted by the oxygen, leading to an uneven distribution of electrical charges in the tetrahedron: the corners are more negatively charged, the center is more positively charged (Holleman, 2001). In quartz the Si–O bond length is 1.61 Å and the Si–O–Si angle is 144.3° (Rösch, 2000). In amorphous SiO₂ these two parameters have random distributions, but their mean values are about the same as in quartz (Iler, 1979). In contrast, the tetrahedron remains almost perfect with only a very small deviation in the O–Si–O angle of 109.5° in quartz. In other silica modifications the 144° Si-O-Si angle is different, while the angles inside the SiO₄ tetrahedron (defined by the O-Si-O bond) remain basically the same (Rösch, 2000). Table 3.5 lists angles and distances for a few silica modifications (Rösch, 2000). Overall, in SiO₂, the Si–O–Si bond lengths vary from 1.55 to 1.65 Å while the bond angles vary from 136° to 180° and these changes are found to correlate to changes in the band gap energy from 8.4 to 11 eV (O'Mara, 1990).

Table 3.5. Examples in variations in silica structural modifications (Rösch, 2000)

<table>
<thead>
<tr>
<th>Modification</th>
<th>Si-O-Si Angle</th>
<th>Si-O Distance (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Quartz</td>
<td>144°</td>
<td>0.161</td>
</tr>
<tr>
<td>β-Quartz</td>
<td>153°</td>
<td>0.162</td>
</tr>
<tr>
<td>α-Cristobalite</td>
<td>147°</td>
<td>0.160</td>
</tr>
<tr>
<td>β-Cristobalite</td>
<td>151°</td>
<td>0.158-0.169</td>
</tr>
<tr>
<td>α-Tridymite</td>
<td>ca.140°</td>
<td>0.154-0.171</td>
</tr>
<tr>
<td>β-Tridymite</td>
<td>180°</td>
<td>0.153-0.155</td>
</tr>
</tbody>
</table>
Ceramic materials are typically hard and inert, and therefore are well known for their excellent mechanical and thermal properties, as well as superb resistance against corrosion and chemical erosion (Greenwood, 1984). These tributes make ceramic materials widely used in many applications, including the fabrication of electronic and photonic devices, sensors, electrodes, catalyst supports, and drug delivery components (Greenwood, 1984). Nanostructured ceramics are much more attractive to study than their bulk counterparts due to the size- and surface-dependent properties. Over the past several decades, a large number of approaches have been developed for processing ceramics into nanostructured materials, with notable examples based on sol–gel chemistry, pyrolysis, and hydrothermal treatment.

3.4. Reactants Used in This Work

In order to have a key understanding of the material synthesis in the future chapters it is important to evaluate key parameters such as each reactant’s molecular structure, melting point, boiling point, and solubility in water. Increased porosity has been achieved through use of zinc chloride and potassium hydroxide as chemical activation reagents. TEOS and the silsesquioxane
(3-aminopropyl) triethoxysilane have been used as silica sources. Carbon sources include sucrose, phenol-resol, carbon nanotubes, poly(acrylic) acid, and the highly aromatic 3,4,9,10-perylenetetracarboxylic dianhydride. The structure directing agent of choice used to synthesize the various ordered mesoporous materials is Pluronic F127.

Table 3.6. Properties of reactants: used throughout this work

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Zinc (II) Chloride</th>
<th>Sucrose</th>
<th>Tetraethyl orthosilicate</th>
<th>Sodium Hydroxide</th>
<th>Hydrochloric Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Formula</td>
<td>ZnCl₂</td>
<td>C₁₂H₂₂O₁₁</td>
<td>Si₄C₈H₂₀O₄</td>
<td>NaOH</td>
<td>HCl</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>136.315</td>
<td>342.30</td>
<td>208.33</td>
<td>40.00</td>
<td>36.46</td>
</tr>
<tr>
<td>Appearance</td>
<td>White solid</td>
<td>White solid</td>
<td>Colorless liquid</td>
<td>White crystals</td>
<td>Colorless liquid</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>2.907</td>
<td>1.587</td>
<td>0.94</td>
<td>2.13</td>
<td>1.19</td>
</tr>
<tr>
<td>Melting Point (°C)</td>
<td>292</td>
<td>189-191</td>
<td>-77</td>
<td>318</td>
<td>-62.25</td>
</tr>
<tr>
<td>Boiling Point (°C)</td>
<td>732</td>
<td>166-169</td>
<td>1388</td>
<td>50.5</td>
<td></td>
</tr>
<tr>
<td>Vapor Pressure (mm Hg)</td>
<td>1 at 428 °C</td>
<td>2 at 20 °C</td>
<td>1 at 739 °C</td>
<td>190 at 25 °C</td>
<td></td>
</tr>
<tr>
<td>Water solubility</td>
<td>Soluble</td>
<td>Soluble</td>
<td>Decomposes</td>
<td>Soluble</td>
<td>Soluble</td>
</tr>
</tbody>
</table>
Table 3.7. Properties of reactants: used throughout this work (continued)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Phenol</th>
<th>Formaldehyde</th>
<th>Pluronic F-127</th>
<th>Nitric Acid</th>
<th>Sulfuric Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Formula</td>
<td>C₆H₅O</td>
<td>CH₂O</td>
<td>PEO₁₀₆⁻·PPO₇₀⁻·PEO₁₀₆⁻</td>
<td>HNO₃</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>Molecular Weight (g/mol)</td>
<td>94.11</td>
<td>30.03</td>
<td>~12,600</td>
<td>63.01</td>
<td>98.08</td>
</tr>
<tr>
<td>Appearance</td>
<td>transparent solid</td>
<td>colorless liquid</td>
<td>white powder</td>
<td>colorless liquid</td>
<td>colorless liquid</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>1.07</td>
<td>1.11</td>
<td></td>
<td>1.51</td>
<td>1.84</td>
</tr>
<tr>
<td>Melting Point (°C)</td>
<td>40.5</td>
<td>-15</td>
<td>53-57</td>
<td>-42</td>
<td>-2</td>
</tr>
<tr>
<td>Boiling Point (°C)</td>
<td>181.7</td>
<td>98</td>
<td>121</td>
<td>327</td>
<td></td>
</tr>
<tr>
<td>Vapor Pressure (mm Hg)</td>
<td>0.35 at 20° C</td>
<td>33.2 at 20° C</td>
<td>2.78 at 20° C</td>
<td>0.3 at 20° C</td>
<td></td>
</tr>
<tr>
<td>Water solubility</td>
<td>Soluble</td>
<td>Soluble</td>
<td>Soluble</td>
<td>Soluble</td>
<td>Soluble</td>
</tr>
</tbody>
</table>
Table 3.8. Properties of reactants: used throughout this work (continued)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Potassium Hydroxide</th>
<th>3, 4, 9, 10-perylenetetracarboxylic dianhydride</th>
<th>3-aminopropyl triethoxysilane</th>
<th>Tetrahydrofuran</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Formula</td>
<td>KOH</td>
<td>C₂₄H₄₈O₆</td>
<td>C₉H₂₃NO₃Si</td>
<td>C₄H₈O</td>
</tr>
<tr>
<td>Molecular Weight (g/mol)</td>
<td>56.1056</td>
<td>392.32</td>
<td>221.37</td>
<td>72.11</td>
</tr>
<tr>
<td>Appearance</td>
<td>white solid</td>
<td>dark red powder</td>
<td>colorless liquid</td>
<td>colorless liquid</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>2.044</td>
<td>1.764</td>
<td>0.949</td>
<td>0.889</td>
</tr>
<tr>
<td>Melting Point (°C)</td>
<td>280</td>
<td>350</td>
<td>-70</td>
<td>-108.4</td>
</tr>
<tr>
<td>Boiling Point (°C)</td>
<td>1327</td>
<td>755.8</td>
<td>217</td>
<td>66</td>
</tr>
<tr>
<td>Vapor Pressure (mm Hg)</td>
<td>1 at 714 °C</td>
<td>&lt; 10 at 100° C</td>
<td>129 at 20° C</td>
<td></td>
</tr>
<tr>
<td>Water solubility</td>
<td>Soluble</td>
<td>Insoluble</td>
<td>Reacts w/ water</td>
<td>Solubility in water 30%</td>
</tr>
</tbody>
</table>
Table 3.9. Properties of solvents used throughout this work

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Ethanol</th>
<th>Water</th>
<th>Petroleum Ether</th>
<th>Acetone</th>
<th>Poly(acrylic acid)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>C₂H₆O</td>
<td>H₂O</td>
<td>C₃H₆O</td>
<td>(C₃H₄O₂)ₙ</td>
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</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>46.07</td>
<td>18.02</td>
<td>86.18</td>
<td>58.08</td>
<td>1.2</td>
</tr>
<tr>
<td>Appearance</td>
<td>colorless liquid</td>
<td>colorless liquid</td>
<td>colorless liquid</td>
<td>colorless liquid</td>
<td>colorless liquid</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>0.789</td>
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<td>0.64</td>
<td>0.791</td>
<td>1.2</td>
</tr>
<tr>
<td>Melting Point (°C)</td>
<td>-114</td>
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<td>-70</td>
<td>-95 - -93</td>
<td></td>
</tr>
<tr>
<td>Boiling Point (°C)</td>
<td>78</td>
<td>100</td>
<td>38-60</td>
<td>56-57</td>
<td>116</td>
</tr>
<tr>
<td>Vapor Pressure (mm Hg)</td>
<td>59.3 at 20°C</td>
<td>17.5 at 20°C</td>
<td>40 at 25°C</td>
<td>231 at 25 °C</td>
<td>18 at 20° C</td>
</tr>
<tr>
<td>Water solubility</td>
<td>Soluble</td>
<td>Insoluble</td>
<td>Soluble</td>
<td>Soluble</td>
<td>Soluble</td>
</tr>
</tbody>
</table>

3.5. Electrospinning

Electrospinning is an interesting process for producing non-woven fibers, and is considered a simple and effective technique for making polymer fibers, inorganic fibers, and composite fibers with average diameters ranging from micro to nanometers. Depending on the specific polymer being used, a wide range of fabric properties such as strength, porosity, surface functionality, etc. can be achieved. Scanning electron microscope (SEM) images are generally used to characterize electrospun nanofibers.

In this work, electrospinning was explored as an additional process to fabricate carbon silica composite materials with carbon nanotubes incorporated into its matrix. The properties of these materials as fibers are being explored.
Previous work with membranes has shown that the incorporation of CNTs will significantly improve the mechanical and electrical properties of the nano-fibrous materials (Kim, 2006). This may be a result of the high porosity within the membranes and the excellent wrapping of the polymers around the CNTs (Kim, 2006). A comparison of the electrical conductivity performance between ordered carbon-silica nanotubes composites to those fabricated into nanofibers via electrospinning will be studied in this work. In addition, the ability for carbon nanotubes to better disperse within the carbon silica network has been examined.

Electrospinning is a process in which high voltage is used to create an electrically charged jet of a polymer solution, or melt, which dries or solidifies to leave a polymer fiber (Fang, 1997; Kim, 1999). A metering pump attached to the plunger of a syringe generates a constant pressure and flow of the fluid through the pipette, resulting in the initiation of a droplet forming (Gupta, 2003). The pump is maintained at a constant and slow rate (typically, less than 1 ml/hr). The driving force is provided by a high voltage source which is typically in the range of 5-30 kV, and the setup can be ran on either positive or negative polarity (Ramakrishna, 2005). One electrode is placed into the spinning solution/melt or on its needle (< 100 µm in diameter) and the other separated some distance (5-30 cm) is attached to a collector of opposite polarity in order to establish a static electric field as seen in the illustration in Figure 3.4 (Gupta, 2003).

The electric field is administered to the end of a capillary tube that contains the polymer fluid held together by its surface tension (Doshi, 1995). A charge on the surface of the liquid is induced. Mutual charge repulsion causes a force opposite to the surface tension (Doshi, 1995). As the intensity of the electric field increases the hemispherical surface of the fluid at the tip of the capillary tube elongates to form a conical shape known as the Taylor cone (Taylor, 1969). With the increasing electric field, a critical value is attained when the repulsive electrostatic
force overcomes the surface tension and a charged jet of fluid is ejected from the tip of the Taylor cone. In electrospinning the cone angle is about 30°. For liquids with a finite conductivity, charged droplets are dispersed from the tip of the Taylor cone and are delivered to the target (Frenot, 2003). If the liquid consists of a polymer melt or of a polymer in solution, and the concentration of that polymer is sufficiently high to cause molecular chain entanglement, a fiber, rather than a droplet, is drawn from the tip of the Taylor cone (Frenot, 2003). Adjusting the flow of the fluid (polymer sample) and the magnitude of the electric field controls the spinning rate (Ramakrishna, 2005). The following parameters affect the process: (a) molecular weight, (b) molecular-weight distribution and architecture (branched, linear etc.) of the polymer, (c) solution properties (viscosity, conductivity, and surface tension), (d) electric potential, (e) flow rate and concentration, (f) distance between the capillary and collection screen, (g) ambient parameters (temperature, humidity, and air velocity in the chamber), and (h) motion of the target screen (Ramakrishna, 2005).

Figure 3.4. Illustration of an electrospinning apparatus (Wilkes; Gupta, 2003)
The discharged polymer solution jet undergoes a whipping process in which the solvent evaporates, leaving behind a charged polymer fiber that lays itself randomly on a grounded collecting metal surface (Shin, 2001). Splaying occurs when the radical forces from the electrical charges carried by the jet become larger than the cohesive forces within the jet, and the single jet divides into many charged jets (with approximately equal diameters and charge per unit length) before the fibers deposit on the collector (Ramakrishna, 2005). The splaying process of the primary jet into multiple filaments is thought to be responsible (together with the elongation due to the acceleration of the jet by electrical forces) for the unusually small diameter fibers which can be produced by electrospinning (Ramakrishna, 2005).

During electrospinning, instabilities are induced by coupling of the liquid strand with the electric field (through the field-induced transport of charges into the liquid strand), in particular, the axisymmetric instability and bending (or whipping) instability (Greiner, 2007). In the case of the charge-driven axisymmetric instability, a statistical variance of the jet's radius causes a modulation of the surface charge density (Greiner, 2007). In turn, this modulation generates tangential forces, which couples to the radius modulation and amplifies it (Greiner, 2007). The end result of such a coupling loop is the formation of beads, which are aligned along the fiber like pearls on a string (Greiner, 2007). By varying the spinning parameters, bead formation can be prevented. In the actual fiber formation bending instabilities develop (Greiner, 2007). Bending instabilities occur at high charge densities and fields, and they can typically be enhanced by increasing the electrical conductivity of the polymer solution, for example by the addition of additives (Greiner, 2007). The loop diameters increase with time during the motion towards the counter electrode (with velocities on the order of meters per second) (Matthews, 2002). During this process, the jet is highly stretched and reduced (Matthews, 2002). Along these
reduced fibers, bending occurs again and is followed by the formation of a new set of coils (Matthews, 2002). This procedure is repeated until the fibers solidify or become resistant towards these instabilities due to their extreme thinness.

It is possible to obtain carbon ceramic composite nanofibers by directly electrospinning a sol solution. However, the inappropriate rheological properties and the rapid hydrolysis rate of metal alkoxides make it very difficult to control the electrospinning process (Dai, 2011). To solve these problems, one has to introduce an additional polymer into the solution as a matrix to adjust the rheological properties (Dai, 2011). Hence, a typical spin-able precursor solution should contain an alkoxide, a carbon precursor such as resol, a typical surfactant directing agent, an addition polymer as an additive to increase viscosity, and a relatively volatile solvent such as ethanol (Dai, 2011). Poly(acrylic acid) (PAA) is a common polymer employed as a matrix due to its high solubility in ethanol or water and its good compatibility with many metal alkoxides.

Electrospinning is advantageous for many reasons, particularly since properties of the fibers can be designed in advance and controlled to a high degree. By choosing a suitable polymer and solvent system, nanofibers with diameters in the range of 20-2000 nm can be made with a large surface area per unit mass due to the high length to diameter ratio and small pore sizes (Frenot, 2003). Due to the inherent properties of the electrospinning process, which can control the deposition of polymer fibers onto a target substrate, nanofibers with complex and three-dimensional shapes can be formed (Frenot, 2003). Nanofibers also provide a connection between the nanoscale world and the macroscale world, since the diameters are in the nanometer range and the lengths are kilometers. As a consequence to solving the emerging energy crisis, increased attention has focused on applying electrospinning in the preparation of porous fiber mats as electronic components including materials for electrodes and separators in devices such
as batteries and supercapacitors (Miao, 2010). Electrospun fiber mats are capable of improving battery power, increasing energy density of capacitors, and enhancing fuel cell and solar cell efficiency (Miao, 2010).

3.6. Characterization Techniques

The textural and chemical characterization of the samples fabricated in this work was performed by various techniques. Gas adsorption measurements were employed to determine the surface area and pore-size distribution of the synthesized carbon-based nanoporous materials. Microscopy techniques were utilized to examine both surface morphology and internal pore structure. The chemical nature of the prepared materials was analyzed through analyzing sample mass loss and x-ray diffraction patterns.

3.6.1. BET Analysis

Nitrogen adsorption isotherms were obtained at 77K using a Micromeritics ASAP 2020 Surface Area and Pore Size Analyzer (Micromeritics Instrument Corporation, Norcross, GA). The procedure is based on the quantity of gas adsorbed by a porous material at constant temperature and at increasing levels of pressure (Sing, 1985). A curve is obtained (the isotherm of adsorption) which is correlated to the distribution of pore sizes within the solid (Sing, 1985). Many fluids can be used depending on the dimension of the pores to be measured.

Gas sorption (both adsorption and desorption) on the clean surface of porous nanocomposites is the most popular method for determining the surface area as well as the pore size distribution. During a gas sorption experiment, the material is initially heated at 200°C for 5 hours and degassed by vacuum force and inert gas purging to remove adsorbed foreign molecules. The sample material is next placed in a vacuum chamber at a constant and very low temperature, usually at the temperature of liquid nitrogen (77K/-195.6 °C), and subjected to a
wide range of pressures, to generate adsorption and desorption isotherms. Various amounts of
gas molecules will be adsorbed or desorbed at different doses of the gas (the adsorbate).
Knowing the area occupied by one adsorbate molecule, \( \sigma \) (for example, \( \sigma = 0.162 \text{ nm}^2 \) for
nitrogen), and using an adsorption model, the total surface area of the material can be determined
(Bruanuer, 1938). The most well known and widely used is the BET equation for multilayer
adsorption:

\[
\frac{P}{n(P_0-P)} = \frac{1}{cn_m} + \frac{c-1}{cn_m} \frac{P}{P_0}
\]  

(3.2)

In Equation 3.2, \( P \), \( P_0 \), \( c \), \( n \), \( n_m \) are the adsorption pressure, the saturation vapor pressure, a
constant related exponentially to enthalpy of adsorption in the first adsorbed layer, the amount
adsorbed (moles per gram of adsorbent) at the relative pressure \( P/P_0 \), and the monolayer capacity
(moles of molecules needed to make a monolayer coverage on the surface of one gram of
adsorbent), respectively (Bruanuer, 1938). Through the slope and intercept of a plot of \( P/[n(P_0-
P)] \) against \( (P/P_0) \), \( n_m \) can be resolved. The specific surface area, \( S \), can then be calculated with
\( N_A \), Avogadro’s number, and area occupied by one molecule, \( \sigma \) (Bruanuer, 1938):

\[
S = N_A n_m \sigma
\]

(3.3)

The specific surface area that can be determined by gas sorption ranges from 0.01 to over 3000
\( \text{m}^2/\text{g} \) (Sing, 1985). Specific surface areas \( (S_{\text{BET}}) \) were calculated by the BET method using the
adsorption branch in a relative pressure range from 0.04–0.25. Determination of pore size and
pore size distribution of porous materials can be made from the adsorption/desorption isotherm
using an assessment model, suitable for the shape and structure of the pores (Sing, 1985). The
range of pore sizes that can be measured using gas sorption is from a few angstroms up to about
half a micron.
The classical pore size model developed by Barrett, Joyner and Halenda (BJH), which is based on the Kelvin equation and corrected for multilayer adsorption, is most widely used for calculations of pore volume and pore size within the mesopores (Barrett, 1951). In the BJH procedure the Kelvin equation (Equation 3.4) is used to calculate the radius $R_K$ of the meniscus curvature of liquid present in the capillaries which are assumed to be cylindrical (Thomson, 1870; Thomson, 1871). The Kelvin equation predicts pressure at which adsorptive will spontaneously condense (and evaporate) in a cylindrical pore of a given size (Thomson, 1870; Thomson, 1871). The computation for the corresponding calculation starts from the high-pressure end of the isotherm and proceeds toward the point of closure of the hysteresis loop (Barrett, 1951).

\[
R_K = \frac{2\gamma \cdot V_M}{\ln \frac{P_0}{P} \cdot RT} \cos \theta
\]  

(3.4)

Within equation 3.4 $P$ is the equilibrium pressure, $P_0$ is the vapor pressure over a flat surface at the same temp, $\gamma$ is the liquid surface tension, $V_M$ is the molar volume of the condensed adsorptive, $\theta$ is the contact angle between the solid and condensed phase, $R$ is the gas constant, and $T$ is the temperature (Thomson, 1870; Thomson, 1871). When nitrogen is used as the sorption gas $V_M$ is equal to 34.68 cm$^3$/mol and $\gamma$ is equal to 8.77 x 10$^{-3}$ N/m, typically the contact angle is assumed to be zero, implying that the solid is perfectly wetted by adsorption. Condensation occurs in pores that already have some multilayers on the walls. The BJH model relates the size of the pores to the pressure at which capillary condensation occurs within the cylindrical pores at a layer thickness $t$ (Barrett, 1951). Therefore, the pore size is calculated from the Kelvin equation and the selected statistical thickness ($t$-curve) equation. The pore diameter is calculated using the kelvin radius, $R_K$, and the addition of the thickness of the adsorbed layer...
present on the wall of the pores for a given pressure (Equation 3.5) (Harkins, 1944; Harkins, 1944; Barrett, 1951).

\[
d_{\text{BJH}} = \frac{4Y \cdot V_M}{\ln P_a \cdot RT} + 2t
\]  

(3.5)

The total pore volume (Equation 3.6) is derived from the amount of vapor adsorbed at a relative temperature close to unity (assuming pores are filled with liquid adsorbate) (Barrett, 1951).

\[
V_{\text{pore}} = V_{\text{liq}} = \frac{P_a \cdot V_{\text{ads}} \cdot V_M}{RT}
\]  

(3.6)

Within Equation 3.6, \(V_{\text{ads}}\) is volume of gas adsorbed, \(V_{\text{liq}}\) is the volume of liquid \(N_2\) in pores, \(V_M\) is the molar volume of liquid adsorbate (\(N_2 = 34.7 \text{ cm}^3/\text{mol}\)), \(P_a\) is the ambient pressure, and \(T\) is the ambient temperature (Barrett, 1951). The porosity of each synthesized carbon-based material was calculated by multiplying the weight of each sample being analysed by the ratio of total pore volume to total geometrical volume of each sample. The later, total geometrical volume was calculated by multiplying the calculated surface area by the measured thickness of each sample which ranged from 0.35-0.50 nm based on the Harkins and Jura t-plot analysis (Harkins, 1944; Harkins, 1944).

The t-plot method is most commonly used to determine the external surface area and micropore volume of microporous materials. Multi-layer formation is modeled mathematically to calculate a layer “thickness, \(t\)” as a function of increasing relative pressure \((P/P_0)\) (Harkins, 1944; Harkins, 1944). The resulting t-curve is compared with the experimental isotherm in the form of a t-plot. That is, experimental volume adsorbed is plotted versus statistical thickness for each experimental \(P/P_0\) value. The linear range lies between monolayer and capillary condensation. The slope of the t-plot \((V/t)\) is equal to the “external area”, i.e. the area of those pores that are not micropores (Harkins, 1944; Harkins, 1944). Mesopores and macropores on the
outside surface are able to form a multilayer, whereas micropores, which have already been filled, cannot contribute further to the adsorption process. This equation approximates the adsorption in mesopores and macropores on a flat surface in a narrow pressure range just above complete filling of micropores, but below vapor condensation in mesopores (Harkins, 1944; Harkins, 1944). This assumption may be valid, if micropores are small and super-micropores are not present. It is recommended to initially select a \( P/P_0 \) range 0.2-0.5, and subsequently adjust it to find the best linear plot. The adsorption within this pressure region may be described by a simple linear dependence: 
\[
a(x) = a_{\text{micro, max}} + k S_{\text{ext}} \ t_{\text{layer}}(x) \quad \text{where} \quad x = P/P_0, \quad a_{\text{micro, max}} \text{ is the adsorption in saturated micropores,} \quad S_{\text{ext}} \text{ is the external surface area (pores larger than micropores),} \quad t_{\text{layer}}(x) \text{ is the estimated statistical thickness of adsorbed layer by Harkins-Jura (HJ) equations, and} \quad k \text{ is a coefficient equal to } 1/(4.3532 \ t_{\text{mono}}) \text{ (Harkins, 1944; Harkins, 1944). Within the } t\text{-plot calculated thickness values are within the range of 0.354 nm (i.e. } t_{\text{mono}} \text{ and 0.5 nm.}
\]

3.6.2. SEM

The JEOL-6700F FE-SEM (JEOL Ltd., Japan) was used for scanning electron microscopy to examine surface morphology. The SEM is an instrument that produces a largely magnified image by using electrons instead of light to form an image (Reimer, 1998). Data is collected over a selected area on the surface of the sample, and a two-dimensional image is generated that displays spatial variations in these properties (Reimer, 1998). Areas ranging from approximately 1 cm to 5 \( \mu \text{m} \) in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from approximately 20-30,000X and spatial resolution of 50 to 100 nm) (Reimer, 1998).

A beam of electrons is produced at the top of the microscope by an electron gun, which is shown in Figure 3.5 (a). The electron beam follows a vertical path through the microscope,
which is held within a vacuum. The beam travels through electromagnetic fields and lenses, which focus the beam towards the sample. Once the beam hits the sample, electrons and x-rays are ejected from the sample Figure 3.5(b). Detectors collect these x-rays, backscattered electrons, and secondary electrons and convert them into a signal that is sent to a screen similar to a television screen, producing the final image. The signals that derive from electron-sample interaction reveal information about the sample including external morphology (texture), chemical composition, crystalline structure, and orientation of materials making up the sample (Goldstein, 2003). The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in semi-quantitatively determining chemical compositions, using energy dispersive x-ray spectroscopy (EDS) (Goldstein, 2003).

Figure 3.5 Illustrations of (a) how an SEM operates and (b) the electrons and x-rays emitted from an SEM sample (Klesel)
3.6.3. TEM

Transmission electron microscopy (TEM) provides information on internal structures in thin-sections, ranging from 70-100 nm. TEM experiments were conducted on a Philips CM120 operated at 120 kV (Philips/FEI Inc., Eindhoven, The Netherlands). The TEM samples were suspended in ethanol and supported on a copper grid. The TEM collects the electrons that are transmitted through specimens. The TEM can also facilitate the analysis of features at the atomic scale (in the range of a few nanometers) using electron beam energies in the range of 60 to 350 keV (Fultz, 2008). Visual representation of pore size and pore distribution can be viewed with TEM images. This is due to the TEM’s ability to capture cellular and sub-cellular structures which can be viewed in great detail (Fultz, 2008).

The TEM provides a means to go beyond the magnification and resolution limits of light microscopes, allowing for magnification of up to 100,000x and resolutions in the nanometer range. A beam of electrons are focused on a single pinpoint spot or element on the sample being studied (Egerton, 2005). The electrons interact with the sample and only those that go past unobstructed hit the phosphor screen on the other side as seen in Figure 3.6 (Egerton, 2005). At this point, the electrons are converted to light and an image is formed.
The dark areas of the image correspond to areas on the specimen where fewer electrons were able to pass through (either absorbed or scattered upon impact). The lighter areas are regions where more electrons pass through, although the varying amounts of electrons in these areas enable the user to see structures and gradients. For crystalline materials, the specimen diffracts the incident electron beam, producing local diffraction intensity variations that can be translated into contrast to form an image (Egerton, 2005). In the case of amorphous materials, contrast is achieved by variations in electron scattering as the electrons traverse the chemical and physical differences within the specimen (Egerton, 2005).

3.6.4. XRD

Powder X-ray diffraction (XRD) patterns were obtained using a PANalytical X’Pert Pro X-ray diffractometer. Cu Kα radiation with $\lambda = 1.5418$ Å was utilized and the copper anode was operated at 40 kV and 30 mA. XRD is a rapid analytical technique primarily used for phase
identification of a crystalline material and can provide information on unit cell dimensions. The information obtained includes types and nature of crystalline phases present, structural makeup of phases, degree of crystallinity, amount of amorphous content, and size and orientation of crystallites.

X-ray diffractometers consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector (Cullity, 1978). X-rays are electromagnetic radiations of wavelength between about 0.02Å and 100Å; note 1 Å is about the same size as an atom. X-rays are generated by a process in a cathode ray tube by applying a current to heat a filament which produces electrons (Cullity, 1978). The electrons are then accelerated towards a copper target by applying a high voltage (15-60kV), followed by the electrons being bombarded on the copper target (Cullity, 1978). When electrons have sufficient energy to dislodge the inner shell electrons of the copper target, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being Kα and Kβ (Warren, 1969). Kα consists, in part, of Kα1 and Kα2. Kα1 has a slightly shorter wavelength and twice the intensity as Kα2 (Warren, 1969). Filtering, by foils or crystal monochromators, is required to produce monochromatic X-rays needed for diffraction. Kα1 and Kα2 are sufficiently close in wavelength such that a weighted average of the two is used (Warren, 1969). These X-rays are collimated and directed onto the sample, which has been ground to a fine powder (typically to produce particle sizes of less than 10 microns).

The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle θ while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of 2θ (Als-Nielsen, 2001). The instrument used to maintain the angle and rotate the sample is termed a goniometer (Als-Nielsen, 2001). As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. The scattering
of x-rays will occur on multiple planes with identical atomic arrangements with a spacing value designated as d, which is illustrated in Figure 3.7(a) (Als-Nielsen, 2001). When a focused X-ray beam interacts with the planes of the atoms, part of the beam is transmitted, part is absorbed by the sample, part is refracted and scattered, and part is diffracted as seen in the schematic of Figure 3.7(b) (Als-Nielsen, 2001). When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and a peak of intensity occurs (Bragg, 1913).

![Figure 3.7](image)

Figure 3.7. Schematics showing (a) the reflection of X-rays from two planes of atoms within a solid and (b) the X-ray beam path as it interact with a sample.

The condition for constructive interference in which the path difference between two waves:

(Bragg, 1913)

\[ 2\lambda = 2d \sin \theta \]  \hspace{1cm} (3.7)

For constructive interference between these waves, the path difference must be an integral number of wavelengths: (Bragg, 1913)

\[ n\lambda = 2\lambda \]  \hspace{1cm} (3.8)
These results leads to Bragg’s equation: (Bragg, 1913)

$$n\lambda = 2d \sin \theta$$  (3.9)

The variables in Bragg’s equation include: $\theta$ which is the angle of incidence of the x-ray, $n$ is the order of interference, and $\lambda$ is the wavelength of the incident radiation (Bragg, 1913). The Bragg law requires that $\theta$ and $\lambda$ be matched for diffraction (Bragg, 1913). The condition may be satisfied by varying, $\lambda$, or varying the orientation of a single crystal. Diffraction occurs from crystallites which are oriented at the angle to satisfy the Bragg condition (Bragg, 1913).

A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a computer (Pecharsky, 2009). The peaks collected within a spectrum represent the positions where the X-ray beam has been diffracted by the crystal lattice. The set of d-spacings, the distance between adjacent planes of atoms, represent the unique "fingerprint" of the polycrystalline material which can be easily calculated from the 2$\theta$ values (Pecharsky, 2009). X-rays are diffracted by each atom differently, depending on what atoms make up the crystal lattice and how these atoms are arranged (Pecharsky, 2009). The unit cell parameters were calculated from the formula: $a_0 = 2d/\sqrt{3}$. XRD will be used to verify if the various fabricated nanomaterials discussed in future sections having crystalline features.

3.6.5. TGA

Thermogravimetric analysis was conducted on a Perkins-Elmer Pyris 6 TG Analyzer. In this technique the change in sample weight (mass) is measured while the sample is heated at a constant rate (or at constant temperature) using a thermobalance (micro balance) within a controlled atmosphere under air (oxidative) or nitrogen (inert) (Sibilia, 1988). This characterization method is effective for quantitative analysis of thermal reactions that are accompanied by mass changes. The analysis provides a measure of the reaction kinetics.
associated with structural decomposition, evaporation, oxidation, corrosion, moisture adsorption/desorption, dehydration, combustion, and gas evolution which involve mass loss (or mass gain) (Sibilia, 1988). A simplified diagram for the instrumentation is illustrated in Figure 3.8.

![Simplified diagram of TGA instrumentation](image)

**Figure 3.8.** A simplified diagram illustrating the key components within a TGA (Sibilia, 1988).

The micro-balance plays a significant role. During sample measurement the change in sample mass affects the equilibrium of the balance (Duncan, 2006). This imbalance is fed back to a force coil, which generates additional electromagnetic force to recover equilibrium (Duncan, 2006). The amount of additional electromagnetic force is proportional to the mass change.

The system allows for the sample to be simultaneously weighed and programmed to be heated or cooled, and the mass, time, and temperature data to be recorded and processed. In TGA, mass loss is observed if a thermal event involves loss of a volatile component (Sibilia, 1988). Thermogravimetric analysis has been used extensively to determine the thermal stability of materials at temperatures up to 1500°C (Sibilia, 1988). Samples in this study were heated from 25-1000°C under nitrogen at 5°C/min to measure weight changes of the product. The
composition of various nanocomposite materials with carbon and silica content will be
determined based on carbon weight loss.

3.6.6. Four Point Probe: Conductivity Analysis

Electrical resistivity is a key physical property of all materials. The electrical resistivity of a material is a number describing how much that material resists the flow of electricity. Electrical resistivity is measured in units of ohm-meters (Ω-m) and is represented by the Greek letter ρ. For example, the electrical wires in overhead power lines and buildings are made of copper or aluminum because these materials have very low resistivities (about 20 nΩ-m), as opposed to material like some types of plastic (which can have resistivities of about $1 \times 10^{18}$ Ω-m) (Hummel, 2001). Electrical conductivity is represented by the Greek letter σ, and is defined as the inverse of the resistivity.

The four point probe is a device for measuring resistivity, especially surface resistivity (ohms-cm$^2$). Within the four point probe arrangement the two outer probes are for the source current, while the two inner probes sense the resulting voltage drop across the sample (Smits, 1958). The four probes rest on the medium with a certain preset pressure in order to obtain the values from which the surface or bulk resistivity is calculated (Smits, 1958). Thin samples are best for four point probe calculations as the simplified equations assume the sample thickness is smaller than the probe spacing, (for example 1.5 mm) (Schuetze, 2004). Each specimen is sampled multiple times in order to average out any bias (Schuetze, 2004). The contact resistance between the probes and the sample could be observed from the I-V plots and is not significant (Schroder, 1990). Prior to making the resistance measurements, samples are annealed in high temperature furnaces in order to increase the particle-particle contact (Schroder, 1990).
Figure 3.9. An illustration of the four-point probe measurement used to calculate resistivity to determine electrical conductivity (Do, 2010).

The volume resistivity was measured by compressing the substrate powder at high pressure (1000-5000 psi) between two copper electrodes (Do, 2010). A known electrical current ($i$) was passed through the substrate and the voltage ($V$) was measured between two fixed points at a pre-determined distance along the compressed sample (Do, 2010). The resulting voltage was used to calculate the substrate resistivity, $\rho$, (Equation 3.10) in $\Omega$-cm, where area is the cross-sectional area of the sample and $L$ is the distance in between the two inside leads of the four-point probe (Do, 2010).

$$\rho \text{ [ } \Omega \text{-cm]} = \frac{V \text{ [volts]}}{i \text{ [amperes]}} \times \frac{\text{Area}[\text{cm}^2]}{L[\text{cm}]} \hspace{1cm} (3.10)$$

The relation between composition, pore structure, and conductivity will be explored by four-point probe. Ideally, it is expected that samples with higher carbon content and well-connected porosities are projected to have higher conductivity values.

3.6.7. Fabrication of Electrode and Electrochemical Measurements for Capacitance

Microporous carbon and carbon based materials with MWCNTs incorporated in the carbon network have been assembled into electrodes to evaluate capacitance performance. Electrodes were obtained by coating an active mass of approximately 1–3 mg onto each current collector (0.5 $\times$ 0.5 cm). The as-synthesized carbon based nanomaterials, and commercially
available activated carbons were assembled together to form electrodes. Electrodes have been prepared by synthesizing slurries consisting of active materials, carbon black (as a conductive agent), and a binder followed by coating on nickel foam. 80% of the active material (synthesized carbon based materials), 10% carbon black, and 10% poly(vinylidene fluoride) (PVDF), were all dispersed in N-methylpyrrolidinone (NMP), followed by sonication and mechanical stirring to form homogenous slurries. The homogenous slurries were coated onto nickel-foam substrates and dried at 80 °C for 10 min under vacuum. Next the samples were pressed at a pressure of 2 MPa and further dried under vacuum at 100 °C for an additional 12 hours. Solvent evaporation and pressing produced dry electrodes.

The classic electrochemical measurements, including cyclic voltammetry (CV) and galvanostatic charge-discharge have been conducted. Platinum foil and an Ag/AgCl electrode have been used as the counter electrode and the reference electrode, respectively. The electrochemical measurements were conducted using a Solartron 1860/1287 Electrochemical Interface (Solartron Analytical, Oak Ridge, TN) apparatus. The electrolyte solutions used were aqueous 1M sulfuric acid (H₂SO₄) and organic 1M tetraethylammonium tetrafluoroborate (NEt₄BF₄) in propylene carbonate (PC) solution and CV measurements were carried using cut-off voltages of –1.5 and 1.2 V versus Ag.

The capacitance, power, and energy density were calculated based on the total mass or volume of both the anode and cathode materials. Energy density is calculated using the previously reported Equation 1.7

\[ E = \frac{1}{2} CV^2 \]  

where \( C \) is the capacitance and \( V \) is the cell-operation potential. The maximum power density was calculated using a version of Equation 1.8 modified for mass
\[ P_{\text{max}} = \frac{V^2}{4RM} \]  \hspace{1cm} (3.11)

where \( R \) is the equivalent series resistance (ESR) and \( M \) is the total mass of anode and cathode materials. The discharge curve of galvanostatic cycles were used to calculate the specific capacitance \( C_s \) (F/g).

\[ C_s = \frac{I}{dV/dt} \approx \frac{I}{\Delta V/\Delta t} \]  \hspace{1cm} (3.12)

In Equation 3.12, \( I \) is the constant discharge current density, \( \Delta V \) is the voltage difference in the discharge cycle, and the slope of the discharge curve (scan rate) is represented by \( dV/dt \).

3.6.8. Durability Testing Via Rotating Disc Electrode

3.6.8.1. Overview/Description

Materials have been fabricated to examine the effects of ceramic/carbon composition and pore structure to corrosion based on resistance to oxidative consumption of the carbon phase. Since testing catalyst support materials contained within the membrane electrode assembly in fuel cells is quite intricate and time-consuming, a straightforward alternative was developed on the basis of hydrodynamic rotating electrodes (Gloaguen, 1994; Schmidt, 2003). Methods utilizing hydrodynamic electrodes have been used to clarify and understand the kinetics of the electrochemical reaction mechanism of the catalyst support material at the electrode (cathode and/or anode) surface.

The advantages of hydrodynamic methods include high precision measurements and quickly attainable steady-state diffusion (Albery, 1971). In studying electrochemical reactions it is essential to separate the electrochemical processes occurring on the electrode surface from those processes that affect the transport of the reactants and the reaction products (Bard, 2000). The key point is to understand the combined effects of mass transport (how fast oxygen travels to
the electrode) and fundamental kinetics (how fast the oxygen reduces once it reaches the electrode). Electrochemical measurements in agitated solutions allow a quantitative description of the mass transfer stage and permit correction for it during analysis of the kinetics of the heterogeneous conversion reaction (Bard, 2000).

Among the hydrodynamic electrode methods, the most convenient and widely-used systems are the rotating disc electrode (RDE) and rotating ring disc electrode (RRDE) techniques. The thin-film rotating disc methods have proven to be a very effective means for studying high surface area catalysts with relatively little effort (Schmidt, 1998; Schmidt, 2003). Both the RDE and RRED techniques have been widely used to explain in detail the oxygen reduction mechanism at the catalyst, evaluate the stability of the catalyst, and to find out the optimum operating conditions (Wang, 2006). The major advantage of the RDE technique is that the construction of the electrochemical cell is rather simple irrespective of the electrode materials. The RDE just consists of a disc of the electrode material imbedded in a rod of an insulating material, for example platinum embedded in a Teflon shield which is rotated in solution at a constant angular velocity (Fried, 1965). A schematic representation of the commonly-used form of the RDE is given in Figure 3.10 (a) (Albery, 1971).

Convection occurs near the disc surface. In addition there is a thin layer rotating along with the disc electrode, the convection velocity of solution from the disk surface to distance Z is distributed as shown in Figure 3.10 (b) (Mayrhofer, 2008). A glassy carbon rotating disc electrode coated with a thin layer of a supported catalyst may be used to reduce dissolved oxygen in an electrolyte solution (Paulus, 2001; Schmidt, 2001; Paulus, 2002; Gasteiger, 2005). The most popular way to immobilize a supported electrocatalyst is by using Nafion® as the “glue” which sticks the carbon supported catalyst particles to the glassy carbon disc (Schmidt, 1998;
Schmidt, 2003). By gradually increasing the rotation rate of the RDE, the rate of mass transport of the dissolved oxygen to the electrode surface increases. Initially, the reduction current at the disk electrode is governed by this mass transport (the rate at which oxygen is arriving at the electrode) (Bard, 2000). As the rotation rate increases, the current increases as the amount of oxygen arriving at the electrode surface increases. Eventually, at a high enough rotation, the rate at which oxygen arrives at the electrode surface approaches the rate at which the supported electrocatalyst reduces the oxygen (Bard, 2000). At this point, the current signal measured at the disc electrode begins to be governed by the kinetic properties of the catalyst (Bard, 2000). It is at these higher rotation rates that the measured disk current begins to yield kinetic information (Paulus, 2001; Schmidt, 2003).
3.6.8.2. Theoretical Derivation of Governing Equations for the RDE Technique

The RDE system is a valuable experimental tool because it evaluates the effects of convection (the transport of the reactants in the solution due to the solvent's flow) and diffusion (the transport of the reactants in the solution due to the non-uniform concentration of the reactants as these are used) on chemical reactions (Fried, 1965). The RDE is a convective electrode system for which the convective-diffusion equation has been rigorously solved at the
steady-state condition with laminar flow. The mathematical application of voltammetry is determined by first examining the flux of species A:

$$J_A \left[ \frac{\text{mol}}{\text{cm}^2 \cdot \text{s}} \right] = -D_A \nabla C_A - \frac{nF}{RT} D_A C_A \nabla \Phi + \vec{v} C_A$$  \hspace{1cm} (3.13)$$

where $D_A \ [\text{cm}^2/\text{s}]$ is the diffusivity of species A, $C_A \ [\text{mol/cm}^3]$ the concentration of species A, $n$ is the number of electrons per molecule of electro-active species involved in the electrode reaction, $\Phi \ [\text{V}]$ the potential, $F$ faraday’s constant, $T$ the absolute temperature, $R$ gas constant, and $\vec{v} \ [\text{cm/s}]$ represents the velocity of a volume element. The first term on the right-hand side of the flux equation represents diffusion, the second term represents migration, and the last term represents convection (Schmidt, 2003). For solutions containing an excess of supporting electrolyte, the ionic migration term can be neglected (Schmidt, 2003). The velocity vector $\vec{v}$ which represents the motion of the solution is analyzed in cylindrical coordinates due to the symmetry of the system. The concentration with respect to time is provided by the equation below:

$$\frac{\partial C_A}{\partial t} = -\nabla J_A$$ \hspace{1cm} (3.14)$$

Assuming that migration is absent and that $D_A$ is not a function of $r$, $z$, $\theta$, and concentration, the general convective-diffusion equation can be determined by combining the Equations 3.13 and 3.14:

$$\frac{\partial C_A}{\partial t} = D_A \nabla^2 C_A - \vec{v} \nabla C_A$$ \hspace{1cm} (3.15)$$

Assuming one-dimensional diffusion and convection for the Laplacian operator $\nabla^2$, Equation 3.15 simplifies to the 1-D convection-diffusion equation:

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial z^2} - \nu_z \frac{\partial C_A}{\partial z}$$ \hspace{1cm} (3.16)$$
3.6.8.2.1. Obtaining the Velocity Profile

Before solving the convective-diffusion equation for the concentration profiles \( C_A(r, z, \theta) \) and subsequently for the currents from the concentration gradients at the electrode surface, the expression for the velocity profile \( \vec{v} \) should be obtained in terms of \( r, z, \theta \), and the rotation rate \( \omega \) [rad/s] (Schmidt, 2003). For an incompressible fluid, \( \vec{v}(r, z, \theta) \), is obtained by the solution of the continuity equation and Navier–Stokes equation with the appropriate boundary conditions. The incompressible continuity equation is given by

\[
\nabla \cdot \vec{v} = 0 \tag{3.17}
\]

and the Navier–Stokes equation per unit volume for a fluid is given by:

\[
\rho \frac{d\vec{v}}{dt} = -\nabla p + \mu \nabla^2 \vec{v} + f \tag{3.18}
\]

Within Equation 3.18 \( \rho \) [g/cm\(^3\)] is the density of solution, \( p \) [atm] pressure, \( \mu \) [(g/cm s) \equiv \text{poise}] the viscosity of solution, and \( f \) [N/cm\(^3\)] denotes the force per unit volume element of the fluid by gravity. In this case, the term on the right hand side is used to represent frictional forces (drags) (Schmidt, 2003). In electrochemical problems only the steady state velocity profile is of interest, therefore \( \frac{d\vec{v}}{dt} = 0 \).

The value of \( \vec{v}(r, z, \theta) \) of a fluid near a rotating disc can be obtained by solving the hydrodynamic equations under the steady-state conditions. Qualitatively, the fluid at the surface of the spinning disc is dragged along with the disc, and the solution is propelled outwards from the center in a radial direction due to centrifugal force (Bard, 2000). The act of rotation drags material to the electrode surface where it can react. The fluid at the disc surface is replenished by a flow normal to the surface (Bard, 2000). Assuming that the gravitational effects are absent, and that there are no special flow effects at the edge of the disc, the velocity of each direction is
given by $v_r = 0$, $v_z = 0$, and $v_\theta = \omega r$ at the disc surface of $z = 0$ (Schmidt, 2003). This implies that the solution is dragged along at the surface of the disc at the angular velocity $\omega$ (Schmidt, 2003). In contrast, when $z$ approaches $\infty$, $v_r = 0$, $v_\theta = 0$, and $v_z = -v_L$. This means that far from the disc, there is no flow in the $r$ and $\theta$ directions, but the solution flows at a limiting velocity toward the disc in the $z$ direction (Schmidt, 2003). The treatment by von Karman and by Cochran yielded the values of the velocities in the form of an infinite series in terms of the dimensionless variable $\gamma$.

$$\gamma = \left(\frac{\omega}{v}\right)^{1/2} z$$

(3.19)

In cases in which $z$ or $\gamma$ have small values, the velocity in each direction can be written in analytical expression by:

$$v_r = r\omega F(\gamma) = r\omega (a\gamma - \frac{1}{2}b\gamma^2 + ...)$$

(3.20)

$$v_\theta = r\omega G(\gamma) = r\omega (1+by + \frac{1}{3}a\gamma^3 + ...)$$

(3.21)

$$v_z = (\omega v)^{1/2} H(\gamma) = (\omega v)^{1/2} (-a\gamma^2 + \frac{1}{3}b\gamma^4 + ... )$$

(3.22)

with $a = 0.51023$ and $b = -0.6159$. For the RDE employed for electrochemical studies, the important velocities are $v_r$ and $v_z$. Near the surface of the rotating disk, these velocities are given in approximate form by:

$$v_z = (\omega v)^{1/2} (-a\gamma^2) = -0.51 \omega^{3/2} v^{-1/2} z^2$$

(3.23)

$$v_r = (r\omega)(a\gamma) = 0.51 \omega^{3/2} v^{-1/2} r z$$

(3.24)
3.6.8.2.2. Solving 1-D Convection Diffusion Equation for Flux at the Electrode

Once the velocity profile has been determined, the 1-D convective-diffusion equation for the RDE (Equation 3.16), utilizing convenient coordinates with the appropriate boundary conditions, can be solved. First considering the steady-state limiting current condition in which \( \omega \) is fixed and a steady velocity profile is attained, a potential step in the limiting current region, where the concentration at \( z = 0 \) \( C_A^{z=0} \) equals zero, will cause the appearance of a current transient similar to that transient observed in the absence of convection (Schmidt, 2003). However, in contrast to the short times where the current decays toward zero with time in an unstirred solution, the current of the RDE decays to a steady-state value at a planar electrode (Schmidt, 2003). Under these conditions, the concentrations near the electrode are no longer functions of time, and the steady-state convective-diffusion equation can be written in terms of cylindrical coordinates as follows:

\[
v_r \left( \frac{\partial C_A}{\partial t} \right) + \frac{v_\theta}{r} \left( \frac{\partial C_A}{\partial \theta} \right) + v_z \left( \frac{\partial C_A}{\partial z} \right) = D_A \left[ \frac{\partial^2 C_A}{\partial z^2} + \frac{\partial^2 C_A}{\partial r^2} + \frac{1}{r} \frac{\partial C_A}{\partial r} + \frac{1}{r^2} \left( \frac{\partial^2 C_A}{\partial \theta^2} \right) \right]
\]  

(3.25)

For the limiting current condition at \( y = 0 \), it is noted that \( C_A^{z=0} = 0 \) and \( \lim_{z \to \infty} C_A = C_A^\infty \) where \( C_A^\infty \) [mol/cm\(^3\)] is the bulk concentration of species A. In addition, due to the symmetry in consideration, \( C_A \) is not a function of \( \theta \), therefore \( \frac{\partial C_A}{\partial \theta} = \left( \frac{\partial^2 C_A}{\partial \theta^2} \right) = 0 \). Also, \( v_z \) does not depend upon \( r \) according and at \( z = 0 \), \( \frac{\partial C_A}{\partial r} = 0 \).

\[
v_z \left( \frac{\partial C_A}{\partial z} \right) = D_A \left( \frac{\partial^2 C_A}{\partial z^2} \right)
\]  

(3.26)

By substituting the value of \( v_z \) and rearrangement of Equation 3.26 the following solution is obtained
\[
\frac{\partial^2 C_A}{\partial z^2} = \frac{Z^2}{B} \left( \frac{\partial C_A}{\partial z} \right)
\]  
(3.27)

with \( B = 0.51 D_A \omega^{3/2} v^{1/2} \). This equation can be solved directly by substitution and integration. In this case \( Z = \frac{\partial C_A}{\partial z} \) so that \( \frac{\partial Z}{\partial z} = \frac{\partial^2 C_A}{\partial z^2} \) and at \( z = 0 \) \( Z_0 = \left( \frac{\partial C_A}{\partial z} \right)_{z=0} \)

\[
\frac{\partial Z}{\partial z} = -\frac{z^2}{B} Z
\]  
(3.28)

\[
\int Z_0 \frac{\partial Z}{\partial z} \frac{1}{Z} = -\frac{1}{B} \int_0^Z z^2 \, dz
\]  
(3.29)

\[
\frac{Z}{Z_0} = \exp \left( -\frac{z^3}{3B} \right)
\]  
(3.30)

\[
\frac{\partial C_A}{\partial z} = \left( \frac{\partial C_A}{\partial z} \right)_{z=0} \exp \left( -\frac{z^3}{3B} \right)
\]  
(3.31)

\[
\int_0^\infty dC_A = \left( \frac{\partial C_A}{\partial z} \right)_{z=0} \int_0^\infty \exp \left( -\frac{z^3}{3B} \right) \, dz
\]  
(3.32)

The definite integral on the right side is obtained by making a substitution and is determined to be \( 0.8934(3B)^{1/3} \) (Schmidt, 2003). Thus,

\[
C_A^\infty = \left( \frac{\partial C_A}{\partial z} \right)_{z=0} 0.8934 \left( \frac{3D_A \omega^{3/2} v^{1/2}}{0.51} \right)^{1/3}
\]  
(3.33)

In a rotating disk electrode, the electrolytes are made to flow past the electrode by convection. During the process, when the rotation speed increases the flux of the electro-active species to the surface of the electrode increases by convection resulting in the current increasing. The current \( I \) [A] is the flux at the electrode surface is

\[
I = nF A_e D_A \left( \frac{\partial C_A}{\partial z} \right)_{z=0}
\]  
(3.34)
in which $A_{ea}$ is the electrochemically active area, gives the variations of concentration and overpotential along the $z$ coordinate of the catalytic layer. From Equations 3.33 and 3.34 the Levich equation for boundary layer diffusion limited current is determined by the mass transport properties of the RDE

$$I_D [A] = nF A_{ea} \left( \frac{D_A}{\delta_0} \right) C_A^\infty = 0.62 nF A_{ea} D_A^{2/3} \nu^{-1/6} \omega^{1/2} C_A^\infty$$

(3.35)

in which $\delta_0$ [cm] is the diffusion layer thickness (for RDEs $\delta_0 = 1.61 D_A^{1/3} \omega^{-1/2} \nu^{-1/6}$). The Levich equation models the variation of diffusion and solution flow around a rotating disk electrode (RDE) (Wang, 2006). In the vicinity of the rotating disc, the component of velocity of the solution normal to the disk diminishes until it becomes zero at the surface of the disk; diffusion, therefore, gradually predominates over convection as the mode of mass transport of the electroactive species to the electrode surface (Wang, 2006). Thus, the concentration gradient, within a very short distance from the rotating disk electrode, closely resembles that at a stationary electrode (Wang, 2006).

For non-limiting current conditions, a change takes place only in the integration limits of Equation (3.32) which yields

$$C_A^\infty - C_A^{z=0} = \left( \frac{\partial C_A}{\partial z} \right)_{z=0} \int_0^\infty \exp \left( -\frac{z^3}{3B} \right) dz$$

(3.36)

$$I = 0.62 nF A_{ea} D_A^{2/3} \nu^{-1/6} \omega^{1/2} (C_A^\infty - C_A^{z=0}) = I_D \left( \frac{C_A^\infty - C_A^{z=0}}{C_A^\infty} \right)$$

(3.37)

The deviation of the plot of $I$ vs. $\omega^{1/2}$ from a straight line that intersects the origin suggests that some kinetic step is involved in the charge transfer reaction. For example, for a totally irreversible reaction, the disk current is:

$$I_{\text{Disk}} = nF A_{ea} k_f(E) C_A^{z=0}$$

(3.38)
with \( k_f(E) = k_0^0 \exp(-\alpha n F \eta / RT) = k_0^0 \exp[-\alpha n F (E - E_{eq}) / RT] \) in which \( k_0^{0} \) [cm/s], \( \alpha \) [–], \( \eta \) [V] are the standard rate constant of electrochemical reaction \( O + ze \rightarrow R \), the transfer coefficient for reduction, the overpotential, i.e., the difference between the electrode potential \( E \) [V] and the equilibrium potential \( E_{eq} \) [V], respectively.

\[
I = n F A_{eq} k_f(E) C_A \left( 1 - \frac{1}{I_L} \right)
\]  

(3.39)

After further rearrangement the kinetic current density, which is the kinetic current of the reaction of a reactive species at the electrode surface in the absence of any mass transfer is determined (Schmidt, 2003).

\[
I_K = n F A_{eq} k_f(E) C_A^{\infty}
\]

(3.40)

At long times when \( t \rightarrow \infty \) or large values of \( t \) the effects of convection is significant than that of the diffusion component. The Koutecky–Levich equation is obtained from the kinetic limited current and diffusion limited current.

\[
\frac{1}{I} = \frac{1}{I_D} + \frac{1}{I_K} = \frac{1}{I_K} + \frac{1}{0.62 n F A_{eq} D_A^{2/3} v^{1/6} \omega^{1/2} C_A^{\infty}}
\]

(3.41)

The oxygen reduction of the Pt electrode proceeds by the following two path ways:

\[
O_2 + 4H^+ + 4e^- \rightarrow 2H_2O
\]

(3.42)

\[
O_2 + 2H^+ + 2e^- \rightarrow H_2O_2
\]

(3.43)

To determine the oxygen reduction pathway, the rotating disc voltammograms should be measured as a function of the rotation rate \( \omega \) by scanning the applied potential \( E \) in an oxygen-saturated acidic solution (Paulus, 2001). In the rotating disc voltammograms, the experimentally measured current is related to \( \omega \) by the Koutecky–Levich equation (Paulus, 2001).
3.6.8.2.3. Applications of RDE for Fuel Cell Analysis

The RDE method has been used extensively to study the kinetics of catalytic oxygen reduction of the hydrogen-oxygen PEM fuel cells at the cathode since it is a rate-limiting step (Gasteiger, 2005). Activation overpotential occurs almost entirely due to the cathode because of the slow oxygen reduction reaction at the cathode. The strong inhibition of the cathodic oxygen reduction reaction (ORR) results in high overpotentials and therefore, significant deterioration in the energy conversion efficiency of a PEM fuel cell (Gasteiger, 2005).

In order to determine the mass activity ($A/\text{g}_\text{Pt}$) and the specific activity ($\mu A/cm^2_{\text{Pt}}$), the complete utilization of the catalyst surface, the electrochemically active area ($A_{\text{ea}}$), along with highly reproducible catalyst loadings are required (Mayrhofer, 2008). By employing the RDE, the $A_{\text{ea}}$ value for Pt/C electrodes can be determined easily by analyzing the cyclic voltammograms (CVs) measured on the Pt/C coated RDE in a deaerated acidic solution (Mayrhofer, 2008). The $A_{\text{ea}}$ value of the Pt/C electrode can be estimated from the hydrogen adsorption/ desorption charge of a layer in the potential range from 0.05 to 0.4 $V_{\text{RHE}}$ called the $H_{\text{upd}}$ (under potentially deposited hydrogen) region in a CV plot (Mayrhofer, 2008). The $A_{\text{ea}}$ value has been calculated from the hydrogen desorption charge divided by the adsorption charge corresponding to the formation of a hydrogen monolayer of $210 \mu C/cm^2$. Traditionally the $H_{\text{upd}}$
area is used for high surface area catalysts due to ready accessibility and convenience of CV’s (Kinoshita, 1977; Schmidt, 1998).

The roughness factor \( r_f \) is the ratio of the surface area covered with platinum to the geometric surface are of the electrode (Mayrhofer, 2008).

\[
rf = \frac{A_{\text{real}}}{A_{\text{geo}}} = \frac{\text{real Pt surface area}}{\text{geometric area of the electrode}}
\] (3.45)

By analyzing the linear plot of the calculated roughness factor \( \left[ \frac{\text{cm}^2}{\text{cm}_{\text{geo}}} \right] \) at various Pt loading values \( \left[ \frac{\mu g}{\text{cm}_{\text{geo}}} \right] \) for catalyst with 1 nm diameters in which the slope of the plot equals the electrochemical active surface area (ECA) in \( \text{m}^2/\mu g_{\text{Pt}} \) of the high surface area catalyst (Mayrhofer, 2008). The specific current density or specific activity \( j_{\text{SA}} \) (\( \mu A/\text{cm}^2_{\text{real}} \)) can easily be calculated from the calculation of measured current when the geometric surface area \( A_{\text{geo}} \) of the electrode equals the real surface area \( A_{\text{real}} \) of the catalyst (Mayrhofer, 2008).

\[
j_{\text{SA}} \left( \frac{\mu A}{\text{cm}^2_{\text{Pt}}} \right) = \frac{\text{current density}}{\text{Pt active surface area}} = \frac{i_K}{A_{\text{real}}} = \frac{i_D \times i}{i_D - i} \times \frac{1}{r_f \times A_{\text{geo}}}
\] (3.46)

The mass activity of a catalyst is another useful intrinsic measure of the catalytic activity (Mayrhofer, 2008). Specific and mass activity are closely related to each other and the mass activity can be calculated using the specific current density by substituting the roughness factor with the Pt loading per geometric surface area \( L_{\text{Pt}} \), leading to:

\[
j_{\text{MA}} \left( \frac{A}{\text{mg}_{\text{Pt}}} \right) = \frac{\text{current density}}{\text{Pt loading}} = j_{\text{SA}} \times \frac{r_f}{L_{\text{Pt}}}
\] (3.47)

The mass activity reflects the gain/cost factor of a catalyst and is therefore of major importance in the development of economical catalysts for application (Mayrhofer, 2008).

3.6.8.3. Testing Details and Parameters
These experimental details were developed using the Automatic Catalyst Characterization System at the General Motors Global Research and Development Center and published by Do, et. al. in “Niobium-doped titanium oxide for fuel cell application” (Do, 2010).

For this work, a uniformly dispersed suspension was formed from the ultrasonication of the supported catalyst (synthesized active material), water, isopropanol, and Nafion®. Typically, the catalyst dispersions were prepared by mixing 5 mg of catalyst in 5 mL aqueous solution containing 1 mL of isopropyl alcohol and 30 mL of 5 wt. % Nafion® solution (4:1:0.0017 v/v) followed by 12 min ultrasonication. The supported catalyst dispersion is prepared by quantitatively dispersing a known amount of catalyst in a known volume of solvent (500 to 1000 µg of catalyst per milliliter of solvent). An aliquot of catalyst suspension was drop coated onto a polished 5 mm diameter glassy carbon substrate, leading to a Pt loading of about 0–20 µgPt/cm²geo with 10–20 wt. % Nafion®. The synthesized catalyst films were dried under flow N₂ at room temperature to evaporate the solvent. From the concentration of the catalyst in the dispersion and using a known volume dispensed on to the disk electrode, an estimate of the amount of catalyst in the thin film is possible.

A Pyrex® cell was filled with about 0.1 L of 0.1 M HClO₄ electrolyte and covered with a Teflon® cap. A reverse hydrogen electrode (RHE) reference was placed in a separate beaker and connected to the cell by a bridge tube filled with the same electrolyte. A Luggin capillary brings the reference to within a few millimeters of the thin film working electrode. The counter electrode is a platinum mesh connected to the cell through a coarse frit. The electrode film was immersed at open-circuit as the electrolyte was being actively sparged with argon, and it was activated by cycling 400 times between 50 and 1100 or 1200 mV at 1 V/s. Once the CV current was stabilized by the rapid cycling, three additional voltage sweeps were run at 20 mV/s. The Pt
surface area was estimated by the charge of the under potential deposited (UPD) hydrogen assuming 210 μA/cm². Oxygen was dispersed for a minimum of 30 min to initially saturate the electrolyte and then continuously throughout the ORR measurement. At successive rotation speeds of 1600, 900, 400, and 100 rpm, the film was initially held at +150 mV for 60 s then swept to +1100 mV at 5 mV/s. Diffusion through the film can be ignored due to the fact that there is no significant difference in activity between 1600 rpm and the extrapolated speed and the significantly low thin thickness of the film.

Another method to analyze carbon based substrates with platinum nanoparticles incorporated (loaded) onto the matrix is accelerated gas-phase thermal oxidation in which the total the mass lost is monitored. The performance of an electrocatalyst is simulated by an accelerated gas-phase thermal oxidation method by evaluating the performance of long periods of electrochemical cycling and a potential hold test. In this method substrates are sintered at 250°C for 30 hours in a helium gas (with 0.7% O₂ and 8% H₂O) stream at 50 sccm. The substrates are also evaluated by cyclic voltammetry, using a three-electrode cell filled with 0.5M H₂SO₄ at 80°C. Voltage cycling was conducted at a rate of 10mV/s over a range of 0 ≤ E≤ 1.2V vs. the hydrogen reference electrode.

This chapter has provided a thorough discussion on the physical properties and chemical structure of the various types of carbon and silica. Synthesized carbon silica nanocomposites which will be discussed in details in the upcoming chapters are categorized with the amorphous classification. However, the materials have crystallites within their structures that hold them together. Carbon nanotubes, which are also used, have chemical structure similar to graphite due to similar hybridization and the folding of a one atom thick graphite sheet to construct the nanotubes. Values of boiling points and melting points have been provided for all reactants used.
to fabricate carbon based materials in this work. These values are especially important when examining the effects of porogens to enhance porosity and surface area. All the characterization techniques used in this work has been overviewed. Microscopy techniques have been used to examine both the external and internal morphologies of all materials. Distinction of ordered versus disordered pore distribution has been made apparent by x-ray diffraction spectra. Surface area and porosity calculations are provided from adsorption/desorption isotherm analysis. Examining the change in weight lost provides information on the composition of materials which can be compared with semi-qualitative EDX spectra. Electrospinning has been explored as an additional fabrication technique to evaluate the effects of carbon nanotubes within carbon silica networks, especially enhanced conductivity. And lastly, electrochemical analyses for both durability and capacitance provide insight to whether the synthesized materials have the capabilities to improve renewable energy storage and conversion applications.
CHAPTER 4: THE IMPACT OF POROGENS FOR ENHANCED POROSITY AND SURFACE AREAS FOR MESOPOROUS CARBON-BASED MATERIALS

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4.1. ABSTRACT

The key obstacles preventing the commercialization of automotive-scale fuel cells are cost and durability of materials. Current materials used for the catalyst support of electrocatalytic applications, such as carbon black, are continuously exposed to highly oxidative environments, which lead to carbon corrosion. Corrosion-resistant mesoporous carbon-ceramic nanocomposites can be designed and fabricated by incorporating the conductivity of low-cost carbon materials with the chemical robustness of ceramic inorganic materials, thus creating a family of conductive, sturdy, chemically stable, porous nanocomposites which can be used for the next generation of durable electrocatalyst supports.

Chemical activation methods through the use of zinc chloride have been employed to tune the surface area, pore volume, and pore-size distribution of the fabricated carbon-ceramic materials, since precise porosity modifications are essential to enhance the features of the carbon-based supported catalyst layer. Randomly disordered porous nanocomposites were synthesized using a simple self-assembly process with a ceramic cluster (hydrolyzed tetraethyl orthosilicate) and a carbon precursor (sucrose). Carbon-ceramic nanocomposites with ordered crystalline pore structures were constructed from a sol gel route using a surfactant directing agent (Pluronic F127), an inorganic component (hydrolyzed tetraethyl orthosilicate), and an oligomeric
assembling block (phenol and formaldehyde). Pore size control was achieved by tuning the concentration of the activation reagent, in which increasing the amount of ZnCl$_2$ resulted in improved pore structures (pore volume 0.1-0.55 cm$^3$/g) and larger pore sizes (2-5nm). In the disordered pore system, the highest surface area of 802.33 m$^2$/g was obtained with 17.63 wt.% ZnCl$_2$, 15.87 wt.% sucrose, and 10.93 wt.% TEOS hydrolyzed in ethanol and water, resulting in a composition of carbon at 49% confirmed by TGA. 2D hexagonal ordered porous carbon-silica nanocomposites with the addition of 10.16 wt. % ZnCl$_2$, resulted in 51.6% increase in surface area to 599.02 m$^2$/g, and a composition of 59% carbon and 41% silica. Preliminary conductivity studies concluded that an increase in carbon content leads to higher conductivity. Optimization of carbon content and increased surface areas and pore sizes through the use of porogens will lead to carbon-silica composites with promising corrosion resistant features.

4.2. INTRODUCTION

In the future hydrogen will be a dominant fuel, converted into electricity in fuel cells, leaving only water as a bi-product. Despite the high interest in fuel cell development there are many technological challenges which must be overcame before fuel cells are commercially viable and widely adopted. There are still numerous questions concerning the optimal characteristics of carbon based materials for fuel cell electrodes.

The two primary issues preventing widespread commercialization of fuel cells are cost and durability (He, 2005). Fuel cell costs must be dramatically reduced to meet the US Department of Energy’s (DOE) target of $30/kW by 2015 to be competitive with virtually every type of power application (He, 2005). The major technical barrier for the acceptance of fuel cells as a practical power source is durability under a wide range of operational conditions (Wilkinson, 2003). This issue is due to the continuous exposure of fuel cells to highly oxidizing
environments, which leads to significant performance deterioration and future device failure (He, 2005). The driving force for oxidative degradation of the porous catalyst support is the air electrode’s constant exposure to oxygen during operation, creating a wet, acidic, highly oxidative environment (Reiser, 2005). Carbon corrosion induces porosity changes causing the structure to collapse from an interconnected network to a dense carbon layer with mainly isolated pores which can significantly contribute to decreased performance potential. The resulting decrease in porosity and pore size of the carbon support hinders mass transport, leading to severe fuel cell performance loss.

Figure 4.1. Illustration of a carbon supported catalyst layer within the cathode electrode of a hydrogen proton exchange membrane (PEM) fuel cell (Adopted from (Lister, 2004))

The main requirements for suitable fuel cell catalysts supports as illustrated in Figure 4.1 are high surface area, good electrical conductivity, suitable porosity to allow good reactant flux, and high stability in fuel cell environment. Current efforts towards corrosion-resisted catalyst supports have focused on engineering existing nanoporous carbon materials to improve their durability or seeking alternative catalyst supports. The most commonly used catalyst support is
high purity carbon black (Conductex® 975 or Vulcan® XC-72): a low cost, easily available, particulate amorphous carbon material with surface areas ranging 250-1200 m$^2$/g and adequate conductivity (> 1 S/cm) (He, 2005). Carbon blacks have high specific surface area contributed mostly by non-interconnected micropores less than 1 nm in size. This result in a disadvantage for catalyst support materials because the pores of the amorphous material are difficult to access and have poor connectivity. Alternative support materials have been explored; which are different from carbon black at both the nanoscopic level in terms of their structural conformation and pore texture and at the macroscopic level in terms of their form. The materials include various nanostructured carbon materials such as mesoporous carbons (Joo, 2001), carbon aerogels (Anderson, 2002; Ye, 2003), carbide derived carbons, and carbon-nanotubes (Li, 2003; Wang, 2004). Compared with carbon blacks, overall mesoporous carbons contain higher surface areas and lower amounts or the absence of micropores. However, all the previously mentioned carbon based materials face the same corrosion issue as that of carbon black.

The appropriate choice and modification of reagents for carbon support can influence catalyst properties. Ceramic materials are highly stable in corrosive environments, however, making low cost conductive ceramic materials with adequate electronic conductivity and controlled pore structure remains challenging. In this work, a new generation of mesoporous corrosion resisted fuel cell catalyst support materials can be designed by incorporating the conductivity and low cost of carbon based materials with the chemical robustness of ceramic materials. Precise control over the composition and interconnected pore structure of the nanocomposites balances the conductivity, transport efficiency, and corrosion resistance, providing novel robust materials for catalyst support applications. Since a strict control of the pore size is mandatory to optimize the properties of the catalyst layer, chemical activation
methods have been utilized to modify the surface area, pore volume, and pore-size distribution of
the as-made carbon-ceramic composites.

4.3. Experimental Approach and Characterization Techniques

4.3.1. Chemicals

Zinc (II) Chloride (98%, Sigma Aldrich), Sucrose (99.5%, Sigma), Tetraethyl orthosilicate (98%,
Sigma Aldrich), Sodium Hydroxide (97%, Sigma Aldrich), Hydrochloric Acid (37%, Sigma
Aldrich), Ethanol (99.5%, Sigma Aldrich), Phenol (99%, Sigma Aldrich), Formaldehyde (37%,
Sigma Aldrich), and Poly(propylene oxide)-poly(ethylene oxide)-poly(propylene oxide) triblock
copolymer Pluronic F-127 (MW = 12,500, Sigma) were all used as received. Distilled water was
used in all experiments.

4.3.2. Incorporation of Porogens into Randomly Disordered Mesoporous Carbon-Silica
Composites

Porous carbon-silica nanocomposites were synthesized utilizing a sol-gel process, in
which tetraethyl orthosilicate (TEOS) was the silica source, sucrose was the carbon source, and
zinc chloride was the chemical activation agent, followed by high temperature carbonization
under nitrogen. In a typical synthesis 2.08g of TEOS, 1.08g of distilled (DI) water, 2.76g of
Ethanol (EtOH), and 8.10 µL of hydrochloric acid (HCl) (molar ratio TEOS:H₂O:EtOH:HCL =
1:6:6:0.01) were pre-hydrolyzed at 60 °C for 4 hours to form the silica precursor. Separately, the
carbon precursor was prepared by dissolving 0.9g of sucrose and 1.0g of ZnCl₂ in 2.0g of DI
water by shaking, stirring, and ultrasonication, until a homogenous mixture was apparent. The
carbon precursor was then added into the silica precursor solution and stirred for 2 hours. The
homogenous mixture was poured into glass dishes to initiate the evaporation of water and ethanol at 25°C for approximately 24 hours, resulting in transparent films being formed. Next, thermo-polymerization occurred at 80°C in an oven for 1 day. During this step, zinc chloride is inserted into the carbon-silica matrix, in which the impregnated zinc chloride later dehydrates the sucrose to form a carbon skeleton. This is confirmed from the colorless transparent gels gradually turning to dark brown during this drying step. After removal from the oven, the evaporation of solvent and both the condensation and hydrolysis of TEOS is complete, and dark brown silica/ZnCl₂/sucrose composites are formed. The composites were carbonized in a tubular furnace under the following conditions: 1°C/min from 80°C-600°C, 5°C/min from 600°C - 900°C, and held at 900°C for 4 hours. A systematic study was completed to determine the effects of carbon content, silica content, and activation agent content on pore size distribution and surface area. Table 4.1 lists the amounts of adjusted reactants: (a) the variation of ZnCl₂ (constant carbon and silica content), (b) variation in sucrose (constant ZnCl₂ and silica content), and (c) variation in silica precursor (constant ZnCl₂ and carbon content).

<table>
<thead>
<tr>
<th>Trial</th>
<th>Variation of ZnCl₂</th>
<th>Variation of Sucrose</th>
<th>Variation of TEOS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ZnCl₂ (g)</td>
<td>ZnCl₂ (wt. %)</td>
<td>Sucrose (g)</td>
</tr>
<tr>
<td>1</td>
<td>0.2</td>
<td>2.22</td>
<td>0.8</td>
</tr>
<tr>
<td>2</td>
<td>0.4</td>
<td>4.34</td>
<td>1.0</td>
</tr>
<tr>
<td>3</td>
<td>1.0</td>
<td>10.18</td>
<td>1.2</td>
</tr>
<tr>
<td>4</td>
<td>1.5</td>
<td>14.53</td>
<td>1.8</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>2.0</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1. Variations in (a) ZnCl₂, (b) Sucrose, and (c) TEOS, respectively with all other reactants held constant to make disordered carbon-silica nanocomposites.
4.3.3. Incorporation of Porogens into Ordered Mesoporous Carbon-Silica Composite

The co-assembly of inorganic (silica) and organic (phenol and triblock copolymer surfactant) phases from the sol gel process and subsequent carbonization is utilized to prepare silica-carbon nanocomposites. A systematic study was initially completed to determine the effects of carbon content (phenolic resin), silica content, and a surfactant directing agent F-127 content in order to make carbon-silica mesoporous nanocomposites with optimized composition, pore size distribution, and surface area. Porogens, ZnCl₂, were added to an optimized chemistry to tune surface areas, pore volumes, and pore sizes of ordered mesoporous carbon silica composites. Initially, a large batch of resol (phenol and formaldehyde) precursor was made using 12.2 g of phenol, 2.6 g of 20 wt. % NaOH, and 21 g of formaldehyde. The solution was heated while stirring to 75°C under reflux, and later neutralized at room temperature to pH 7 by 0.6M HCl. Water was removed by vacuum evaporation below 50°C, and the final viscous product was dissolved in ethanol making a 20 wt. % resol solution. Next, 3.6 g of F-127 was dissolved in 16.0 g of ethanol with 2.0 g of 0.2M HCl and stirred for 1 hour at 40°C. Then 4.16 g of hydrolyzed TEOS (molar ratio TEOS: H₂O: EtOH: HCl = 1:6:6:0.01) and 12.5 g of 20 wt. % resol/ethanol solution were added to the surfactant mixture and stirred for 2 hours. Five trials were conducted requiring additional stirring of varying amounts of zinc chloride solution (0, 1.39, 2.75, 5.33, and 10.16 wt. % respectively, dissolved in 2.0 g of DI water) for 30 minutes into the carbon-silica matrix.

Next, the mixtures were poured into glass dishes and dried in air at 25°C for 1 day to evaporate the ethanol, then placed in an oven and thermopolymerized at 100°C for 1 day. After removal from the oven, the evaporation of solvent and condensation and hydrolysis of TEOS
was complete and orange/brown transparent silica/organic nanocomposites were formed. The nanocomposites were then carbonized in a tubular furnace, heating under nitrogen at 1°C/min from 100°C-600°C, 5°C/min from 600°C-900°C, and held at 900°C for 4 hours.

4.3.4. Characterization

Nitrogen adsorption/desorption isotherms were determined at 77K using a Micromeritics ASAP 2020 Surface Area and Pore Size Analyzer (Micromeritics Instrument Corporation, Norcross, GA) to calculate the Brunauer Emmett Teller (BET) specific surface area using adsorption data in a relative pressure range from 0.04 to 0.25. Samples were degassed in vacuum at 200°C for 5 hours. Barrett Joyner Halenda (BJH) model was used to calculate pore size distributions and pore volumes derived from the adsorption isotherm. The total pore volume was estimated from the adsorption amount at a relative pressure (P/P₀) of 0.97. The micropore volumes and surface areas were calculated from the V-t plot method. The JEOL-6700F FE-SEM (JEOL Ltd., Japan) was used for scanning electron microscopy to examine surface morphology. TEM experiments were conducted on a Philips CM120 operated at 120 kV (Philips/FEI Inc., Eindhoven, The Netherlands) providing information on internal structures and morphologies. Powder X-ray diffraction (XRD) spectra were obtained using a PANalytical X’Pert Pro X-ray diffractometer. Ni-filtered Cu Kα radiation with λ = 1.5418 Å and the copper anode was operated at 40 kV and 30 mA. XRD was utilized to identify crystallinity and provide information on unit cell dimensions. The unit cell parameters were calculated from the formula \[ a = \frac{2d_{10}}{\sqrt{3}} \]. The composition of the various nanocomposite materials with carbon and silica content will be determined based on carbon weight loss using thermogravimetric analysis (TGA) on a Perkins-Elmer Pyris 6 TG Analyzer at a heating rate of 5°C/min from 25-1000°C under nitrogen.
4.4. Results/Discussion

4.4.1. Chemically Activated Randomly Disordered Mesoporous Carbon-Silica Nanocomposites

The addition of carbon particles into a silica network and direct carbonization yields mesoporous carbon-silica nanocomposites. Disordered porous nanocomposites have been synthesized using a simple self-assembly process with a ceramic cluster, silicate species; carbon precursor, sucrose; and porogens, chemical activation agents in aqueous media. Chemical activation is a method used to improve the adsorption properties of carbon materials. ZnCl$_2$ dissolved in water was incorporated into the carbon-silica matrix and above the zinc chloride melting point of 283°C a mobile liquid is formed as zinc chloride decomposes. Once the boiling point of ZnCl$_2$ is met at a higher temperature of 732°C a serve reaction occurs between the zinc compound and both the carbon and silica atoms. The result of this interaction is the increased carbon burn off which creates new pores from the atomic layers of carbon and silica widening. The carbon-silica nanocomposites are disordered due to different polymerization rates of inorganic and organic species, which destroy their co-assembly and lead to disordered arrangements. The porosity of the carbon-silica nanocomposites can be tuned by adjusting the amount of activation agent. These sets of experiments were conducted to optimize the composition and pore structure of the nanocomposites to achieve improved durability, adequate electron transport, and efficient mass transport.

4.4.1.1. Variation in Activation Agent

Variations in porosity were initially examined by altering the amount of zinc chloride used during synthesis. For many years it has been recognized that certain forms of physisorption
hysteresis are associated with capillary condensation in mesoporous media and that the type of hysteresis loop is governed to some extent by both the pore shape and the nature of the network (Greggs, 1982). Everett and Haynes have shown mathematically that capillary condensation is accompanied by an irreversible entropy change, and resulting in hysteresis (Everett, 1972). Nitrogen isotherms of the carbon-silica composites synthesized with various amounts of ZnCl₂ exhibit distinct hysteresis loops which are generally found with well defined mesoporous adsorbents. As shown in Figure 4.2(a), increasing the amount of ZnCl₂ resulted in increased nitrogen intakes. Type IV isotherms with H2 hysteresis become more apparent as the amount of ZnCl₂ used in the procedure increases. The three well distinguished regions of the adsorption isotherm (a) the linear increase of the adsorbed volume at low pressure due to monolayer adsorption on the pore walls, (b) a sharp increase in adsorbed volume at intermediate pressure due to capillary condensation, and (c) a subsequent linear increase in the adsorbed volume versus pressure at high pressure due to multilayer adsorption on the outer surface are clearly shown at higher zinc chloride contents. Therefore, increased capillary condensation and hysteresis is due to the increased amounts of zinc chloride resulting in more porosity, and larger pore sizes and pore volumes.

The sample with the least amount of zinc chloride 2.22 wt. % shows more of a H4 hysteresis loop when zoomed in from 0-40 cm³ STP/g of volume adsorbed-desorbed. The isotherm is nearly parallel over a wide range of P/P₀. The type H4 loop shown here is associated with narrow slit like pores and is indicative of microporosity. Examining the distribution of mesoporous to microporous surface areas and volumes (Figure 4.2 (a) and (b), respectively) the wide yet narrow type H4 hysteresis loop in the 2.22 wt. % ZnCl₂ sample is due to the composite having 87% of its surface area and 85% of its pore volume microporous. This implies that
incorporation of even small amounts of porogens induces the development of pores, initially micropores. Increased concentration of porogens will contribute to the development of mesopores.

The pore size distribution (dV/dD vs. D) of the various zinc chloride samples were calculated from the N\textsubscript{2} isotherm data using BJH methodology. Figure 4.2(b), shows a trend with a narrow pore size distribution with both increased pore volume and pore diameter with increased ZnCl\textsubscript{2} content. Based on the results reported in Table 4.3, an overall trend of increased surface areas and pore volumes with increased zinc chloride concentrations is exhibited. An approximate 90% increase in both surface area and pore volume occurs with increasing zinc chloride content from 2.22 to 14.53 wt. %. The degree of activation is evaluated from the amount of ZnCl\textsubscript{2} incorporated into the carbon precursor, this ranges from \(\sim 0.15\) to \(1^2/3\) grams of zinc chloride to 1 gram of carbon precursors (sucrose). It is clear that surface area and pore volume control is achieved by tuning the concentration of the activation reagent. The pore diameters reported in Table 4.2 are relatively small ranging from 2-4nm; however larger pore sizes can by synthesized by using higher concentrations of zinc chloride.
Figure 4.2. (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution of disordered mesoporous carbon-silica composites prepared with variations in chemical activation reagent (zinc chloride) content; the amounts of the carbon precursor and silica precursor are held constant.

Table 4.2. Total Surface Areas, Total Pore Volumes, and Pore Sizes of disordered mesoporous carbon-silica composites varied by ZnCl$_2$ content

<table>
<thead>
<tr>
<th>Variation in ZnCl$_2$</th>
<th>Surface Area (m$^2$/g)</th>
<th>Pore Volume (cm$^3$/g)</th>
<th>Pore Size (nm)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.22</td>
<td>50.73</td>
<td>0.025</td>
<td>2.00</td>
<td>2.93</td>
</tr>
<tr>
<td>4.34</td>
<td>321.44</td>
<td>0.108</td>
<td>2.99</td>
<td>18.18</td>
</tr>
<tr>
<td>10.18</td>
<td>349.77</td>
<td>0.186</td>
<td>3.29</td>
<td>25.20</td>
</tr>
<tr>
<td>14.53</td>
<td>447.67</td>
<td>0.285</td>
<td>3.68</td>
<td>37.91</td>
</tr>
</tbody>
</table>

By examining the distribution of mesoporous surface area to microporous surface area (Figure 4.3 (a)), there is a significant shift to higher mesoporosity with the addition of only 4.34 wt. % of ZnCl$_2$ to the carbon and silica precursors. The surface areas are on the order of 70% mesoporous. Figure 4.3 (b) shows a decrease in microporosity pore volume with the increasing amounts of ZnCl$_2$, leading to the sample with the highest amount of zinc chloride having 79% of its pore volume mesoporous. Thus, pore diameters widen (increase) with higher concentrations of porogens within the carbon silica network.
Figures 4.3. The distribution between mesoporous and microporous (a) surface areas and (b) pore volumes of disordered porous carbon-silica composites with variations in ZnCl$_2$ content.

Figures 4.4 and 4.5 show the SEM and TEM images of carbon/silica nanocomposites prepared with and without the addition of zinc chloride. The samples without ZnCl$_2$ have smooth surfaces and nonporous structures. The introduction of zinc chloride into the process results in samples with disordered porous structure and rough surface morphologies. The TEM images with 14.53 wt. % of ZnCl$_2$ displayed pores on the order of 4 nm, which is comparable to the 3.68 nm BJH adsorption isotherm pore diameter measurement. These results confirmed that the interaction between zinc chloride and carbon precursors under high temperature leads to the formation of pore structures inside the carbon-silica composites. The higher the amount of zinc chloride incorporated into the precursor solution, the higher the porosity of the obtained nanocomposites.
Figure 4.4. SEM 3kV images at (a) 2K magnification and (b) 50K magnification and (c) TEM images of a carbon-silica composite prepared with 0.0 wt. % of ZnCl₂.

Figure 4.5. SEM 10kV images at (a) 1.2K and (b) 50K magnification and (c) TEM images of disordered mesoporous carbon-silica composites prepared with 14.53 wt. % of zinc chloride.

The framework composition of the disordered mesoporous carbon-silica composites were determined by thermogravimetric analysis (TGA) of the carbonized products. The organic-inorganic composition is represented as weight percentage of carbon and silica, in which the TGA curves show combustion of the organic phase. For the sample with the highest concentration of porogens, 14.53 wt. % ZnCl₂, TGA shows a significant weight loss of 34% in the temperature range of 450-600 °C under nitrogen for the carbon-silica composite, as seen in Figure 4.6 (a). Increased porosity (pore size and pore volume) resulted in higher carbon content within the composites. Thus, the usage of porogens tunes surface area, pore size distribution, and composition. It should be noted that based on the original amounts of reactants, 2.08g of
hydrolyzed TEOS and 0.9g of sucrose in solution (which were held constant), the mass ratio of silica to carbon was 2.31: 1, which is reflected in all the samples having a higher content of silica.

(a) \hspace{1cm} (b)

![Graph](image)

Figure 4.6. (a) TGA curves and (b) carbon and silica composition of randomly disordered mesoporous carbon-silica nanocomposites with varying concentrations (wt. %) of ZnCl₂ in aqueous solution

<table>
<thead>
<tr>
<th>ZnCl₂ wt. %</th>
<th>% Silica</th>
<th>% Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.22</td>
<td>92</td>
<td>8</td>
</tr>
<tr>
<td>4.34</td>
<td>82</td>
<td>18</td>
</tr>
<tr>
<td>10.18</td>
<td>76</td>
<td>24</td>
</tr>
<tr>
<td>14.53</td>
<td>66</td>
<td>34</td>
</tr>
</tbody>
</table>

4.4.1.2. Variation in Carbon Precursor

These sets of experiments were conducted to examine the changes in porosity and surface areas based on varying the concentration of the sucrose precursor. In this case the amounts of activation agent, ZnCl₂, and silica precursor solution were kept constant. The nitrogen uptake decreased with increasing carbon content. As seen in Figure 4.7(a), all the nanocomposites exhibited type-IV isotherms with distinct capillary condensation steps suggesting mesoporous size distributions. H2 hysteresis is evident, implying that all the samples have local components of non-uniformity. The hysteresis loops decreased in size with increasing carbon content reflecting, a decrease in pore size when increased amounts of sucrose were used.
The overall surface area does not significantly decrease with variation in carbon content, for example there is only a 4.64% decrease in surface area when comparing the range of 8.23-18.31 wt. % of sucrose in aqueous solution (Table 4.3). The mesoporous surface areas of the carbon-silica composites, shown in Figure 4.8(a), decreased from 75% at the lowest carbon content of 8.23 wt. % to approximately 60% at the highest carbon content of 18.31 wt. %, indicating the presence of more microporous features with the increased concentration of carbon precursor. Furthermore, microporosity is a feature resulting from excess sucrose. When aqueous sucrose solution is used as a carbon precursor, additional microporosity is formed due to the elimination of water and the extensive thermal decomposition of sucrose. Consequently, the resulting carbon within the carbon silica matrix contains hierarchical features with increased micropores embedded within the walls of the mesopores.

Increased microporosity is also in direct accordance with the findings in the previous section 4.4.1.1. With increasing sucrose content (keeping the same mass of ZnCl\textsubscript{2} within each trial constant) less zinc chloride was incorporated into the sample leading to samples with more microporosity. The ratio of grams of zinc chloride to grams of sucrose varied from 1.25 to 0.5 with higher concentrations of sucrose added to each successive trial. Note, the surface areas stayed within the range of 360-390 m\textsuperscript{2}/g, similar to sample trial #3 in section 4.4.1.1 (variation of ZnCl\textsubscript{2}) with 10.18 wt. % ZnCl\textsubscript{2} due to the percentage of ZnCl\textsubscript{2} being 9.15-10.25 wt. % (decreasing with increasing sucrose content) within this case of varying carbon precursor. In addition, the contribution of the silica precursor was also analogous to sample trial #3 in the variation of ZnCl\textsubscript{2} case in which the amount of silica precursor was on the order of 19.04-21.39 wt. % (decreasing with increasing sucrose content).
The total pore volume does significantly change due to carbon content. The total pore volume decreases by more than 54% with increasing carbon content from 8.23-18.31 wt. % of sucrose. There is a significant increase in microporous volume at higher carbon content (Figure 4.8(b)), with approximately 54% microporous volume at the highest carbon content. Increasing the amount of carbon content resulted in lower pore size distribution (Figure 4.7(b)), with most of the pores distributed at both approximately 3.2 nm and 4.0 nm.

It is known that increased carbon content will lead to higher conductivity. Previous findings by this research group in which Pt nanoparticles were deposited onto the mesoporous carbon-silica to construct an electrode reported that when the carbon content is higher than 56%, the conductivity of the carbon-silica nanocomposite can reach 6.6 S/cm, which is adequate for fuel cell device applications (Hu, 2007). This indicates that a balance needs to be made between required pore size and increased carbon content for higher electrical conductivity. Based on the data in Section 4.4.1.1., if larger pore sizes are needed, an increase in the amount of activation agent should be used to result in composites with both high porosity and pore size, and high carbon content for improved electrical conductivity.
Figure 4.7. (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution of disordered mesoporous carbon-silica composites prepared with variations in the carbon source content, sucrose; the amounts of the amount of zinc chloride in solution and hydrolyzed TEOS are held constant.

Figure 4.8. The distribution between mesoporous and microporous (a) surface areas and (b) pore volumes of porous carbon-silica composites with variations in aqueous sucrose concentrations.
Table 4.3. Total Surface Areas, Total Pore Volumes, and Pore Sizes of disordered mesoporous carbon silica composites varied by sucrose content.

<table>
<thead>
<tr>
<th>Variation in Sucrose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sucrose (wt. %)</td>
</tr>
<tr>
<td>8.23</td>
</tr>
<tr>
<td>10.08</td>
</tr>
<tr>
<td>11.85</td>
</tr>
<tr>
<td>16.79</td>
</tr>
<tr>
<td>18.31</td>
</tr>
</tbody>
</table>

The carbon composition increased by only 8% when the concentration of carbon precursor was increased over a range of 8.23 to 18.31 wt. %, with an average composition of 80% silica and 20% carbon. Again the effects of the chemical activation reagent, ZnCl$_2$, had a tuning effect on compositional changes due to the amount of ZnCl$_2$ changing by ~1% between the highest and lowest carbon precursor concentration, resulting in limited compositional changes. As seen in Figure 4.9(a), the major weight change occurred between 450°C and 750°C.
Figure 4.9. (a) TGA curves and (b) carbon and silica composition of randomly disordered mesoporous carbon silica nanocomposites with varying concentrations (wt. %) of sucrose in aqueous solution.

4.4.1.3. Variation in Silica Precursor

The purpose of silica in the carbon-silica network is to improve durability by decreasing weight loss of carbon in an oxidative environment. These sets of experiments were conducted to examine the changes in porosity and N₂ uptake, based on changes in the amount of silica precursor used, in which the amounts of activation reagent, ZnCl₂, and carbon precursor solution were kept constant. Adding water to the solution hydrolyzes the TEOS so it is able to polymerize. Ethanol is used as a co-solvent since it is miscible with both TEOS and water, which allows both substances to be in the same phase so they can react. Hydrochloric acid is an acidic catalyst that helps to make the reactions go faster.

N₂ sorption isotherms and pore size distribution curves of carbon-silica nanocomposites with different silica contents are shown in Figure 4.10, and the corresponding pore
characteristics including BET surface areas, pore volume, and pore diameter are summarized in Table 4.4. All the nanocomposites exhibited type-IV curves with H2 hysteresis indicating mesoporous material. Based on Figure 4.10 (a), hysteresis loops increased in size with increasing silica content suggesting that pore sizes should increase with increasing TEOS content. However, nitrogen uptake decreased with increasing silica precursor content. The overall surface area decreased by 56% with the increase in TEOS from 10.93 to 23.02 wt. %. Lower silica content had more microporous features (Figures 4.11 (a) and (b)).

Figure 4.10. (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution of disordered mesoporous carbon-silica composites prepared with variations in the silica content; the amounts of the carbon precursor and activation reagent are held constant.

By keeping the amount of sucrose and ZnCl₂ constant at 0.9g and 1.0g respectively, varying concentrations of zinc chloride are incorporated into the carbon-silica matrix valued from 8.85-17.63 wt. % (decreasing with increasing silica content). This trend is reflected in the highest surface area value of 802.33 m²/g with 17.63 wt. % ZnCl₂ and only 10.93 wt. % TEOS hydrolyzed in ethanol and water, this proving that at high concentrations of activation reagent surface area values area able to drastically increase.
Table 4.4. Total Surface Areas, Total Pore Volumes, and Pore Sizes of mesoporous carbon-silica composites varied by silica content.

<table>
<thead>
<tr>
<th>Variation in Silica Precursor</th>
<th>TEOS (wt. %)</th>
<th>Surface Area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
<th>Pore Size (nm)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10.93</td>
<td>802.33</td>
<td>0.164</td>
<td>3.37</td>
<td>26.62</td>
</tr>
<tr>
<td></td>
<td>13.26</td>
<td>700.86</td>
<td>0.170</td>
<td>3.13</td>
<td>20.76</td>
</tr>
<tr>
<td></td>
<td>15.16</td>
<td>587.69</td>
<td>0.193</td>
<td>3.28</td>
<td>18.73</td>
</tr>
<tr>
<td></td>
<td>23.02</td>
<td>345.42</td>
<td>0.182</td>
<td>3.49</td>
<td>17.18</td>
</tr>
</tbody>
</table>

Figure 4.11. (a) TGA curves and (b) carbon and silica composition of as made randomly disordered mesoporous carbon silica nanocomposites with varying concentrations (wt. %) of TEOS hydrolyzed in water and ethanol.

The TG analysis confirmed increasing carbon content when using lower concentrations of hydrolyzed TEOS, as seen in Figure 4.11. As previously mentioned, the highest concentration of zinc chloride solution at 17.63 wt. % was incorporated into the carbon silica matrix when using 10.93 wt. % TEOS resulting in a nanocomposite with the highest composition of carbon at 49%.
Figure 4.12. The distribution between mesoporous and microporous (a) surface areas and (b) pore volumes of mesoporous carbon-silica composites varied by TEOS content.

The type of pore structure can be easily controlled by adjusting the ratio of silicate to sucrose used in the starting solution. The carbon content will always be kept high (over 50%) in order to maintain sufficient conductivity within the nanocomposite. Since the objective is to improve the durability and robustness of carbon by molecular level mixing of ceramic materials it is important to understand the effects of porosity due to the amount of silica added to the composite. Higher surfaces areas are achieved at lower silica concentrations; however the composite is more microporous (Figure 4.12). The composite can be tuned to be more mesoporous by increasing the amount of zinc chloride, which will also lead to increases in pore sizes and pore volumes.

4.4.2. Chemically Activated Ordered Mesoporous Silica-Carbon Nanocomposites

Molecular level mixing of carbon and ceramics was conducted to form robust 2-D hexagonal nanocomposites with enhanced corrosion resistance. The co-assembly of the Pluronic
F-127 surfactant, silica, and phenolic resins via sol-gel polymerization, followed by carbonization to decompose the surfactant, lead to the generation of mesoporous carbon silica composites with ordered channel structure. The phenolic resin known as resol (phenol & formaldehyde) is used as a precursor which is composed of a multi-connected benzene ring framework has independently demonstrated reproducible synthesis of highly ordered mesoporous polymers and carbon frameworks with \( p6m \) symmetry via EISA of triblock copolymers (Meng, 2005). Triblock copolymer F-127 was selected as a template mainly due to its long poly ethylene oxide (PEO) chains, which can from strong hydrogen bonding interactions and favor the organization of ordered nanocomposite mesostructures. The preferential evaporation of ethanol progressively enriches the concentration of the copolymer and drives the organization of resol-copolymer composites into an ordered liquid crystalline mesophase. The ordered mesophase is solidified by the cross-linking of resols induced by thermopolymerization. Compositions and pore structures have been tuned through the use of ZnCl\(_2\) added to the carbon silica network to enhance surface area and porosity.

Similar to the results with randomly disordered mesoporous carbon silica, the incorporation of porogens into a carbon silica network, which self assembles into ordered pore structure, resulted in carbon silica networks with increased surface areas, pore volumes, and pore sizes. As seen in Figure 4.13(a), the area within the hysteresis loops became larger with the addition of increasing concentrations of zinc chloride in aqueous solution, reflecting increased mesoporosity. This is also confirmed by examining the distribution of mesoporous to microporous surface areas, in which the mesoporous contribution increased by 20% using the highest concentration of ZnCl\(_2\) (Figure 4.14). Larger surface areas are the result of increased nitrogen uptakes through the use of chemical activation reagents, a maximum surface area of
599.03 cm$^2$/g resulted in a 52% increase with 10.16 wt. % ZnCl$_2$ decomposing in the carbon-silica network (Table 4.5). A narrow pore size distribution was centered between ~4.00-4.08 nm, as shown in Figure 4.13(b).

![Figure 4.13](image)

Figure 4.13. (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution of ordered mesoporous carbon-silica composites prepared with variations in the activation reagent (zinc chloride) concentration; the amounts of the carbon precursor and silica precursor are held constant.

Table 4.5. Total Surface Areas, Total Pore Volumes, and Pore Sizes of ordered mesoporous carbon-silica composites varied by ZnCl$_2$ content.

<table>
<thead>
<tr>
<th>Variation in ZnCl$_2$</th>
<th>Surface Area (m$^2$/g)</th>
<th>Pore Volume (cm$^3$/g)</th>
<th>Pore Size (nm)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnCl$_2$ (wt. %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>395.11</td>
<td>0.199</td>
<td>3.73</td>
<td>18.26</td>
</tr>
<tr>
<td>1.39</td>
<td>415.30</td>
<td>0.226</td>
<td>3.96</td>
<td>18.69</td>
</tr>
<tr>
<td>2.75</td>
<td>436.07</td>
<td>0.242</td>
<td>4.23</td>
<td>21.20</td>
</tr>
<tr>
<td>5.35</td>
<td>474.32</td>
<td>0.343</td>
<td>4.43</td>
<td>26.33</td>
</tr>
<tr>
<td>10.16</td>
<td>599.02</td>
<td>0.555</td>
<td>4.56</td>
<td>35.48</td>
</tr>
</tbody>
</table>
Figure 4.14. The distribution between mesoporous and microporous (a) surface areas and (b) pore volumes of ordered porous carbon-silica composites varied by ZnCl$_2$ content.

The XRD spectra reflect that the crystalline features become more disordered with the introduction and increased concentrations of zinc chloride within the ordered mesoporous carbon-silica network. In addition, the crystalline peak intensity decreases with higher concentrations of chemical activation reagent in use. The original sample with 0 wt. % zinc chloride has two resolved diffraction peaks which are indexed at 10 and 20 are part of the two-dimensional (2-D) hexagonal symmetry space group $p6m$. The strong XRD peak shifted leftward with higher concentration of zinc chloride (Figure 4.15). Due to the use of porogens, the strong peak at 0.8504° ($a_0 = 11.99$ nm) shifted to $\sim 0.6^\circ$ ranging from 0.61-0.68° with d spacing ranging from 14.47-12.97 nm, respectively ($a_0 = 16.70-14.98$).

The change in crystallinity to more disordered and less uniformed pore structure is also evident by TEM. Figure 4.16 shows that the pore structures within the TEM images become less resolved with the introduction of porogens within the carbon silica composite. The pore structure appears to be more distorted. This may be due to the interaction between the zinc compounds...
with the carbon and silica atoms within the carbon silica network at temperatures higher than 732°C during carbonization resulting in the widening of the atomic layer leading to some disorder within the pores. The surface morphologies seen in the SEM images in Figure 4.17 appear to be rougher with the contribution of higher porosity by the incorporation of zinc chloride.

TGA curves show weight losses of 45-59% between 405°C to 615°C for carbon-silica composites when zinc chloride is used to increase porosity. The carbonized composite with the highest zinc chloride content consisted of 59% carbon and 41% silica. The incorporation of zinc chloride as a porogens resulted in increased carbon content when more pores were formed in the carbon-silica network.
Figure 4.15. Powder XRD of ordered mesoporous carbon-silica composites prepared with resol and F-127 as the carbon precursor; TEOS as the silica precursor; and (a) 0 wt. %, (b) 1.39 wt. %, (c) 2.75 wt. %, (d) 5.35 wt. %, and (e) 10.16 wt. % aqueous zinc chloride added as a porogen.

Figure 4.16. TEM images of ordered mesoporous carbon/silica prepared with resol and F-127 as the carbon precursor, TEOS as the silica precursor and (a) 0 wt. %, (b) 2.75 wt. %, and (c) 10.16 wt. % aqueous zinc chloride added as a porogen.
Figure 4.17. SEM images 10kV at lower magnification (a-c) and higher magnification (d-f) of ordered mesoporous carbon/silica prepared with resol and F-127 as the carbon precursor, TEOS as the silica precursor, and (left panel) 0 wt. %, (center panel) 2.75 wt. %, and (right panel) 10.16 wt. % aqueous zinc chloride added as a porogen.

Figure 4.18. (a) TGA curves and (b) carbon and silica composition of as made ordered mesoporous carbon silica nanocomposites with varying concentrations (wt. %) of ZnCl$_2$ in aqueous solution.
4.4.3. Conductivity and Durability Results

Preliminary corrosion resistant durability studies were conducted by placing 20mg of the as-made carbon-silica catalyst supports in 1.5 M sulfuric acid solution at approximately 60°C for 30 minute intervals, removed, and rinsed with water and filtered based on a previous study by Uchida (Uchida, 1995). It was observed that the color of the sulfuric acid solution gradually changed. The change in color of the sulfuric acid solution is indicative of carbon support dissolution. The time was recorded for when the carbon-silica nanocomposite was completely dissolved. An optimized chemistry was used for the randomly disordered composite of 5 samples with molar ratios of 0.25:1 (8.42%:20.48%), 0.5:1 (15.54%:18.88%), 1:1 (25.88%:15.74%), 1.5:1 (29.44%:11.93%), and 2:1 (35.75%:10.86%) sucrose: silica, respectively with the amount of zinc chloride held constant at 2.72g (7.2-13.58 wt.% decreasing in concentration with higher sucrose concentration). Samples with higher concentrations of silica took longer to dissolve in highly acidic environments, as shown in Figure 4.19(a).
Electrically conductivity measurements of 0.15, 0.37, 0.78, 1.56, and 2.17 S/cm were obtained from four point probe measurements (Figure 4.19(b)), which are significantly less than obtained values from activated carbon ranging from 5-35 S/cm. It is evident that optimization of conductivity is due to increased carbon content. Further work of including carbon nanotubes in the carbon-silica matrix can provide tuning of electrical conductivity. Platinum nanoparticles (~10µgPt/cm²) were deposited on as-prepared carbon-silica support materials for fuel cell electrodes. Commercially produced Vulcan XC-72 activated carbon was used as a test reference material. Previously, standard accelerated thermal sintering experiments were conducted as an oxidation test to evaluate durability, with carbon-silica aerosol particles with 10% silica (Hu, 2007). Hu et al. reported weight loss of carbon-silica nanocomposite of only 3% after one sintering test as compared with activated carbon with a 40% weight loss. In this case, durability testing was completed using electrochemical testing on the rotating disc electrode. The findings summarized in Table 4.6 are significantly lower than those produced from activated carbon.
Even though the as-prepared chemically activated carbon-silica nanocomposites had large BET surface areas ranging from 140-600 m²/g, the pore size was only tuned on the range of 4-8 nm. Adequate pore size for fuel cell supports need to be on the order of 12-20 nm to obtain adequate platinum loading to achieve increased specific surface areas and specific activity. Thus, higher concentrations of chemical activation should be used to obtain larger pore sizes to optimize durable carbon support materials for fuel cells.

Table 4.6. Rotating Disc Electrode Electrochemical Testing Results

<table>
<thead>
<tr>
<th>Sucrose (wt. %)</th>
<th>Loading (µgₚt/cm²)</th>
<th>Specific Surface Area (m²/gₚt)</th>
<th>Mass Activity (A/mgₚt)</th>
<th>Specific Activity (µA/cm²ₚt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.42</td>
<td>10</td>
<td>31</td>
<td>0.031</td>
<td>59</td>
</tr>
<tr>
<td>15.54</td>
<td>10</td>
<td>34</td>
<td>0.037</td>
<td>62</td>
</tr>
<tr>
<td>25.88</td>
<td>10</td>
<td>37</td>
<td>0.041</td>
<td>79</td>
</tr>
<tr>
<td>35.75</td>
<td>10</td>
<td>49</td>
<td>0.045</td>
<td>88</td>
</tr>
<tr>
<td>Vulcan-XC72</td>
<td>14</td>
<td>86</td>
<td>0.110</td>
<td>130</td>
</tr>
</tbody>
</table>

4.5. Conclusion

Durability is a significant technical barrier for the acceptance of fuel cells as a practical power source. The main requirements for suitable carbon-based supports for fuel cells are: high surface area, good electrical conductivity, suitable porosity to allow good reactant flux, and high stability in fuel cell environment. Mesoporous corrosion resisted fuel cell catalyst supports can be designed by incorporating the conductivity and low cost of carbon based materials with the chemical robustness of ceramic materials. Chemical activation methods have been used to tune the surface area, pore volume, and pore-size distribution of the fabricated carbon ceramic materials. Disordered porous nanocomposites were synthesized using a simple self-assembly process with a silicate species, sucrose, and zinc chloride as a chemical activation reagent in aqueous media. The porosity of the carbon-silica nanocomposites is tuned by adjusting the
amount of activation agent. Increased concentrations of porogens resulted in larger surface areas, pore volumes, and pore sizes contributing to the development of mesopores. Increased porosity (pore size and pore volume) resulted in higher carbon content within the composites. Changes in aqueous sucrose solutions resulted in the presence of more microporous features with increasing concentrations of carbon precursor.

The co-assembly of the Pluronic F-127 surfactant, silica, and phenolic resins via sol-gel polymerization, followed by carbonization to decompose the surfactant, lead to the generation of mesoporous carbon silica composites with ordered 2-D hexagonal channel structure. Similar to the results with randomly disordered mesoporous carbon silica, the incorporation of porogens into a carbon silica network, which self assembles into ordered pore structure, resulted in carbon silica networks with increased surface areas, pore volumes, and pore sizes. In addition, the incorporation of zinc chloride as a porogens resulted in increased carbon content when more ordered pores were formed in the carbon-silica network. Preliminary corrosion resistance testing concludes that additional optimization of the synthetic routes to produce carbon-silica composites with increased pore sizes shall lead to corrosion resistance features better than activated carbon. Increased activation agent concentration should be explored to tune the pore size.
5.1. Abstract

Highly conductive multi-walled carbon nanotubes were incorporated into mesoporous carbon-based networks to improve electrical conductivity. Functionalized MWNTs provided additional conductive pathways into the polymer network. Evaporation induced self-assembly (EISA) at room temperature of carbon, consisting of a phenol-resin and Pluronic F-127 as a structure directing surfactant was mixed at the molecular level with hydrolyzed TEOS, with the addition of carbon nanotubes at 0, 0.05, 0.5, and 1 wt. %. The presence of carbon nanotubes were confirmed from SEM, TEM, increased carbon weight loss in thermogravametric analysis, increased nitrogen uptakes with in IV-isotherms, and XRD shifts to larger unit cell values \(a_0\). Increased carbon nanotube concentrations resulted in increased surfaces areas ranging from 195.15-574.62 m\(^2\)/g, and improved electrical conductivity. An order of magnitude increase in conductivity, 1 S/cm, was achieved with the addition of 0.5 wt. % CNTs. Dispersion issues due to the agglomeration of CNTs during the drying process prevented each nanotube from being loaded over a maximum interfacial area. In order to improve the dispersion of carbon nanotubes...
within the carbon-silica network, electrospinning was explored as a method to provide improved alignment of the carbon nanotubes. Electrospun fibers resulted in samples with the highest surface areas (333.36 m²/g) and concentrations of CNTs (1.0 wt. %) achieving 2.09 S/cm of conductivity. Capacitance measurements were calculated to examine if improved conductivity results in higher capacitance values. The best capacitance performance was 148 F/g carbon-based mesoporous composites with 0.5 wt. % CNTs in an aqueous electrolyte with a 2.0 mV/s scan rate. An 80% increase in capacitance occurs with the addition of 0.5 wt. % CNTs.

5.2. Introduction

Extensive research has been conducted on improving the macroscopic properties of polymers and other carbon-based materials by incorporating nanotubes into the polymer matrix. Carbon nanotubes (CNTs) exhibit superior mechanical, thermal, and electrical properties, attracting great interest as advanced nano-reinforcements in various types of polymer composites (Tomànek, 2000). The graphite nature of the CNT lattice results in a fiber with high strength, stiffness, conductivity, and aspect ratios (small diameter and long length), which lead to promising performance characteristics for a variety of nano-material applications (Pierson, 1993; Dresselhaus, 1996). These properties offer CNTs great potential for a variety of applications including: field emission devices, hydrogen storage, chemical sensors, nano-electronic devices, energy storage, structural materials, fibers, and heterogeneous catalyst supports (Thostenson, 2001; Ajayan, 2003; Coleman, 2006; Tan, 2007). Even using relatively low loadings (concentrations), the inclusion of nanotubes has greatly demonstrated enhanced macroscopic properties for the polymers (Ma, 2010).
The electrical properties and electric current carrying capacity of carbon nanotubes are approximately 1000 times higher than copper wires (Collins, 2000). This feature has motivated a number of attempts to fabricate CNT/polymer nanocomposites in the development of high performance composite materials where carbon nanotubes are dispersed within polymer networks to improve the electrical conductivity (Pötschke, 2002). The network-like structures of CNTs introduce conducting paths that considerably improve the conductivity and other electrochemical properties of the composites (Golikand, 2010). Furthermore, the carbon nanotubes low dissipation energy enables them to carry tremendous current densities as well (Dresselhaus, 1996).

The electrical conductivity of such composites depends significantly on the concentration of the conducting phase and the extent of its continuity. With gradually increasing carbon nanotube concentrations, composites undergo a percolation transition where the electrical conductivity of the composite jumps up several orders of magnitude (Liu, 2004). This behavior is attributed to the formation of a conducting network of carbon nanotube content that is at or above the percolation threshold. Kymakis et al. reported the electrical and optical properties of single-walled carbon nanotube (SWCN)/poly(3-octylthiophene) composites (Kymakis, 2002). As the nanotube concentration increased from 0 to 20 wt. %, the conductivity of the casting films increased by five orders of magnitude. In this case, the percolation threshold was about 11 wt. % (Kymakis, 2002). Unfortunately, the percolation threshold values led to difficulties in establishing definite conclusions about the electrical conductivity from previously published studies of various polymer composites (Kymakis, 2002). The reported levels of CNT loading required to achieve a percolation concentration (an appreciable increase in electrical conductivity) vary widely, ranging from 0.002 to over 4%, depending on the type of CNTs and
the processing techniques used to produce the nanocomposites (Grimes, 2000). One of the other issues leading to a variety of reported data includes the impurities and structural defects inherent in MWNT’s, which leads to difficulties in obtaining reproducible samples due to the tendencies of variations from batch to batch of the produced MWNTs (Kymakis, 2002).

While carbon nanotube composites have shown great promise, inadequate dispersion is the most cited process limitation in nanocomposites that contain MWNT’s. Due to the significant bundling tendency (agglomeration) of carbon nanotubes, early investigators struggled to find appropriate processing methods that had the ability to disperse the nanotubes adequately throughout the matrix. For CNT/polymer nanocomposites, ‘good dispersion’ has two different meanings: i) ‘disentanglement’ of bundled CNTs or agglomerates, which is ‘nanoscopic dispersion’ and ii) ‘uniform distribution’ of individual CNTs or CNT agglomerates throughout the nanocomposites, which is more of ‘micro- and macroscopic’ dispersion.

Improved dispersion of CNTs in the polymer matrix is of great use for modifying the physical properties of the polymer matrix (Moniruzzaman, 2006). It is important that the individual nanotubes are distributed uniformly throughout the matrix and well-separated from each other; the presence of agglomerates is extremely undesirable, particularly if the carbon-based matrix does not fully penetrate the agglomerate during processing (Moniruzzaman, 2006). The agglomerating tendency and poor dispersibility of carbon nanotubes (CNTs) in common solvents is caused by electrostatic interactions and strong inter-tube van der Waals interactions. With good dispersion each nanotube is loaded individually over a maximum interfacial area.

Solution blending has been utilized to disperse carbon nanotubes within the nanocomposite network. Solution blending involves dispersion of nanotubes with high powered wand sonication in a polar solvent with medium to low viscosity. The most common techniques
used to fabricate CNT-composite materials are solution casting, melt processing, wet spinning, and electrospinning. Electrospinning is an interesting process for producing non-woven fibers and is considered a simple and effective technique for the making of polymer fibers, inorganic fibers, and composite fibers with average diameters ranging from micro to nanoscales. In this process, a fiber is drawn from a polymer solution or a melt by applying high electrostatic forces to deposit on a metallic collective screen.

Carbon nanotubes provide an alternative way to improve the electrical properties of insulating ceramics. The conductivity of carbon-based nanocomposites are limited by the intrinsic conductivity of amorphous carbon materials, which has a conductivity value of $3.33 \times 10^{-2}$ S/cm (Stransfield, 1914). MWNTs have conductivity measurements from $1.2 \times 10^3$-5.1x10$^6$ S/cm (Liu, 2004). Originally, carbon silica nanocomposites were synthesized (via a sol-gel processing with EISA at room temperature) to improve durability through enhanced porosity and tuning composition. Chemically modified MWNTs with carboxyl, ketone, and hydroxyl groups have been added to similar chemistries to determine if electro-conductivity improvement is possible (Gao, 2005). Electrospinning is also being explored as an additional process to fabricate hybrid carbon silica materials (Ramakrishna, 2005). The properties of these materials as fibers are being explored; in particular, the ability for carbon nanotubes to be better dispersed in a more viscous carbon silica network has been examined.

In this work, the influence on MWNT’s on the electrical conductivity performance and capacitance behavior as a function of loading and sample preparation of ordered carbon-silica nanocomposites are explored. The synthesis and characterization of carbon-based-carbon nanotube nanocomposites fabricated using EISA at room temperature and electrospinning are
being reported. These materials need to be further developed as potential electrode material for energy conversion and storage systems such as fuel cells and supercapacitors.

5.3. Experimental Approach & Characterization

5.3.1. Chemicals

Nitric acid (70%, Sigma Aldrich), Sulfuric acid (95-98%, Sigma Aldrich), Tetraethyl orthosilicate (TEOS) (98%, Sigma Aldrich), Sodium Hydroxide (97%, Sigma Aldrich), Hydrochloric Acid (37%, Sigma Aldrich), Ethanol (99.5%, Sigma Aldrich), Phenol (99%, Sigma Aldrich), Formaldehyde (37%, Sigma Aldrich), Poly(acrylic acid) (MW = 450,000, Sigma Aldrich), and Poly(propylene oxide)-poly(ethylene oxide)-poly(propylene oxide) triblock copolymer Pluronic F-127 (MW = 12,500, Sigma) were all used as received. Distilled water was used in all experiments. Multi-walled carbon nanotubes were synthesized using a catalytic chemical-vapor deposition in a nanoagglomerate fluidized bed. Commercially available activated carbon (Yihuan Carbon Co., Ltd. Fuzhou, China) was used for electrode fabrication.

5.3.2. Functionalizing Multi-walled Carbon Nanotubes

In order to modify the surface chemistry and improve dispersion, the carbon nanotubes were subjected to oxidation. Treating carbon nanotubes with nitric acid or other oxidants purifies and creates various functional groups such as –COOH, -OH, and –C=O on the nanotubes’ surfaces. According to previous reports by Gao, oxidizing carbon nanotubes by boiling in concentrated HNO₃ will create approximately 10²¹ active sites per gram of carbon nanotubes (Gao, 2005). The multi-walled carbon nanotubes were immersed in mixture of H₂SO₄ and HNO₃ with a volume ratio of 1:3. H₂SO₄ absorbs the water produced by HNO₃ and the carbon
nanotubes, and makes the reaction continuous (Gao, 2005). Oxidized nanotubes were obtained by refluxing 12.0g of multi-walled carbon nanotubes in 100 mL of HNO₃ and 300 mL of H₂SO₄ at 100°C for 100 minutes (Gao, 2005). The carbon nanotubes were washed with distilled water and separated by centrifugation, and later filtered. The yield is about 4 grams (33.33%). The functionalized carbon nanotubes were ground into fine powder via ball milling. Note, ball-milling leads to CNTs with decreased aspect ratios, but provides improved dispersion within polymer networks of composite materials.

5.3.3. Incorporation of MWNTs into Ordered Mesoporous Silica-Carbon Composite

5.3.3.1. EISA at Room Temperature

The co-assembly of inorganic (silica) and organic (phenol and triblock copolymer surfactant) phases from the sol gel process and subsequent carbonization is utilized to prepare silica-carbon nanocomposites. Initially, a large batch of resol precursor was made using 12.2g of phenol, 2.6g of 20 wt. % NaOH, and 21g of formaldehyde. The solution was heated while stirring to 75°C under reflux, and later neutralized at room temperature to pH 7 by 0.6M HCl. Water was removed by vacuum evaporation below 50°C, and the final viscous product was dissolved in ethanol making a 20 wt. % resol solution. Next, 3.6 g of F-127 was dissolved in 16.0g of ethanol with 2.0g of 0.2M HCl and stirred for 1 hour at 40°C. Then 4.16g of TEOS and 12.5g of 20 wt. % resol/ethanol solution were added to the surfactant mixture and stirred for 2 hours. Five trials were conducted requiring additional stirring and ultrasonication of varying amounts of carbon nanotubes in an water: ethanol (4:1%vol) solution (0, 0.05, 0.5, and 1.0 wt. % respectively, dissolved in 2.0g of DI aqueous solution) for 1 hour into the carbon silica matrix.
Next, the mixtures were poured into glass dishes and dried in air at 25°C for 1 day to evaporate the ethanol, then placed in an oven and thermopolymerized at 100°C for 1 day. After removal from the oven, the evaporation of solvent, and condensation and hydrolysis of TEOS was complete. The nanocomposites were then carbonized in a tubular furnace, heating under nitrogen at 1°C/min from 100°C-600°C, 5°C/min from 600°C-900°C, and held at 900°C for 4 hours.

5.3.3.2. Additional Thermal EISA Methods

Thermal drop casting was conducted in a glove box under the flow of nitrogen. The carbon nanotubes/silica/polymer mixture from the aforementioned synthetic approach was dropped onto a heated silica wafer, as opposed to casting in glass dishes and dried at room temperature. The temperature of the wafer was approximately 100-120°C. The solidified material was collected off of the wafer and carbonized in the tubular furnace to 900°C at 1°C/min, 5°C/min from 600°C-900°C, and held at 900°C for 4 hours.

In the aerosol assisted method, the carbon nanotubes/silica/carbon precursor was generated into an aerosol dispersion within a tubular reactor heated to 650°C using a commercialized atomizer (Model 3076, TSI, Inc., St Paul, MN) operated with nitrogen as a carrier/atomization gas. The aerosol equipment consists of three parts: (a) the Pneumonic atomizer, (b) the tube furnace, and (c) the collecting filter. The atomizer produces aerosol droplets from the carbon-nanotubes/silica/polymer solution by use of high pressurized carrier gas. In the drying zone prior to the entrance of tube furnace, the solvent (in this case a mixture of ethanol and water) of the aerosol droplets is evaporated while the solution concentration of droplets is increased. In the heating zone within the tube furnace, pyrolysis takes place at 650°C.
In the filter region, the products are cooled down and collected on the filter paper. The sample is collected on filter paper and retrieved by dissolving the filter paper in acetone. The final product was then carbonized in a tubular furnace to 900°C at 1°C/min.

5.3.4. Electrospinning

The reactants used for electrospinning are the same as the previous section with the addition of poly(acrylic acid) (PAA) to increase viscosity of the precursor used for electrospinning. PAA was added to the combined polymer-silica solution prior to the addition of the carbon nanotube solution. The amount of each chemical used includes: 1.5g F-127, 2.5g ethanol, 1.0g 2.0M HCl, 2.08g TEOS, 1.0g Resol in 20 wt.% ethanol, 2.85g PAA, and varying amounts of carbon nanotubes (0, 0.05, 0.5, and 1.0 wt.%). The entire solution with carbon nanotubes was ultrasonicated for 1 hour to obtain a homogenous dispersion, before immediately being drawn in a syringe and electrospun.

The prepared solution was added to a 10-mL plastic syringe with a 0.5 mm diameter needle tip. The feeding rate of the polymer solution was controlled by a syringe pump at 1.0 mL/h. The electrospinning voltage (15 kV) was applied to the needle and the distance between the needle tip and collector was 11 cm. At a critical voltage, the jet of the polymer solution came out from the needle tip and was collected on the collector. When the solvent evaporated, a non-woven carbon-silica-carbon nanotube mat was formed. The electrospun fibrous material was carbonized in a tubular furnace, heating under nitrogen at 1°C/min from 100°C-600°C, 5°C/min from 600°C-900°C, and held at 900°C for 4 hours.
5.3.5. Characterization

Nitrogen adsorption isotherms were determined at 77K using a Micromeritics ASAP 2020 Surface Area and Pore Size Analyzer (Micromeritics Instrument Corporation, Norcross, GA) to calculate the Brunauer Emmett Teller (BET) specific surface area using adsorption data in a relative pressure range from 0.04 to 0.25. Samples were degassed in vacuum at 200°C for 5 hours. Barrett Joyner Halenda (BJH) model was used to calculate pore size distributions and pore volumes derived from the adsorption isotherm. The total pore volume was estimated from the adsorption amount at a relative pressure (P/P₀) of 0.97. The micropore volumes and surface areas were calculated from the V-t plot method. The JEOL-6700F FE-SEM (JEOL Ltd., Japan) was used for scanning electron microscopy to examine surface morphology. TEM experiments were conducted on a Philips CM120 operated at 120 kV (Philips/FEI Inc., Eindhoven, The Netherlands) providing information on internal structures and morphologies. Powder X-ray diffraction (XRD) spectra were obtained using a PANalytical X’Pert Pro X-ray diffractometer. Ni-filtered Cu Kα radiation with λ = 1.5418 Å and the copper anode was operated at 40 kV and 30 mA. XRD was utilized to identify crystallinity and provide information on unit cell dimensions. The unit cell parameters were calculated from the formula a = 2d₁₀/√3 . The composition of the various nanocomposite materials with carbon and silica content will be determined based on carbon weight loss using thermogravimetric analysis (TGA) on a Perkins-Elmer Pyris 6 TG Analyzer at a heating rate of 5°C/min from 25-1000°C under nitrogen.

5.3.5.1. Conductivity

Four-point probe analysis was completed to obtain the resistivity of the as-prepared samples. The carbonized samples were compressed at high pressure (5000 psi) between two
copper electrodes, and a known electrical current (I) was passed through the sample and the measured voltage (V) was measured between two points at a known distance along the compressed sample (Do, 2010). The measured voltage was used to calculate the samples resistivity.

5.3.5.2. Capacitance Measurements

Carbon based materials with MWNTs incorporated in the carbon network have been assembled into electrodes to evaluate capacitance performance. Electrodes were obtained by coating an active mass of approximately 1–2 mg onto each current collector (0.5 × 0.5 cm). Electrodes have been prepared by synthesizing slurries consisting of active materials, carbon black (as a conductive agent), and a binder followed by coating on nickel foam. The slurries consist of 80% of the active material (synthesized carbon based materials), 10% carbon black, and 10% poly(vinylidene fluoride) (PVDF) which were all dispersed in N-methylpyrrolidinone (NMP). The as-prepared samples were ultra-sonicated and mechanically stirred forming a homogenous mixture. The homogenous slurries were coated onto nickel-foam substrates and dried at 80°C for 10 min under vacuum. Next, the samples were pressed at a pressure of 2 MPa and further dried under vacuum at 100 °C for an additional 12 h to produce dry electrodes.

Cyclic voltammetry have been conducted for electrochemical testing. Platinum foil and an Ag/AgCl electrode have been used as the counter electrode and the reference electrode, respectively. The electrochemical measurements were conducted on a Solartron 1860/1287 Electrochemical Interface (Solartron Analytical, Oak Ridge, TN) apparatus. The electrolyte solutions used were aqueous 1M H₂SO₄ and aqueous 0.2M NaCl. CV measurements were
carried using cut-off voltages of –1.5 V and 1.2 V versus Ag, and scan rates of 2, 5, 10, 20, 50, and 100 mV/s.

The capacitance, power, and energy density can be calculated based on the total mass or volume of both the anode and cathode materials. Energy density is calculated using Equation 5.1

\[ E = \frac{1}{2} CV^2 \]  

(5.1)

where \( C \) is the capacitance and \( V \) is the cell-operation potential. The discharge curve of galvanostatic cycles were used to calculate the specific capacitance \( C_s \) (F/g).

\[ C_s = I/(dV/dt) \approx I/(\Delta V/\Delta t) \]  

(5.2)

In equation 5.2, \( I \) is the constant discharge current density, \( \Delta V \) is the voltage difference in the discharge cycle, \( \Delta t \) is the time taken for the voltage drop, and the slope of the discharge curve (scan rate) is represented by \( dV/dt \).

5.4. Results/Discussion

5.4.1. EISA at Room Temperature

Functionalized multi-walled carbon nanotubes were added to a homogenously mixed carbon precursor of phenol resin, F-127 surfactant, and hydrolyzed TEOS. In these studies the addition of carbon nanotubes on the range of 0.05-1.0 wt. % provided a significant increase in surface area (Table 5.1). The size effect of CNTs based on them having small diameters (nanometer scale) with high aspect ratios (>1000) leads to increased surface areas when CNTs are incorporated into composites as fillers. The surface area increased by 40% from the addition of 0.05 wt. % CNTs. The nitrogen isotherms in Figure 5.1 reflect type IV isotherms with H2 hysteresis indicating that these materials are highly mesoporous. The introduction of the carbon nanotubes to the carbon-silica networks provides a small order of microporosity, less than 6%,
both in surface area and volume to the composites (Figure 5.2). Another feature based on the size effect of CNTs, is additional microporosity introduced into the polymer/carbon-based system due to the addition of very short distance between the polymer matrix and the CNTs. This effect (short distances between polymer matrix and CNTs) also results in the properties of the composites being largely modified even at an extremely low content of CNTs.

(a)  
(b)  

Figure 5.1. (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution of mesoporous ordered carbon-silica with multi-walled carbon nanotubes incorporated into the carbon-silica matrix

(a)  
(b)  

Figure 5.2. The distribution between mesoporous and microporous (a) surface areas and (b) pore volumes of ordered carbon-silica composites with multi-walled carbon nanotubes added to the carbon-silica network
Table 5.1. Total Surface Areas, Total Pore Volumes, and Pore Sizes of ordered carbon-silica composites with the addition of multi-walled carbon nanotubes.

<table>
<thead>
<tr>
<th>Incorporation of Carbon Nanotubes (wt. %)</th>
<th>0.0 % CNTs</th>
<th>0.05 % CNTs</th>
<th>0.5% CNTs</th>
<th>1.0% CNTs</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET Surface Area (m$^2$/g)</td>
<td>195.16</td>
<td>272.97</td>
<td>405.33</td>
<td>574.62</td>
</tr>
<tr>
<td>Pore Volume (cm$^3$/g)</td>
<td>0.531</td>
<td>0.249</td>
<td>0.541</td>
<td>0.728</td>
</tr>
<tr>
<td>Pore Diameter (nm)</td>
<td>3.64</td>
<td>3.89</td>
<td>4.80</td>
<td>5.08</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>26.83</td>
<td>27.65</td>
<td>38.51</td>
<td>40.23</td>
</tr>
</tbody>
</table>

Table 5.2. Total Surface Areas and Pore Sizes of 0.5% HF silica etched ordered carbon-silica composites with the addition of multi-walled carbon nanotubes used for capacitance measurements.

<table>
<thead>
<tr>
<th>Incorporation of Carbon Nanotubes (wt. %)</th>
<th>0.0 % CNTs</th>
<th>0.05 % CNTs</th>
<th>0.5% CNTs</th>
<th>1.0% CNTs</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET Surface Area (m$^2$/g)</td>
<td>1272.45</td>
<td>1398.11</td>
<td>1601.58</td>
<td>1754.25</td>
</tr>
<tr>
<td>Pore Diameter (nm)</td>
<td>4.91</td>
<td>5.03</td>
<td>5.11</td>
<td>5.22</td>
</tr>
</tbody>
</table>

X-ray diffraction patterns were taken to determine if the porosity of these amorphous carbon-based materials contained some distribution of ordered pore structure. The XRD spectra have a strong 2θ peak around 0.5 degrees, reflecting that the sample has some degree of ordered mesoporosity. This strong peak can be indexed at (10) reflection associated with 2D hexagonal $p6m$ symmetry (Zhao, 1998). The sample without any carbon nanotubes peak was located at 0.54°, however the addition of the nanotubes shifted the peak left to approximately 0.48-0.49°, creating larger unit-cell parameter values $a_0$, on the order of 20 nm due to increased carbon content from the nanotubes.
Figure 5.3. (a) Powder XRD patterns and (b) unit cell, \(a_0\), values of mesoporous order carbon-silica nanocomposites with various amounts carbon nanotubes added to the carbon-silica network.

The framework composition was examined through TGA analysis shown in Figure 5.4 (a). The initial carbon-silica composite with no carbon nanotubes had approximately a 20% weight loss in the temperature range of 485-630°C attributed to the carbon compound within the nanocomposite. This reflects a carbon-silica nanocomposite with 79.22% silica and 20.78% carbon. This was also confirmed by energy-dispersive X-ray (EDX) spectroscopy (Figure 5.4(b)) which provided a semi-quantitative atomic ratio of Si: C: O 81.40: 13.58: 5.03, respectively. Assuming that most of the oxygen atoms are bonded to Si to form silica, since Si-O is thermodynamically more favorable to form than C=O with bond energies of 452 kJ/mol and 745 kJ/mol, respectively. It should be noted that based on the original amounts of reactants, 4.16g of hydrolyzed TEOS and 12.5g of 20 wt. % resol in ethanol (which were held constant), the mass...
ratio of silica to carbon precursor was 1.66: 1. This is reflected in all the samples having a higher content of silica. Incorporating and increasing the concentration of carbon nanotubes within the carbon-silica network resulted in weight loss increases of 5.3%, 9.8%, and 21.8% respectively, reflecting a definite increase in carbon content.

The incorporation of carbon nanotubes within the carbon-silica matrix provided a significant increase in conductivity (Figure 5.5). However, the conductivity value decreased at the highest carbon nanotubes concentration of 1.0 wt. %, which may have been due to dispersion and agglomeration issues. Thus the carbon nanotubes were not uniformly loaded and their properties were not efficiently translated into the carbon-silica composite at high concentrations.

![TGA curves of ordered mesoporous carbon-silica composites with the addition of varied amounts of carbon nanotubes within the carbon-silica network.](a)

![EDX spectrum of an ordered mesoporous carbon-silica composite with 0% CNTs.](b)

Figure 5.4. (a) TGA curves of ordered mesoporous carbon-silica composites with the addition of varied amounts of carbon nanotubes within the carbon-silica network. (b) EDX spectrum of an ordered mesoporous carbon-silica composite with 0% CNTs.
Figure 5.5. Electrical conductivity measurements for carbon nanotubes inside the carbon-silica network made using evaporation induced self-assembly at room temperature

TEM images were taken of the samples with 0.5 wt. % of carbon nanotubes. In Figure 5.6(b) areas of local ordered pore structure are evident, which confirms the XRD peak for crystallinity. However, the pores have some distortion with addition of the carbon nanotubes in comparison to the original ordered mesoporous carbon-silica network. In addition, the dispersion and agglomeration issues as previously discussed are seen looking at the internal pores structures of the carbon-silica-CNT composites. The surface morphology images from the SEM Figures 5.6 (c-d) show the carbon nanotubes (the light colored straw materials) on top of the carbon-silica composite. Some of the carbon nanotubes are also penetrating through the parent carbon-silica network which is seen in the highly magnified image in Figure 5.6(d).
Figure 5.6. (a-b) TEM, (c) SEM 10kV at 3K magnification, and (d) SEM 5kV at 35K images of 0.5 wt. % multi-walled carbon nanotubes within the carbon-silica nanocomposites. (e-f) TEM, (g) SEM 5kV at 3.3K magnification, and (h) SEM 5.6kV @ 35K images the carbon-silica nanocomposites with 0 wt. % carbon nanotubes.
As CNTs are produced they are held in bundles or entanglements consisting of 50 to a few hundred by van der Waals forces. It has been proven that these bundles agglomerate resulting in diminished mechanical and electrical properties of composites as compared with theoretical predictions related to individual CNTs. Thus, the challenge is incorporating individual or at least relatively thin CNT bundles or disentangled CNTs inside a polymer matrix.

During composite synthesis using room temperature, EISA agglomeration was evident after a few hours while the casted samples were drying at room temperature. In response to this issue, the precursor solution of the carbon-based-CNT composite was dried using rapid drying EISA methods of thermal casting and aerosol methods. Increased conductivity was seen with the incorporation of carbon nanotubes in carbon-silica nanocomposites prepared using both thermal casting and the aerosol method (Figure 5.7). However the best conductivity performance of 1 S/cm is seen with evaporation induced self-assembly at room temperature with the addition of 0.5 wt. % of carbon nanotubes. Since solvent evaporation methods did not improve dispersion issues, electrospinning was considered as another method to fabricate composites. Electrospinning is being explored as a technique for the alignment of CNTs in the carbon-silica matrix in order to improve dispersion and reduce agglomeration.
Figure 5.7. Conductivity measurements for carbon nanotubes inside the carbon-silica network made using (a) thermal casting at 100-120°C and (b) the aerosol method.

Capacitance testing was conducted to determine if the introduction of carbon nanotubes resulted in improved capacitance in the as-prepared carbon-based composites. In order to fabricate porous carbon symmetric electrodes with high surface areas, silica was removed from the carbon-silica-CNT composite by etching in 5% hydrofluoric acid. In the case of the carbon-based composites with no silica, the strong XRD peak was located at 0.51° for the sample with no carbon nanotubes and shifted to approximately 0.42-0.43°, indicating that the crystallinity remained in the framework after the silica was removed.

Higher electrical conductivity is required to have high capacitance and high power density in supercapacitors. The presence of mesopores in multi-walled carbon nanotubes allow for easy access of ions at the electrode/electrolyte interface. The thin walls of a carbon nanotube allows for increased capacitance in an electric double-layer capacitor. By adding multi-walled nanotubes to these capacitors, the resistance of the electrodes can be decreased. As seen in Figure 5.8, the sample with the highest conductivity, 0.5 wt. % CNTs, had the highest
capacitance value of 148 F/g with a 2 mV/s scan rate in an aqueous electrolyte. Thus, the capacitor cells with multi-walled nanotubes had higher electron and electrolyte-ion conductivities as compared to cells made from composites that did not have these nanotubes. The cyclic voltammetry results of the four samples with 0, 0.05, 0.5, and 1.0 wt. % CNTs at scan rates of 5, 20, and 50 (mV/s) are displayed in Figure 5.9.

![Figure 5.9](image-url)

Figure 5.9. (a) The calculated specific capacitance of silica etched ordered carbon-silica nanocomposites with varied amounts of carbon nanotubes incorporated into the carbon-silica network at different CV scan rates. (b) Schematic of a cyclic voltammetry curve for the highest reached capacitance from a symmetric capacitor built with carbon-based composite with the addition of 0.5 wt. % CNTs at a 2 (mV/s) scan rate.

For electrodes built exclusively with MWNTs, specific capacitance in a range of 4-135F/g have been calculated (Frackowiak, 2000; Frackowiak, 2001). Thus the 80% increase in capacitance from 82 F/g to 148 F/g in an aqueous electrolyte is directly related to the capacitance provided from the carbon nanotubes. The limited capacitance in the as-made carbon-based carbon nanotube composites may be due to the large pore sizes on the order of 5 nm. Even
though the samples had high surface areas, >1400 m$^2$/g, the best performing electrode materials contain highly electroactive regions through the control of microporous structure. The ideal pore structure would contain the co-existence of mesopores with micropores with good 3D-interconnectivity to ensure rapid ion transport and high pore characteristics of supercapacitors (Shi, 1996). The synthesis of carbon-based-CNT composites must be improved to include more micropores within the mesoporous structure. Chemical activation with potassium hydroxide should be included in the synthetic approach to provide additional induced microporosity, since it is a known porogen for microporosity development (Tseng, 2005).

![Figure 5.9](image_url)

**Figure 5.9.** Voltammetry characteristics at (a) 5 mV/s, (b) 20 mV/s, (c) 50 mV/s of a symmetric capacitor built from silica etched carbon-silica nanocomposites with multi-walled carbon nanotubes carbons incorporated into the carbon-silica network using a 1M H$_2$SO$_4$ electrolyte.

5.4.2. Electrospun Fibers

The fibrous composites of carbon-silica with varied amounts of MWNTs incorporated into the carbon-silica matrix exhibited type-IV isotherms with H1 hysteresis loops (Figure 5.10 (a)). This indicates that the materials have large uniformly ordered mesopores. The nitrogen uptakes increased with increasing concentrations of carbon nanotubes added to the carbon-silica network, which directly increased surface areas as reported in Table 5.3. With the removal of
the silica network from the carbon-silica-CNT composite, fibrous materials ranging from 645-1000 m$^2$/g surface areas were obtained. The pore size distribution calculated from the adsorption branch based on the BJH model shown in Figure 5.10(b) is centered at approximately 4.00 nm with bimodal distribution.

![Figure 5.10](image)

Figure 5.10. (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution of electrospun mesoporous carbon-silica fibers with multi-walled carbon nanotubes added into the carbon-silica matrix

Table 5.3. Total Surface Areas, Total Pore Volumes, and Pore Sizes of Electrospun carbon-silica fibers with the addition of multi-walled carbon nanotubes.

<table>
<thead>
<tr>
<th>Carbon Nanotubes (wt. %)</th>
<th>0.0</th>
<th>0.05</th>
<th>0.5</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Area (m$^2$/g)</td>
<td>135.55</td>
<td>285.35</td>
<td>308.49</td>
<td>333.36</td>
</tr>
<tr>
<td>Pore Volume (cm$^3$/g)</td>
<td>0.32</td>
<td>0.34</td>
<td>0.37</td>
<td>0.45</td>
</tr>
<tr>
<td>Pore Size (nm)</td>
<td>9.10</td>
<td>4.80</td>
<td>5.93</td>
<td>6.47</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>28.91</td>
<td>31.87</td>
<td>36.41</td>
<td>38.02</td>
</tr>
</tbody>
</table>
Table 5.4. Total Surface Areas and Pore Sizes of 0.5% HF silica etched electrospun carbon-silica fibrous composites with the addition of multi-walled carbon nanotubes

<table>
<thead>
<tr>
<th>Carbon Nanotubes (wt. %)</th>
<th>0.0</th>
<th>0.05</th>
<th>0.5</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET Surface Area (m²/g)</td>
<td>545.12</td>
<td>687.78</td>
<td>817.26</td>
<td>1000.75</td>
</tr>
<tr>
<td>Pore Diameter (nm)</td>
<td>10.21</td>
<td>7.56</td>
<td>7.88</td>
<td>8.02</td>
</tr>
</tbody>
</table>

The addition of MWNTs into the electrospun carbon-silica fibrous composites resulted in increased microporosity in both surface areas and pore volumes on the order of 40% and 17% respectively. The enhanced microporosity indicates a better distribution of carbon nanotubes in comparison to the room temperature of self-assembly.

![Figure 5.11](image)

Figure 5.11. The distribution between mesoporous and microporous (a) surface areas and (b) pore volumes of electrospun carbon-silica fibers with multi-walled carbon nanotubes added to the carbon-silica network

The XRD spectra in Figure 5.12 confirm the ordered structure within the electrospun fibers. The strong XRD peak shifted to 1.92° for the sample without carbon nanotubes and the addition of carbon nanotubes resulted in the peak shifting to the left ranging from 1.51-1.73°,
with increasing peak intensity from the addition of more carbon nanotubes. The electrospun fibers had much smaller unit cell values, $a_0$, of approximately 6 nm.

![Graph showing XRD patterns with increasing peak intensity from addition of more carbon nanotubes.](image)

(A) 0 wt.%  
(B) 0.05 wt.%  
(C) 0.5 wt.%  
(D) 1.0 wt.%

<table>
<thead>
<tr>
<th>CNTs</th>
<th>2θ</th>
<th>d-spacing (nm)</th>
<th>$a_0$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0%</td>
<td>1.92°</td>
<td>4.591</td>
<td>5.301</td>
</tr>
<tr>
<td>0.05%</td>
<td>1.74°</td>
<td>5.074</td>
<td>5.859</td>
</tr>
<tr>
<td>0.5%</td>
<td>1.63°</td>
<td>5.427</td>
<td>6.266</td>
</tr>
<tr>
<td>1.0%</td>
<td>1.51°</td>
<td>5.850</td>
<td>6.755</td>
</tr>
</tbody>
</table>

Figure 5.12. (a) Powder XRD patterns and (b) unit cell, $a_0$, values of electrospun mesoporous carbon-silica fibers with various amounts carbon nanotubes added to the carbon-silica network

The initial carbon-silica fibrous composite contained 65% silica and 35% carbon based on thermogravimetric analysis, provided in Figure 5.13(a). The composition of the sample was also determined and compared semi-quantitatively with EDX analysis (Figure 5.13 (b)), in which the atomic ratio of Si: C: O was determined to be 53.15: 34.06: 12.79, respectively. Assuming that the majority of the oxygen content is used to make silica the contribution of silica to carbon is 65.94 to 34.06, respectively. During the TGA process organic combustion for the samples took place between 450°C to 700°C, with each sample needing a higher temperature before the drastic weight change took place. This indicates that the samples with increased amounts of carbon nanotubes have better thermal stability. Incorporating and increasing the concentration of carbon nanotubes within the carbon-silica network resulted in weight loss increases of 8%, 13%, and 29% respectively, reflecting a definite increase in carbon content, and better dispersion of carbon
nanotubes in comparison to the previously reported samples. The electrospun fiber with 1.0 wt.
% carbon nanotubes resulted in sample with 64% carbon and 36% silica.

(a) ![TGA curves](image1)
(b) ![EDX spectrum](image2)

Figure 5.13. (a) TGA curves of electrospun ordered mesoporous carbon-silica fibers with the addition of varied amounts of carbon nanotubes within the carbon-silica network. (b) EDX spectrum of an electrospun ordered mesoporous carbon-silica composite with 0% CNTs.

![Conductivity](image3)

Figure 5.14. Electrical conductivity values of electrospun carbon-silica fibers with the addition of varied amounts of carbon nanotubes within the carbon-silica network.

The higher carbon content is also reflected in higher conductivity within the electrospun composite fibers. Four-point probe measurements produced conductivity values ranging from 0.097-2.09 S/cm, which displayed in Figure 5.14(b). In addition, a trend of increased carbon
nanotube concentration and increased electro-conductivity reflects the presence of less agglomeration issues at higher carbon nanotube concentrations in electrospun fibers. Within the electrospinning process, the high porosity of carbon-silica network and the excellent wrapping of the carbon-based polymers around the CNTs resulted in enhanced conductivity. The alignment of CNTs in the electrospun nanofibers depends upon the dispersion of CNTs in the carbon-silica solution. However, during electrospinning, the alignment of CNTs is expected due to the sink flow and the high extension of the electrospun jet, which leads to less agglomeration. The alignment of CNTs within electrospun fibers has been predicted by a mathematical model reported from Dror et al. (Dror, 2003).

Figure 5.15 shows the SEM images of carbon-silica nanofibers with (a-c) 0.5 wt. % and (d-f) 0 wt. % carbon nanotubes. The pure carbon-silica nanofibers in Figure 5.15 (d-f) are straight with a smoother surface and an average diameter of about 28 nm. The average diameter increased with increasing MWNT concentrations, with the average diameters of about 126 nm with 0.5 wt. % carbon nanotubes.
Figure 5.1. SEM images (a) 10kV at 300 magnification, (b) 20kV at 10K magnification, and (c) 5kV at 25K magnification of 0.5 wt. % multi-walled carbon nanotubes within electrospun carbon-silica fibrous composites. SEM images (d) 5kV at 550 magnification, (e) 10kV at 10K magnification, and (f) 5kV at 25K of electrospun carbon-silica fibrous composites with 0 wt. % carbon nanotubes.

The multi-walled carbon nanotubes are seen within the internal structure through TEM images in Figures 5.16 (a-b). The imbedded carbon nanotubes are in alignment with the same orientation as the electrospun fiber. The ordered pore structure is maintained with the addition of the carbon nanotubes into the mesoporous carbon-silica fibers.
Figure 5.16. TEM images of electrospun carbon-silica composite fibers with (a-b) 0.5 wt. % MWNTs and (c-d) 0 wt. % CNTs

Since higher electrical conductivity is always desired to achieve increased capacitance and power density in supercapacitors, CNTs were introduced into the carbon-silica nanofibers. However, the capacitance results for the electrospun fibers are surprisingly low even though the electro-conductivity showed improvement. This may be due to lower surface areas below 1500 m$^2$/g and large pore sizes ranging from 8-10 nm. The trend of higher capacitance with higher electrically conductive material is evident, even though only a 36.58 F/g capacitance is reached (Figure 5.17).
Figure 5.17. (a) The calculated specific capacitance of silica etched ordered carbon-silica nanocomposites with varied amounts of carbon nanotubes incorporated into the carbon-silica network at different CV scan rates. (b) Schematic of a cyclic voltammetry for the highest reached capacitance from a symmetric capacitor built with carbon-based electrospun fibers with the addition of 1.0 wt. % CNTs at a 2 (mV/s) scan rate.

Figure 5.18. Voltammetry characteristics at (a) 5 mV/s, (b) 20 mV/s, (c) 50 mV/s of a symmetric capacitor built from silica etched electrospun carbon-silica fibrous composites with multi-walled carbon nanotubes carbons incorporated into the carbon-silica network using a 1M H₂SO₄ electrolyte.

5.5. Conclusion

The relationship between composition, pore structure, and conductivity has been explored in carbon-silica nanocomposites and electrospun carbon-silica fibers with MWNTs added to enhance conductivity. Carbon nanotubes exhibit superior mechanical, thermal and electrical
properties, thus leading to high potential for their ability to improve nanocomposite properties. Even using relatively low loadings, the inclusion of nanotubes has greatly demonstrated enhanced macroscopic properties. However, even after a decade of research, the full potential of incorporating CNTs into various carbon-based composites has been severely limited because of the difficulties associated with dispersion of entangled nanotubes during processing and poor interfacial interaction between CNTs and the polymer matrix. The adsorbed MWNT carbon-silica composites and fibers not only achieved improved electrical properties, but also obtained enhanced inherent characteristics, such as high porosity and surface areas. Electrospinning technique has also been used for the alignment of CNTs in the polymer matrix, and produced materials with better electrically conductive properties. Capacitance testing was conducted in order to determine if electrical conductivity leads to improved capacitance. Even though the capacitance values were only on the order of 150 F/g with 1.0 wt. % MWNTs in an aqueous electrolyte, there was a consistent trend of higher capacitance in materials with higher electrical conductivity. Further adjustments to the synthetic approach can lead to materials with improved electrical conductivity and capacitance. This feature has motivated future work to fabricate CNT-carbon-based nanocomposites in the development of high performance composite materials.

CHAPTER 6: ADDITIONAL UNPUBLISHED WORK

6.1. Porous Carbon Tubes from Perylenetetracarboxylic diimide bridged silsesquioxane (PDBS)

6.1.1. Introduction

A novel approach will be used to synthesize nanoporous carbon materials for hydrogen storage applications. Recent studies on the hydrogen storage of carbon-based materials indicate that micropores (< 2nm diameter) are most effective for hydrogen adsorption than mesopores. (Rosi, 2003) The ideal average pore size for hydrogen storage is that which can hold
two layers of adsorbed hydrogen. (Rosi, 2003; Cai, 2004) Therefore, the preparation of uniform microporous carbons with high specific surface is of great interest for hydrogen storage.

It is predicted that bridged silsesquioxane building molecules will assemble and lead to the formation of crystalline materials with ordered structure. Carbonization will lead to crystalline carbon/silica fibers with well-defined layer structure. Finally, silica removal leads to the formation of nanoporous carbons fibers with uniformed nanometer pores. Effects of morphology have been examined by varying the 3,4,9,10-perylenetetracaboxylic dianhydride (carbon precursor) concentration (Table 6.1).

**Table 6.1. Amount of carbon precursor and silane precursor used in the study**

<table>
<thead>
<tr>
<th></th>
<th>(3-aminopropyl) triethoxysilane</th>
<th>3, 4, 9, 10-perylenetetracaboxylic dianhydride</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2mL (8.6mmol)</td>
<td>0.196g (0.5 mmol)</td>
</tr>
<tr>
<td>2</td>
<td>2mL (8.6mmol)</td>
<td>0.392g (1 mmol)</td>
</tr>
<tr>
<td>3</td>
<td>2mL (8.6mmol)</td>
<td>0.49g (1.25 mmol)</td>
</tr>
</tbody>
</table>

6.1.2. Experimental Procedure

6.1.2.1. Chemicals

3,4,9,10-perylenetetracarboxylic dianhydride (97%, Aldrich), 3-aminopropyl triethoxysilane (Sigma Aldrich), Petroleum ether (Fisher Scientific), Acetone (99.7%, Fisher Scientific), and Tetrahydrofuran (99.5%, Fisher Scientific) were all used as received.

6.1.2.2. Synthesis of Porous Carbon Tubes

It is predicted that bridged silsesquioxane building molecules will assemble and lead to the formation of crystalline materials with ordered structure. Carbonization of these materials will lead to crystalline carbon/silica nanocomposites with well-defined layer structure. Finally,
silica removal leads to the formation of nanoporous carbons with uniformed sub nanometer pores. The following details the technical approach.

6.1.2.3. Synthesis of perylenetetracarboxylic diimide bridged silsesquioxane (PDBS)

Typically, 0.392 (1 mmol) of 3, 4, 9, 10-perylenetetracarboxylic dianhydride, the carbon precursor; and 1mL (4.3 mmol) of (3-aminopropyl) triethoxysilane, the silica precursor; were added into a 3 neck flask. The flask was repeatedly evacuated using a vacuum line and flushed with nitrogen. The mixture was stirred for 10 min under nitrogen, and then heated to 110°C using an electronic heating mantle until the liquid silane precursor was no longer visible. This typically occurs within 7-10 hours. During this work, it was found that the flow of nitrogen must be kept to a minimum, if not certain sections of the flask will not be at the desired 110°C resulting in a final product that is not homogenous. After cooling to room temperature, the mixture was washed with 4:1 (v/v) ratio petroleum ether: acetone to remove any excess (3-aminopropyl) triethoxysilane. The final product appeared to be a shiny needlelike red precipitate. Based on previous work reported by Lu, Y. et al., the incorporation of acetone with the petroleum ether greatly improved the ability to remove the perylenetetracarboxylic diimide bridged silsesquioxane (PDBS) product from the glassware. (Yang, 2008) Figure 6.1 shows the reaction and the chemical structure of the PDBS building block, which is stable in open air.
Figure 6.1. Schematic showing the synthesis of perylenetetracarboxylic diimide bridged silsesquioxane (PDBS)(Yang, 2008)

6.1.2.4. Self-directed assembly PDBS to form novel nanocomposite with Tubular Structure.

The above perylenediimide-bridged silsesquioxane (PDBS) solid was first mixed with tetrahydrofuran (THF) to prepare a mixture with a concentration of ~ 8.3 mg/mL based on previous findings that this concentration lead to PDBS assembling into tubes. (Yang, 2008) For example, 1 gram of PDBS crystals requires 120mL of THF. Next, at room temperature a designated volume of petroleum ether was then slowly dropped into the PDBS/THF solution with volume ratio of THF: petroleum ether being 1:5. The polar ends of the PDBS, the propyltriethoxysilane moiety, have good solubility, and the PD moiety has poor solubility in petroleum ether and THF. Increased PDBS concentration promotes assembly. The entire solution was transferred to a flat round glass dish. The solvents evaporated off at room temperature within 18-36 hours. Further hydrolysis and condensation of the triethoxysilane component of PDBS were conducted by exposing the red crystals in acidic solution of (pH = 1) for approximately 36-48 hours. The acidic solution was then centrifuged off with the final product of red crystals remaining.
6.1.2.5. Tubular Carbon Transformation

The red solid was crushed using a milling machine and transferred to a horizontal tube furnace and heated to 900 °C at 1°C/min under the flow of N₂ gas and held for 4 h at 900°C to creating a black carbonaceous solid. Finally the silica template was removed from the carbon-silica composite with 5% HF to obtain a pure carbon product.

6.1.3. Results/Discussion

The purity and chemical structure of the shiny red perylenetetracarboxylic diimide bridged silsesquioxane (PDBS) crystals were examined based on ¹H Nuclear Magnetic Resonance (NMR). Table 6.2 displays the chemical shifts reported in literature in comparison to the chemical shifts obtained in this work using 2mL of silane precursor and 0.392g of carbon precursor. The NMR peaks are very similar to previously reported PDBS data.

Table 6.2. 500 MHz CDCL₃ ¹H NMR Data for PDBS (d = doublet, t = triplet, q = quartet, m = multiplet)

<table>
<thead>
<tr>
<th>Group</th>
<th>Chemical Shift d(ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Literature</td>
</tr>
<tr>
<td>Ar-H</td>
<td>8.20 (d, 4H)</td>
</tr>
<tr>
<td>N-CH₂</td>
<td>4.11 (t, 4H)</td>
</tr>
<tr>
<td>O-CH₂</td>
<td>3.83 (q, 12H)</td>
</tr>
<tr>
<td>N-CH₂CH₂</td>
<td>1.85 (m, 4H)</td>
</tr>
<tr>
<td>OCH₂CH₃</td>
<td>1.24 (t, 18H)</td>
</tr>
<tr>
<td>SiCH₂</td>
<td>0.75 (t, 4H)</td>
</tr>
</tbody>
</table>

All the additional results were obtained after PDBS assembly, solvent evaporation, further hydrolysis and condensation, and lastly carbonization under nitrogen. The surface area, pore volume, and pore size values reported in Table 6.3 increase with increasing carbon content.
for the porous carbon tubes. Figure 6.2(a) shows type IV nitrogen isotherms for all the samples with H1 hysteresis. It is evident that the isotherms are almost vertical and parallel from 0.8-0.95 relative pressure (P/P₀). The H1 loops are indicative of uniform regular ordered arrays of pores. The x-ray diffraction pattern in Figure 6.3 reflects crystallinity with an intense Bragg (001) peaks with a d-spacing of 3.15nm. The strong 2θ peak at 2.8 degrees reflects that the sample has a degree of ordered mesostructure.

![Figure 6.2](image)

**Figure 6.2.** (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution of carbon tubes formed from PDBS

<table>
<thead>
<tr>
<th>Carbon Precursor</th>
<th>0.5 mmol</th>
<th>1 mmol</th>
<th>1.25 mmol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Area (m²/g)</td>
<td>582.55</td>
<td>909.818</td>
<td>1281.62</td>
</tr>
<tr>
<td>Pore Volume (cm³/g)</td>
<td>0.21</td>
<td>0.36</td>
<td>0.51</td>
</tr>
<tr>
<td>Pore Size (nm)</td>
<td>2.92</td>
<td>3.03</td>
<td>3.68</td>
</tr>
</tbody>
</table>

The TEM images (Figure 6.4) show local areas of uniform ordered porosity with pore sizes approximately 2.25 nm in diameter. Initial hydrogen adsorption measurements ranged from 1.4-
2.5 weight % under liquid nitrogen conditions at 77K (Figure 6.5). This suggests that further optimization to increase uniform pore distribution and decreasing pore size may lead to better hydrogen adsorption performance.

Figure 6.3. Powdered x-ray diffraction of carbonized and HF-etched PDBS carbon tubes composed of 1mmol of carbon precursor 3, 4, 9, 10-perylenetetracaboxylic dianhydride

Figure 6.4. TEM images of carbonized and HF-etched PDBS carbon tubes composed of 1 mmol of carbon precursor 3, 4, 9, 10-perylenetetracaboxylic dianhydride
Figure 6.5. Excess hydrogen adsorption at 77K of carbonized and HF-etched PDBS carbon tubes

6.2. Microporous Carbon

6.2.1. Introduction

Porous carbons that possess a well-tailored micropore structure are extremely attractive and now in great demand for the electrodes of electric double-layer capacitors. Previous work have shown that pore sizes less than 1nm greatly contributes to capacitance suggesting that solvated ions were capable of at least partially removing their salvation shell to enter such small pores, which lead to higher capacitance. There is a strong need to adapt the electrode pore size to the electrolyte ions size for maximizing the capacitance and thus specific energy.

Many novel approaches to control pore structure have thus been proposed. Among them, great attention has been paid to the template carbonization method. A variety of inorganic templates including microporous zeolites, mesoporous silicas, and various carbon sources including sucrose, furfuryl alcohol, crylonitrile, propylene, pyrene, vinyl acetate, and acetonitrile
have been used to prepare porous carbons. Using a phenol-formaldehyde oligomer and KOH solution, the carbon precursor and chemical activation agent are homogenously mixed on the molecular level to synthesize very high surface area microporous carbons.

6.2.2. Experimental Approach

6.2.2.1. Chemicals

Phenol (99%, Sigma Aldrich), Formaldehyde (37%, Sigma Aldrich), and Potassium Hydroxide (90%, Sigma Aldrich) were all used as received.

6.2.2.2. Synthetic Approach

High surface area microporous carbons are synthesized by molecular level mixing of a phenol-formaldehyde oligomer, the carbon precursor, and potassium hydroxide (KOH), the chemical activation reagent, into a homogenous solution. Inside a 3 neck round bottom flask under the flow of nitrogen, 26 mmol of phenol (2.44g) was melted at 40°C with stirring, followed by the addition of 2.6 mmol of grinded KOH (0.145g). Then, 0.52 mmol of formaldehyde (4.22g) was added drop wise below 50°C and the entire solution was heated and held at 75°C for 1 hour. 5M KOH was slowly added to the phenol-formaldehyde oligomer solution. The amount of KOH added was based on a ratio of 1.5-2.5 grams of KOH per gram of phenol-formaldehyde oligomer. The oligomer-KOH solution was heated and soaked at 160°C for 12 hours. During this process the solution boiled at about 115°C for approximately 1 hour until most of the water evaporated then the material slowly increased and reached the 160°C temperature. While being heated the phenol-formaldehyde oligomers cross-linked and polymerized under the action of the KOH to form a thermoset polymer, a cured insoluble polymer network. A yellow solid was scrapped out from the inside of the 3-neck flask and transferred into a tubular furnace to undergo carbonization to 900°C at a rate of 1°C/min in an inert atmosphere. The KOH incorporated into
the polymer network acts as a chemical activation agent to create porosity. Previous work by Sabio and Reinoso mentioned that the interaction with KOH is more intense for non-carbonized material. (Molina-Sabio, 2004) During high temperature treatment, the oxygen in KOH can remove cross-linking by oxidation of cross-linking carbon atoms and stabilize carbon atoms in crystallites. (March, 1984) The potassium metal released at activation temperatures may intercalate and force apart the separate layers of the crystallites. (March, 1984) Removal of the potassium salts by washing and the etching of carbon atoms by the activation reaction from the internal volume of the bulk carbon creates microporosity in the structure. (March, 1984) The final carbon network was washed and centrifuged with dilute hydrochloric acid (0.2 M), followed by washing with distilled water to remove any residual KOH or potassium metal from the carbon. The final product was dried in an oven at 150°C for 8 hours.

6.2.3. Results/Discussion

Initially a 5 M KOH solution with ~1.8g of KOH was gradually added to the phenol-formaldehyde oligomer solution while stirring resulting in a ratio of 1.8g of KOH to 1g phenol resin carbon precursor. This resulted in a highly porous carbon with a BET Surface Area of 736.8172 m²/g, pore volume of 0.0306 cm³/g, and BJH Pore Size of 3.30 nm. The t-plot analysis calculated a 612.2397 m²/g microporous surface area, reflecting 83% microporous surface area. The nitrogen isotherm in Figure 6.6 (a) shows a type IV nitrogen isotherm with H4 hysteresis in which the adsorption and desorption branches remain almost horizontal and parallel from a relative pressure (P/P0) range of 0.25-0.8. The type H4 hysteresis provided in Figure 6.6(a) is associated with narrow slit-like pores indicative to microporosity. This is due to the plot having a similar shape to the type I isotherm which has concavity to the relative pressure axis which are
seen by microporous solids having small external surfaces. In this case most of the uptake is governed by accessible micropore volume rather than internal surface area.

Figure 6.6. (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution of porous carbon prepared using 1.8g KOH to 1 gram of phenol resol precursor

Based on these initial findings more extensive research was conducted to synthesize additional porous carbon materials with increased surface area. However, reaction conditions were optimized to maintain the smallest pore sizes possible. The most interesting set of results were obtained using 2.3g KOH in 5M KOH solution to 1 gram of carbon precursor. The BET surface area value reached 1500.43 m²/g; its isotherm is displayed in Figure 6.7(a). Additional isotherm data include a 1.03 cm³/g pore volume and BJH calculated pore size of 3.57 nm. Even though the surface area is considerably large, the calculated capacitance values obtained from current-voltage (CV) measurements were surprisingly low 6.39 F/g at 2(mV/s). This may be due to poor connectivity within the porous network and un-uniform pore sizes distribution within the microporous range to ensure adequate transport of ions for charge storage.
The TEM images in Figure 6.10 (c) and (d) display pore sizes ranging 0.4-0.5 nm, revealing a very microporous structure. The highly porous surface morphology is shown with the SEM image in Figure 6.10 (a).

![Graph](image1)

Figure 6.7. (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution of porous carbon with a 1500 m²/g surface area prepared using 2.3 KOH to 1 gram of phenol resol precursor

![Graph](image2)

Figure 6.8. (a) The calculated specific capacitance of microporous carbon from potassium hydroxide chemical activation at different CV scan rates. (b) Schematic of a cyclic voltammetry for the highest reached capacitance from a symmetric capacitor built with microporous carbon at a 2 (mV/s) scan rate.
Figure 6.9. Voltammetry characteristics at (a) 5 mV/s, (b) 20 mV/s, (c) 50 mV/s of a symmetric capacitor built from microporous carbon from KOH chemical activation using a 1M H$_2$SO$_4$ electrolyte.
Figure 6.10. (a) SEM 10kV at 3,300 magnification, (b-d) TEM images of a microporous carbon prepared using 2.3g KOH to 1 gram of phenol resol precursor.
CHAPTER 7: SUMMARY

Sustainable and environmentally friendly electrochemical energy production is being developed as sources for alternative energy and power. The device performance of electrochemical energy storage and conversion systems greatly depends on the properties of their materials. Nano-materials have attracted great interest for the development of high performance applications due to their unusual mechanical, electrical, and optical properties enhanced by confined dimensions on the nanoscale.

The self-assembly of surfactants and inorganic precursors in dilute aqueous solutions paved the way for strategies to produce a class of mesoporous materials. Initially considerable research was completed to optimize pore structure (size and volume) of silica, resulting in sol gel processing utilizing acidic hydrolysis and condensation with non-ionic block copolymers as structure directing agents leading to optimal ordered pore compositions. However, most other materials could not be synthesized into mesostructures using sol-gel processing, and nanocasting of a variety of materials with mesoporous silicas as hard templates became the leading method to produce mesoporous materials. Later, organic-organic self-assembly was developed providing a simple one-pot synthesis approach for the creation of mesoporous carbon, which was initially difficult to fabricate due to the high formation energy of carbon-carbon bonds. Various carbon-based mesoporous materials have been developed utilizing organic-organic and organic-inorganic self-assembly routes. For example, nanostructured organic-inorganic hybrid materials have been the subject of extensive research because they are able to combine in a single solid both the attractive properties of a mechanically and thermally stable inorganic backbone, and the specific chemical reactivity and flexibility of the organo-functional group.
Nanostructured materials have made a considerable contribution to the process development of low temperature fuel cells, through dispersion of precious metal catalyst and the development of catalyst supports within the membrane electrode assembly. In response to improving carbon catalyst support corrosion resistance, mesoporous carbon-ceramic composites have been synthesized with the hopes that the robust ceramic material provides the needed durability. Carbon nanotubes were added to provide additional electron transport pathways to carbon-based chemistries to enhance electrical conductivity within the nanocomposites. In order to obtain a complete understanding of how carbon and silica mix at the molecular level; it is essential to have a fundamental understanding of the physical properties of carbon and silica. Amorphous carbon and silica with some crystalline features have been synthesized through the use of sol gel chemistry with evaporation induced self-assembly. A detailed description of carbon and its various allotropes have been described in order to understand the effects of carbon nanotubes in comparison to the other carbon allotropes, particularly since carbon nanotubes are composed of rolled graphite.

Porogens were added to the carbon silica sol gel chemistries to control pore structures, surface areas, and compositions. Zinc chloride, the chemical activation reagent of choice, melted within the carbon-silica networks at its melting point, and once evaporation occurred at its boiling point temperature the interaction between zinc and composite atoms result in the widening of the atomic layers within the composite matrix forming additional pores. Increasing the concentration of the activation reagent leads to increased porosity and surface areas, and significant compositional changes. Higher pore sizes are needed for optimal usage of fuel cell carbon-support materials, concentrations of zinc chloride on the order of 25 wt.% is needed to obtain the required 15-20 nm pore size diameters.
The ability to judicially control pore structure (volume and size) is also essential to achieve high performance within supercapacitor electrodes. The pore size distribution of porous carbons influences to a large degree the fundamental performance criteria of carbon-based supercapacitors, since the co-existence of mesopores with small micropores with good 3D-interconnectivity is required for rapid ion transport to maintain the high power characteristics. Electrochemical capacitance testing was explored on carbon-based nanocomposites with carbon nanotubes incorporated into the polymer matrix, to examine if enhanced conductivity results in higher capacitance. This trend was evident based on this work, however the concentration of carbon nanotubes and carbon within the carbon-based composites need to be optimized in order to achieve the best electrical performance. Increased surface areas, pore sizes, pore volumes, and carbon weight lost confirmed that carbon nanotubes were dispersed within the carbon-silica network. However, agglomeration issues resulted in ununiformed loading of carbon nanotubes which prevented the composites from obtaining the maximum effects of the properties of the nanotubes. Electrospinning was explored as method to improve carbon nanotube alignment within the carbon-based composites. Higher electrical conductivity was achieved in the fibrous composites, however the synthetic route needs to better optimized to obtain better capacitance performance. For example porogens that induce microporosity such as potassium hydroxide should be explored as an additive for higher surface areas and smaller pore sizes to achieve improved capacitance behavior.
APPENDIX

APPENDIX A: Additional Experimental Results for Disordered Carbon-Silica Composites

Table A.1. Experiments showing the variations in ZnCl₂, Sucrose, and TEOS, respectively to make disordered carbon-silica nanocomposites

<table>
<thead>
<tr>
<th>Trial</th>
<th>ZnCl₂ (g)</th>
<th>Sucrose (g)</th>
<th>TEOS (g)</th>
<th>H₂O (g)</th>
<th>EtOH (g)</th>
<th>HCl (µL)</th>
<th>Silica Precursor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variation in ZnCl₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| Activation Agent | Carbon Precursor | Silica Precursor
| Trial | ZnCl₂ (g) | Sucrose (g) | TEOS (g) | H₂O (g) | EtOH (g) | HCl (µL) | TEOS (g) | H₂O (g) | EtOH (g) | HCl (µL) |
| 1     | 0.2       | 0.9         | 2.08     | 1.08    | 2.76     | 8.10    | 0.52      | 0.82    | 0.96     | 2.36     |
| 2     | 0.4       | 0.9         | 2.08     | 1.08    | 2.76     | 8.10    | 0.54      | 0.83    | 0.96     | 2.36     |
| 3     | 1.0       | 0.9         | 2.08     | 1.08    | 2.76     | 8.10    | 1.06      | 1.25    | 1.41     | 3.40     |
| 4     | 1.5       | 0.9         | 2.08     | 1.08    | 2.76     | 8.10    | 1.25      | 1.25    | 1.41     | 3.40     |
| Variation in Sucrose |
| Activation Agent | Carbon Precursor | Silica Precursor |
| Trial | ZnCl₂ (g) | Sucrose (g) | TEOS (g) | H₂O (g) | EtOH (g) | HCl (µL) | TEOS (g) | H₂O (g) | EtOH (g) | HCl (µL) |
| 1     | 1.0       | 0.8         | 2.08     | 1.08    | 2.76     | 8.10    | 0.52      | 0.82    | 0.96     | 2.36     |
| 2     | 1.0       | 1.0         | 2.08     | 1.08    | 2.76     | 8.10    | 0.54      | 0.83    | 0.96     | 2.36     |
| 3     | 1.0       | 1.2         | 2.08     | 1.08    | 2.76     | 8.10    | 1.06      | 1.25    | 1.41     | 3.40     |
| 4     | 1.0       | 1.8         | 2.08     | 1.08    | 2.76     | 8.10    | 1.25      | 1.25    | 1.41     | 3.40     |
| 5     | 1.0       | 2.0         | 2.08     | 1.08    | 2.76     | 8.10    | 1.25      | 1.25    | 1.41     | 3.40     |
| Variation in Silica Precursor |
| Activation Agent | Carbon Precursor | Silica Precursor |
| Trial | ZnCl₂ (g) | Sucrose (g) | TEOS (g) | H₂O (g) | EtOH (g) | HCl (µL) | TEOS (g) | H₂O (g) | EtOH (g) | HCl (µL) |
| 1     | 1.0       | 0.9         | 0.62     | 0.32    | 0.83     | 2.46    | 0.04      | 0.06    | 0.11     | 0.36     |
| 2     | 1.0       | 0.9         | 0.83     | 0.43    | 1.10     | 3.27    | 0.04      | 0.06    | 0.11     | 0.36     |
| 3     | 1.0       | 0.9         | 1.04     | 0.54    | 1.38     | 4.08    | 0.04      | 0.06    | 0.11     | 0.36     |
| 4     | 1.0       | 0.9         | 2.60     | 1.35    | 3.44     | 10.22   | 0.04      | 0.06    | 0.11     | 0.36     |
Figure A.1. (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution of disordered mesoporous carbon-silica composites prepared with various amounts of sucrose, and all other precursors constant: 2.72g ZnCl₂ & 4.16g of hydrolyzed TEOS

Figure A.2. The distribution between mesoporous and microporous (a) surface areas and (b) pore volumes of disordered porous carbon-silica composites prepared with various amounts of sucrose and all other precursors constant: 2.72g ZnCl₂ & 4.16g of hydrolyzed TEOS
Table A.2. Total Surface Areas, Total Pore Volumes, and Pore Sizes of disordered mesoporous carbon-silica composites prepared with varied amounts of sucrose in aqueous solution and 2.72g ZnCl$_2$ & 4.16g of TEOS held constant

<table>
<thead>
<tr>
<th>Variation in Sucrose</th>
<th>Sucrose:TEOS (moles: moles)</th>
<th>Sucrose (wt.%)</th>
<th>Surface Area (m$^2$/g)</th>
<th>Pore Volume (cm$^3$/g)</th>
<th>Pore Size (nm)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25:1.0</td>
<td>8.42</td>
<td>615.91</td>
<td>0.265</td>
<td>7.89</td>
<td>12.29</td>
<td></td>
</tr>
<tr>
<td>0.5:1.0</td>
<td>15.54</td>
<td>515.32</td>
<td>0.187</td>
<td>6.42</td>
<td>12.75</td>
<td></td>
</tr>
<tr>
<td>1.0:1.0</td>
<td>25.88</td>
<td>486.48</td>
<td>0.174</td>
<td>5.56</td>
<td>13.02</td>
<td></td>
</tr>
<tr>
<td>1.5:1.0</td>
<td>29.44</td>
<td>336.38</td>
<td>0.135</td>
<td>4.32</td>
<td>22.03</td>
<td></td>
</tr>
<tr>
<td>2.0:1.0</td>
<td>35.75</td>
<td>239.12</td>
<td>0.125</td>
<td>3.82</td>
<td>25.67</td>
<td></td>
</tr>
</tbody>
</table>

Figure A.3. (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution of disordered mesoporous carbon-silica self assembled using thermal casting prepared with different amounts of sucrose and constant amounts of ZnCl$_2$ and TEOS at 1g and 2.08g, respectively.
Figure A.4. The distribution between mesoporous and microporous (a) surface areas and (b) pore volumes of disordered mesoporous carbon-silica self assembled using thermal casting prepared with different amounts of sucrose and constant amounts of ZnCl₂ and TEOS at 1g and 2.08g, respectively.

Table A.3. Total Surface Areas, Total Pore Volumes, and Pore Sizes of disordered mesoporous carbon-silica self assembled using thermal casting prepared with different amounts of sucrose and constant amounts of ZnCl₂ and TEOS at 1g and 2.08g, respectively.

<table>
<thead>
<tr>
<th>Sucrose (wt. %)</th>
<th>Surface Area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
<th>Pore Size (nm)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>28.82</td>
<td>466.69</td>
<td>0.111</td>
<td>2.85</td>
<td>13.05</td>
</tr>
<tr>
<td>31.90</td>
<td>349.69</td>
<td>0.219</td>
<td>3.40</td>
<td>19.68</td>
</tr>
<tr>
<td>37.16</td>
<td>196.43</td>
<td>0.206</td>
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</table>
Figure A.5. SEM images of disordered mesoporous carbon-silica self assembled using thermal casting prepared with (a-b) 28.12 wt. % and 37.16 wt. % sucrose and constant amounts of ZnCl$_2$ and TEOS at 1g and 2.08g, respectively.
Figure A.6. (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution of silica etched with 5.0% HF disordered mesoporous carbon-silica self assembled using thermal casting prepared with different amounts of sucrose and constant amounts of ZnCl$_2$ and TEOS at 1g and 2.08g, respectively.

Figure A.7. The distribution between mesoporous and microporous (a) surface areas and (b) pore volumes of silica etched with 5.0% HF disordered mesoporous carbon-silica self assembled using thermal casting prepared with different amounts of sucrose and constant amounts of ZnCl$_2$ and TEOS at 1g and 2.08g, respectively.
Table A.4. Total Surface Areas, Total Pore Volumes, and Pore Sizes of silica etched with 5.0% HF disordered mesoporous carbon-silica self assembled using thermal casting prepared with different amounts of sucrose and constant amounts of ZnCl₂ and TEOS at 1g and 2.08g, respectively.

<table>
<thead>
<tr>
<th>Sucrose (wt.%)</th>
<th>Surface Area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
<th>Pore Size (nm)</th>
<th>Porosity (%)</th>
</tr>
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<td>1142.43</td>
<td>1.658</td>
<td>5.49</td>
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<td>37.16</td>
<td>987.89</td>
<td>0.971</td>
<td>3.75</td>
<td>32.86</td>
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</table>

Figure A.8. (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution of disordered mesoporous carbon-silica self assembled in the aerosol process prepared with different amounts of sucrose and constant amounts of ZnCl₂ and TEOS at 1g and 2.08g, respectively.
Figure A.9. The distribution between mesoporous and microporous (a) surface areas and (b) pore volumes of disordered mesoporous carbon-silica self assembled in the aerosol process prepared with different amounts of sucrose and constant amounts of ZnCl$_2$ and TEOS at 1g and 2.08g, respectively.

Table A.5. Total Surface Areas, Total Pore Volumes, and Pore Sizes of disordered mesoporous carbon-silica self assembled in the aerosol process prepared with different amounts of sucrose and constant amounts of ZnCl$_2$ and TEOS at 1g and 2.08g, respectively.

<table>
<thead>
<tr>
<th>Sucrose (wt. %)</th>
<th>Surface Area (m$^2$/g)</th>
<th>Pore Volume (cm$^3$/g)</th>
<th>Pore Size (nm)</th>
<th>Porosity (%)</th>
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<td>31.90</td>
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<td>3.54</td>
<td>32.52</td>
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<tr>
<td>37.16</td>
<td>151.24</td>
<td>0.121</td>
<td>4.21</td>
<td>37.03</td>
</tr>
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</table>
Figure A.10. SEM images of disordered mesoporous carbon-silica self-assembled using the aerosol process with (a-b) 28.12 wt. % and 37.16 wt. % sucrose and constant amounts of ZnCl₂ and TEOS at 1g and 2.08g, respectively.
Figure A.11. (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution of silica etched with 5.0% HF disordered mesoporous carbon-silica self assembled in the aerosol process prepared with different amounts of sucrose and constant amounts of ZnCl$_2$ and TEOS at 1g and 2.08g, respectively.

Figure A.12. The distribution between mesoporous and microporous (a) surface areas and (b) pore volumes of silica etched with 5.0% HF disordered mesoporous carbon-silica self assembled in the aerosol process prepared with different amounts of sucrose and constant amounts of ZnCl$_2$ and TEOS at 1g and 2.08g, respectively.
Table A.6. Total Surface Areas, Total Pore Volumes, and Pore Sizes of silica etched with 5.0% HF disordered mesoporous carbon-silica self assembled in the aerosol process prepared with different amounts of sucrose and constant amounts of ZnCl$_2$ and TEOS at 1g and 2.08g, respectively.

<table>
<thead>
<tr>
<th>Sucrose (wt. %)</th>
<th>Surface Area (m$^2$/g)</th>
<th>Pore Volume (cm$^3$/g)</th>
<th>Pore Size (nm)</th>
<th>Porosity (%)</th>
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<td>37.16</td>
<td>527.37</td>
<td>0.512</td>
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Appendix B: Uniformly Ordered Mesoporous Silica-Carbon Nanocomposites

Synthesis of Ordered Mesoporous Silica-Carbon Composites-The co-assembly of inorganic (silica) and organic (phenol and triblock copolymer surfactant) phases from the sol gel process and subsequent carbonization is utilized to prepare silica-carbon nanocomposites.

B.1. Preparation of Resol Precursor

The synthesis of the oligomeric resol was prepared by melting 6.5mmol of phenol (0.61 g) at 40-42°C under N$_2$ in a 3 neck round bottom flask, followed by the addition of 0.65mmol of sodium hydroxide (20% NaOH) (0.13g) with continuous stirring for 10 minutes. Then 13 mmol (1.05g) of formaldehyde (37%) was added drop wise below 50°C. The temperature was then increased to 70°C and continuously stirred for 1 hour. The mixture was cooled to room temperature and then neutralized to approximately pH 7 using 0.6M HCl and tested with Insta Check pH Testpaper. Lastly, the final product was centrifuged to remove any sodium chloride precipitate formed during the neutralization process, and water was removed by vacuum evaporation below 50°C. The final viscous product was dissolved in ethanol making a 20% by weight resol solution.

B.2. Synthesis of Silica-Carbon Composite
The organic precursor was prepared by mixing the obtained resol precursor, with various amounts of triblock copolymer Pluronic F-127 and ethanol. The various amounts of block copolymer used are reported in Table 3.2. In a typical preparation 1g of F-127 is dissolved in 20mL of ethanol by shaking, stirring, and sonication. A homogenous clear mixture of the organic precursor is prepared combining the above mixtures of resol and dissolved F-127, followed by sonication for 10 minutes, and mechanical stirring for an additional 30 minutes. The silicate precursor was prepared by reacting TEOS in an acidic water/ethanol solvent at room temperature under sonication for 30 minutes, and mechanically stirred for 1 hour at room temperature. The molar ratio of reactants was maintained at TEOS:EtOH:H₂O:HCl = 1:6:6:0.01, in which 2.08g of TEOS, 12g of ethanol, 8.1µL of 37% HCL, and 0.9g of DI water were homogenously mixed together. The silicate precursor was added into the organic precursor, and the homogenous mixture was mechanically stirred for 1 hour. Next, the mixture was poured into glass dishes and dried in air at 25°C for 1 day to evaporate ethanol. The samples were then placed in an oven and were thermopolymerized at 100°C for 1 day. After removal from the oven, the evaporation of solvent and condensation and hydrolysis of TEOS was complete and orange transparent silica/organic nanocomposites were formed. The nanocomposites are then carbonized in a tubular furnace. The heating process under nitrogen occurs at 1°C/min from 100°C-600°C, 5°C/min from 600°C-900°C, and held at 900°C for 4 hours. In order to produce 1.5-2.0g of final product the above procedure was scaled by a factor of 5. Table 4.2 list the details for experiments with (a) the variation of surfactant F-127 (constant carbon and silica content), (b) variation in resol (constant surfactant and silica content), and (c) variation in silica precursor (constant surfactant and carbon content). In the case of varying the amount of silica precursor the amount of TEOS used for these experiments are based on using 30%, 40%, 50%, and 125%, of the base
case TEOS amount of 21.17 wt. % (2.08g, 0.01 mol) and maintaining the following molar ratio for the silica precursor solution TEOS:EtOH:H₂O:HCL 1:6:6:0.01.

Table B.1. Experiments showing the variations in (a) F-127/ethanol, (b) silica precursor, and (c) resol, respectively to make ordered carbon/silica nanocomposites

<table>
<thead>
<tr>
<th>Variation in Pluronic F-127</th>
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<th>Silica Precursor</th>
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<td>Formaldehyde (g)</td>
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<table>
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<th>Variation in Silica Precursor</th>
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<th>Silica Precursor</th>
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<td>Formaldehyde (g)</td>
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<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
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<td>Trial</td>
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<td>Formaldehyde (g)</td>
</tr>
<tr>
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Table B.2. Experiments showing the variations in (a) F-127/ethanol, (b) resol, and (c) TEOS, respectively to make ordered carbon/silica nanocomposites

<table>
<thead>
<tr>
<th>Trial</th>
<th>Variation in F-127</th>
<th>Variation in Resol</th>
<th>Variation TEOS</th>
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</thead>
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<tr>
<td></td>
<td>F-127 (g)</td>
<td>Phenol (g)</td>
<td>TEOS (g)</td>
</tr>
<tr>
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<td>F-127 (wt. %)</td>
<td>Phenol (wt. %)</td>
<td>TEOS (wt. %)</td>
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<tr>
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B.3. Variation in amount of surfactant

The pore structure within the carbon-silica nanocomposites is controlled by the surfactant liquid crystalline mesophase, which depends on the type and concentration of surfactant, and reaction conditions. The surfactant (Pluronic F-127) strongly interacts with the resol precursor and can be easily removed with a simple heating treatment. Because they contain many oxygen atoms and have a low glass transition temperature (lower than room temperature), PEO-PPO-PEO copolymers can be easily removed at low temperatures without destroying the resin framework.

The effect of the amount of surfactant used during the synthesis has been examined. Based on this study there seems to be an optimal amount of surfactant to be used in order to have maximum nitrogen uptake. When lower amounts of F-127 were used to make the organic precursor the volume of nitrogen adsorbed/desorbed was significantly low and the hysteresis loops are flat and elongated parallel to the relative pressure axis indicative of H4 hysteresis, as shown in Figure B.1 (a). The H4 loop is associated with microporosity, and there is significantly higher micropore distribution in both surface area and pore volume with the lower surfactant concentrations (Figure B.2 (a) and (b)). In addition, Figure B.1 (b) shows the pore size
distribution is extremely low for the experimental conditions with 0.75 wt. % and 1.33 wt. % (1.25g and 2.5g) of surfactant used in the organic precursor. The lack of surfactant concentration leads to serious framework shrinkage resulting in low surfaces areas and pore volumes. This concludes that a greater amount of surfactant was needed in those experimental conditions in order to obtain more mesoporous features.

In addition to the decreased concentration of surfactant, there are a set of experimental conditions which leads to the conclusion that there can be an excessive amount of surfactant used based on the conditions when 3.19 wt. % (10g) of F-127 was used in the organic precursor. The higher surfactant concentrations exhibit type-IV curves with capillary condensation range of $P/P_0 = 0.47$-0.70 and H1-type hysteresis loops which is typical of large-pore mesoporous materials with cylindrical channels. Type H1 hysteresis is often associated with porous materials with uniform spheres in fairly regular array, which also have narrow distributions of pore size. These results suggest that the samples with higher F-127 concentration consist of an ordered uniform cylindrical mesoporous channels. A narrow pore size distribution is centered at 4.02 nm calculated from the adsorption branch based on the BJH model (Figure B.1 (b)).
Figure B.1. (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution of mesoporous carbon-silica prepared at different surfactant (F-127) concentrations.

Table B.3. Total Surface Areas, Total Pore Volumes, and Pore Sizes of mesoporous carbon-silica composites varied by F-127 content.

<table>
<thead>
<tr>
<th>Variation in F-127</th>
<th>F-127 (wt. %)</th>
<th>F-127 (g)</th>
<th>EtOH (mL)</th>
<th>Surface Area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
<th>Pore Size (nm)</th>
<th>Porosity (%)</th>
</tr>
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<tr>
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<td>1.25</td>
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<td>83.36</td>
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<td>3.29</td>
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<tr>
<td>3.19</td>
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<td>389.15</td>
<td>0.387</td>
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<td>34.73</td>
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</table>
Figure B.2. The distribution between mesoporous and microporous (a) surface areas and (b) pore volumes of mesoporous carbon-silica composites with increased F-127 content.

The powder XRD pattern (Figure B.3) of the synthesized mesoporous carbon-silica composites prepared with various F-127 concentrations shows evidence of 3 reflections at 2θ values between 0.5° and 2° (one strong peak and 2 broad shoulder beak). The XRD patterns suggest thermally stable ordered mesoporous structures. The strong peak at 0.7856° with d spacings of ~11.23 nm (a₀=12.97 nm) is consistent with all 4 samples, the shoulder peak shifts and broadens at various surfactant concentrations. Based on reference comparison from Meng, Y. et.al, the strong peak is identified as (10) associated with 2D hexagonal p6m symmetry. Small-angle X-ray scattering (SAXS) is needed for more resolved peaks.
Figure B.3. Powder XRD patterns of carbon-silica nanocomposites made with various amounts of F127.

B.4. Variation in amount of Phenol (Resol Precursor)

Resol (phenol/formaldehyde) is an expensive precursor which can form four-connected covalently bonded zeolite-like aromatic frameworks by thermal polymerization. The resols are polymerized by phenol and formaldehyde under alkaline conditions. The molar ratio of phenol/formaldehyde/NaOH is 1:2:0.1. In an ideal network of phenolic resins, one benzene ring links via covalent bonds with three other benzene rings through an aliphatic or an ether bridge. The four connected benzene exist in the framework of the mesoporous polymer products. Resol is essential to the successful organization of organic-organic mesostructures due to the large number of hydroxyl groups (-OH) which can interact strongly with the triblock copolymers.
through the formation of hydrogen bonds. The interaction occurs between the hydroxyl groups and the PEO within the blocks of copolymer $\text{PEO}_{106}$-$\text{PPO}_{70}$-$\text{PEO}_{106}$.

Various amounts of resol were used to determine its influences on surface area and pore size distribution. The materials in Figure B.4 (a) show typical type-IV curves with hysteresis loops containing capillary condensation steps in the $P/P_0$ range from 0.45 to 0.65 corresponding to mesoporous structure. The nitrogen adsorption uptake, surface areas, and pore volume, increases with increasing phenol content (Table B.4). The adsorption and desorption isotherms of each sample are not closed, which is attributed to the polymer framework. The BET surface area, pore volume, and mean pore size are calculated to be $642.12 \, \text{m}^2/\text{g}$, $0.204 \, \text{cm}^3/\text{g}$, and $4.98 \, \text{nm}$, respectively for 4.77 wt. % (12.2g, 0.13 mol) of phenol used. The pore size distribution was centered at $4.01 \, \text{nm}$ when 0.68 wt. %, 1.33 wt. %, and 3.70 wt. % of phenol were used.
Table B.4. Total Surface Areas, Total Pore Volumes, and Pore Sizes of mesoporous carbon-silica composites varied by amounts of phenol and formaldehyde.

<table>
<thead>
<tr>
<th>Variation in Phenol</th>
<th>Surface Area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
<th>Pore Size (nm)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.68</td>
<td>257.92</td>
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<td>4.98</td>
<td>13.99</td>
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<td>1.33</td>
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<td>3.70</td>
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<td>4.77</td>
<td>642.12</td>
<td>0.204</td>
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<td>9.73</td>
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</table>

The structural features of the cross-linked phenolic resins possess network structures that are analogous to that of microporous zeolites made of four-connected silicate tetrahedrons and have a covalently bonded infinite framework. An increase in microporous surface area and pore volume occurs with increasing phenol concentration, as seen in Figure B.5 (a).
Figure B.5. The distribution of between mesoporous and microporous (a) surface areas and (b) pore volumes of mesoporous carbon-silica composites with increased phenol and formaldehyde content

The XRD patterns of the mesoporous carbon-silica composites with various amounts of phenol precursors used displays a narrow and intense diffraction peak at a $2\theta$ value of 0.7856°, which can be indexed as a reflection of 10 for a 2-D hexagonal mesostructure (Figure B.6). The d spacing for the strong peak was 11.23 nm and a unit cell parameter $a_0$ of 12.97 nm. This strong diffraction pattern suggests a periodic regularity of the mesostructure. Overall, adjusting the concentration of the resol precursor, results in more microporous internal features and an increase in surface area.
B.5. Variation in amount of Silica Precursor

The effects of the silica precursor on the formation of the nanocomposites surface area and pore size distribution has been examined. Silica serves the purpose of proving robustness and durability to the silica samples by providing additional rigidity to the carbon-silica composites. TEOS reacts with the hydroxyl groups within the phenolic resins. In the acid-hydrolyzed TEOS solution, small oligomers full of Si-OH groups are formed and can form strong hydrogen-bonding interactions with the PEO containing triblock polymers arranged around the triblock copolymer micelles. Silicate oligomers undergo a cooperative process, during which they not only assemble with surfactants, but also condense and cross-link together to form
a silica framework. The tetrahedral structure of the silicate species is able to crosslink around nano-sized resols to generate a robust framework.

Silica samples were made of 2.04 wt. % (2.60g, 12.5mmol), 3.23 wt. % (5.21g, 25mmol), and 6.22 wt. % (31.25g, 150mmol) of TEOS with TEOS: Ethanol: H₂O: HCl molar ratios held constant at 1:6:6:0.01. N₂ sorption isotherms of the mesoporous nanocomposites carbonized at 900°C in N₂ exhibit type-IV curves with H2-type hysteresis loops in which the nitrogen uptake increases with increasing silica concentration and pore size distribution centered at 4.1 nm (Figure B.7). The H2-hysteresis is suggesting that the cylindrical channels are imperfect due to asymmetric shrinkage. The surface area increased approximately 10% from 2.04 wt. % to 3.23 wt. % of TEOS, and 33.3% from 3.23 wt. % to 6.22 wt. % of TEOS (Table B.5). The first samples two samples with the lesser amounts of TEOS had approximately 60% microporous surface area, and with 6.22 wt. % of TEOS the microporous surface area increased to 76% (Figure B.8). The XRD patterns with three peaks suggest thermally stable ordered 2D hexagonal mesoporous structures. The strong peak is at 0.7856° with d spacings of ~11.23nm \((a_0 = 12.97nm)\) is consistent with all 3 samples (Figure B.9). Based on these findings the controllable co assembly of surfactants, resols, and silica species achieved a homogenous distribution of resols and silicates around the triblock copolymer F-127 template. Inorganic silicates and polymer resins coexisted in a well-ordered long range architecture by local micro-phase separation.
Figure B.7. (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution of mesoporous carbon-silica prepared with different amounts of silica precursor TEOS: Ethanol: HCl: H₂O: F-127 =1:6:0.01:6 (molar)

Table B.5. Total Surface Areas, Total Pore Volumes, and Pore Sizes of mesoporous carbon-silica composites varied by amounts of silica precursor.

<table>
<thead>
<tr>
<th>Variation in Silica Precursor</th>
<th>Surface Area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
<th>Pore Size (nm)</th>
<th>Porosity (%)</th>
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<tr>
<td>TEOS (wt. %)</td>
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<td></td>
</tr>
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</table>
Figure B.8. The distribution between mesoporous and microporous (a) surface areas and (b) pore volumes of mesoporous carbon-silica composites with increased silica precursor TEOS:Ethanol:HCl:H$_2$O = 1:6:0.01:6 (molar).

Figure B.9. Powder XRD patterns of carbon-silica nanocomposites made with various amounts of silica precursor.
B.6. Optimization of Ordered Carbon-Silica

Mesoporous polymer-silica nanocomposites were prepared by evaporation induced self-assembly of phenolic resols, silica from acid catalyzed hydrolysis of TEOS, and surfactant F-127 in an ethanol solution. After heating at 900°C in nitrogen, the nanocomposite becomes black and 2 well-resolved diffraction peaks indexed at 10 and 20 reflections are observed in the powder X-ray diffraction patterns for all four samples (Figure B.10). These reflections are part of the two-dimensional (2-D) hexagonal symmetry with space group of \( p6m \). In sample D with 7.76 wt. % (2.0g) F-127 and 6.21 wt. % (1.6g) of resol most intense peak initially started at 0.8026° and shifted to 0.8504° with an increase of both surfactant and resol precursor to 9.05wt % (3.2g) F-127 and 28.28 wt.% (10g) of resol (Sample B). This resulted in the shrinkage in unit cell parameters \( (a_0) \) from 12.7 nm to 11.99 nm.
Figure B.10. Powder XRD patterns of mesoporous carbon-silica nanocomposites with [A] 9.83 wt.% (4.6g) F-127 & 42.77 wt.% (20g) Resol, [B] 9.05 wt.% (3.2g) F-127 & 28.28 wt.% (10g) Resol, [C] 6.86 wt.% (2.0g) F-127 & 17.15 wt.% (5g) Resol, and [D] 7.76 wt.% (2.0g) F-127 & 6.21 wt.% (1.6g) Resol.

Figure B.13 shows the SEM images of the surface morphology of mesoporous carbon-silica composites with hierarchical pore structure synthesized using various amounts of surfactant F-127 as a structure directing agent and carbon precursor (resol) with 20% ethanol. The TEM images also within Figure B.13 reveal very porous nanocomposites with ordered structure (right panel). In the cases of the least amount of resol 6.21 wt.% (Figure B.13 e) and most amount of resol 42.77 wt.% (Figure B.13 h) the ordered structure can be seen on the surface morphology of the SEM images at high magnification of 140K. The surface appears to have hexagonal pores on the order of approximately 7-8 nm. The surfactant-templated approach is a
synthetic route that produces mesoporous materials with tunable surface area, pore diameters, uniform pore size distribution, and controllable pore connectivity.

Figure B.11. (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution of ordered mesoporous carbon-silica composites prepared using variations in surfactant F-127 and oligomer precursor resol in 20 wt. % ethanol with constant hydrolyzed TEOS at 4.16g.

Table B.6. Total Surface Areas, Total Pore Volumes, and Pore Sizes of mesoporous carbon-silica composites prepared using variations in surfactant F-127 and oligomer precursor resol in 20 wt. % ethanol with constant hydrolyzed TEOS at 4.16g.

<table>
<thead>
<tr>
<th>Surfactant and Oligomer Composition</th>
<th>BET Surface Area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
<th>Pore Size (nm)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.83 wt.% F-127 42.77 wt.% Resol</td>
<td>704.55</td>
<td>0.586</td>
<td>4.19</td>
<td>23.76</td>
</tr>
<tr>
<td>9.05 wt.% F-127 28.28 wt.% Resol</td>
<td>457.98</td>
<td>0.443</td>
<td>4.42</td>
<td>27.64</td>
</tr>
<tr>
<td>6.86 wt.% F-127 17.15 wt.% Resol</td>
<td>395.85</td>
<td>0.441</td>
<td>4.82</td>
<td>31.83</td>
</tr>
<tr>
<td>7.76 wt.% F-127 6.21 wt.% Resol</td>
<td>189.96</td>
<td>0.296</td>
<td>6.17</td>
<td>44.52</td>
</tr>
</tbody>
</table>
Figure B.12. The distribution between mesoporous and microporous (a) surface areas and (b) pore volumes of ordered mesoporous carbon-silica prepared using variations in surfactant F-127 and oligomer precursor resol in 20 wt. % ethanol with constant hydrolyzed TEOS at 4.16g. (A) 9.83 wt. % F-127 & 42.77 wt. % Resol, (B) 9.05 wt. % F-127 & 28.28 wt. % Resol, (C) 6.86 wt. % F-127 & 17.15 wt. % Resol, and (D) 7.26 wt. % F-127 & 6.21 wt. % Resol.
Figure B.13. SEM 10kV at 3K magnification (left panel) and 140K magnification (center panel), and TEM (right panel) images of mesoporous carbon–silica prepared with (a-c) 9.05 wt.% F-127 & 28.28 wt.% Resol; (d-f) 9.83 wt.% F-127 & 42.77 wt.% Resol; (g-i) 7.76 wt.% F-127 & 6.21 wt.% Resol; and (j-l) 6.86 wt.% F-127 & 17.15 wt.% Resol.
Appendix C: Carbon Nanotubes in Randomly Disordered Carbon-Silica Composites

Functionalized multi-walled carbon nanotubes were added to a homogenously mixed carbon precursor of sucrose and hydrolyzed silica precursor of TEOS. Based on initial BET sorption isotherms the incorporation of carbon nanotubes into the carbon-silica nanoporous network provided approximately a 9-20% increase in surface areas (Table C.1). As seen in Figure C.1 (a), there is a shift of increased nitrogen sorption uptakes with the addition of the 0.05-1.0 wt. % carbon nanotubes. However, there isn’t a direct correlation between increasing carbon nanotubes concentration and increasing surface area. This implies that randomly distributed disordered pore structures are not the best carbon-silica networks to add carbon nanotubes in order to tune conductivity. The nanotubes are not uniformly loaded individually over a maximum interfacial area. Thus, the nanotubes properties are not efficiently uniformly integrated into the carbon/silica matrix.

Closer inspection of Figure C.1 (a) shows a decrease in hysteresis with the incorporation of the carbon nanotubes reflecting that the incorporation of the nanotubes contributed to more microporosity within the carbon-silica nanocomposite. Based on Figure C.2, microporous surface area and pore volume increased on the order of 12.3% and 18%, respectively with the incorporation of carbon nanotubes. The surfactant templated approach to produce uniformly ordered mesoporous networks is explored in greater detail for carbon nanotubes incorporation.
Table C.1. Total Surface Areas, Total Pore Volumes, and Pore Sizes of disordered carbon-silica composites incorporated with multi-walled carbon nanotubes.

<table>
<thead>
<tr>
<th>Incorporation of Carbon Nanotubes (wt. %)</th>
<th>0.0 % CNTs</th>
<th>0.05 % CNTs</th>
<th>0.5 % CNTs</th>
<th>1.0 % CNTs</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET Surface Area (m^2/g)</td>
<td>245.90</td>
<td>278.54</td>
<td>298.25</td>
<td>268.69</td>
</tr>
<tr>
<td>Pore Volume (cm^3/g)</td>
<td>0.128</td>
<td>0.083</td>
<td>0.104</td>
<td>0.131</td>
</tr>
<tr>
<td>Pore Diameter (nm)</td>
<td>3.52</td>
<td>3.66</td>
<td>3.72</td>
<td>3.75</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>22.79</td>
<td>23.00</td>
<td>18.27</td>
<td>18.11</td>
</tr>
</tbody>
</table>

Figure C.1. (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution of mesoporous disordered carbon-silica incorporated with multi-walled carbon nanotubes.
Figure C.2. The distribution between mesoporous and microporous (a) surface areas and (b) pore volumes of disordered carbon-silica composites incorporated with multi-walled carbon nanotubes

Appendix D: Characterization of thermal casted & aerosol produced ordered carbon-silica composites with carbon nanotubes

Figure D.1. (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution of ordered mesoporous carbon-silica composites prepared using thermal casting at 120°C with multi-walled carbon nanotubes added to the carbon-silica network
Figure D.2. The distribution between mesoporous and microporous (a) surface areas and (b) pore volumes of ordered mesoporous carbon-silica self assembled using thermal casting at 120°C prepared with different amounts of carbon nanotubes added to the carbon-silica network.

Table D.1. Total Surface Areas, Total Pore Volumes, and Pore Sizes of ordered mesoporous carbon-silica self assembled using thermal casting at 120°C prepared with different amounts of carbon nanotubes added to the carbon-silica network

<table>
<thead>
<tr>
<th>Amount of CNTs</th>
<th>0 wt.%</th>
<th>0.5 wt.%</th>
<th>1.0 wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET Surface Area (m²/g)</td>
<td>51.00</td>
<td>61.23</td>
<td>72.63</td>
</tr>
<tr>
<td>Pore Volume (cm³/g)</td>
<td>0.021</td>
<td>0.035</td>
<td>0.051</td>
</tr>
<tr>
<td>Pore Size (nm)</td>
<td>3.23</td>
<td>4.07</td>
<td>5.13</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>11.86</td>
<td>20.40</td>
<td>24.94</td>
</tr>
</tbody>
</table>
Figure D.3. (a) XRD spectra and (b) TGA curves of ordered mesoporous carbon-silica self assembled using thermal casting at 120°C prepared using the aerosol process with multi-walled carbon nanotubes added to the carbon-silica network.

Figure D.4. TEM images of ordered mesoporous carbon-silica self assembled using (a) thermal casting and (b) the aerosol process with 0.5 wt. % CNTs incorporated into the carbon-silica network.
Figure D.5. (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution of ordered mesoporous carbon-silica composites prepared using the aerosol process with multi-walled carbon nanotubes added to the carbon-silica network.

Figure D.6. The distribution between mesoporous and microporous (a) surface areas and (b) pore volumes of ordered mesoporous carbon-silica self assembled using the aerosol process prepared using the aerosol process with multi-walled carbon nanotubes added to the carbon-silica network.
Table D.2. Total Surface Areas, Total Pore Volumes, and Pore Sizes of ordered mesoporous carbon-silica self assembled using the aerosol process with different amounts of carbon nanotubes added to the carbon-silica network

<table>
<thead>
<tr>
<th></th>
<th>CNTs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0 wt.%</td>
</tr>
<tr>
<td>BET Surface Area (m²/g)</td>
<td>34.17</td>
</tr>
<tr>
<td>Pore Volume (cm³/g)</td>
<td>0.056</td>
</tr>
<tr>
<td>Pore Size (nm)</td>
<td>7.23</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>51.51</td>
</tr>
</tbody>
</table>

Figure D.7. (a) XRD spectra and (b) TGA curves of ordered mesoporous carbon-silica self assembled using the aerosol process prepared using the aerosol process with multi-walled carbon nanotubes added to the carbon-silica network
Appendix E: XRD Patterns of Silica Etched Nanocomposites & Fibers with carbon nanotubes

(a) Powder XRD patterns and (b) unit cell, \( a_0 \), values of mesoporous order silica etched with 5.0% HF carbon nanocomposites with various amounts carbon nanotubes added to the carbon-silica network.

Figure E.1

<table>
<thead>
<tr>
<th>CNTs</th>
<th>( \theta )</th>
<th>d-spacing</th>
<th>( a_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00%</td>
<td>0.425°</td>
<td>20.81nm</td>
<td>24.03nm</td>
</tr>
<tr>
<td>0.05%</td>
<td>0.383°</td>
<td>23.04nm</td>
<td>26.60nm</td>
</tr>
<tr>
<td>0.5%</td>
<td>0.401°</td>
<td>22.00nm</td>
<td>25.41nm</td>
</tr>
<tr>
<td>1.0%</td>
<td>0.395°</td>
<td>22.34nm</td>
<td>25.79nm</td>
</tr>
</tbody>
</table>
Figure E.2. (a) Powder XRD patterns and (b) unit cell, $a_0$, values of electrospun silica etched with 5.0% HF mesoporous carbon fibers with various amounts carbon nanotubes added to the carbon-silica network.


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Ramakrishna, S., K. Fujihara, W.-E. Teo, T.-C. Lim and Z. Ma (2005). An Introduction to Electrospinning and Nanofibers.


