ELECTROCHEMICAL DOUBLE-LAYER CAPACITORS BASED ON FUNCTIONALIZED GRAPHENE

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ABSTRACT

Graphene is a promising electrode material for electrochemical double-layer capacitors (EDLCs) used for energy storage due to its high electrical conductivity and theoretical specific surface area. However, the intrinsic capacitance of graphene is known to be low and governed by the electronic side of the interface. Furthermore, graphene tends to aggregate and stack together when processed into thick electrode films. This significantly lowers the ion-accessible specific surface area (SSA). Maximizing both the SSA and the intrinsic capacitance are the main problems addressed in this thesis in an effort to improve the specific capacitance and energy density of EDLCs.

In contrast to pristine graphene, functionalized graphene produced by the thermal exfoliation of graphite oxide contains residual functional groups and lattice defects. To study how these properties affect the double-layer capacitance, a model electrode system capable of measuring the intrinsic electrochemical properties of functionalized graphene was developed. To prevent artifacts and uncertainties related to measurements on porous electrodes, the functionalized graphene sheets (FGSs) were assembled as densely tiled monolayers using a Langmuir-Blodgett technique. In this way, charging can be studied in a well-defined 2D geometry. The possibility of measuring and isolating the intrinsic electrochemical properties of FGS monolayers was first demonstrated by comparing capacitance and redox probe measurements carried out on coatings deposited on passivated gold and single crystal graphite substrates.

This monolayer system was then used to follow the double-layer capacitance of the FGS/electrolyte interface as the structure and chemistry of graphene was varied by

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thermal treatments ranging from 300 °C to 2100 °C. Elemental analysis and Raman spectroscopy were used to determine the resulting chemical and structural transformation upon heat treatment. It was demonstrated that intrinsically defective graphene monolayers can exhibit four-fold higher double-layer capacitance than pristine graphene. High temperature annealing lowered the capacitance until it approached that of pristine graphene. An optimal level of functionalization and lattice disorder is found necessary to retain high double-layer capacitance suggesting that graphene-based materials can be chemically tailored to engineer higher capacitance electrodes.

The second half of this thesis focuses on understanding the factors that control the SSA of FGS aggregates when processed into dense electrodes and the development of a new electrode fabrications strategy to improve the ion-accessible surface area of FGS-based electrodes. Using various processing conditions, it was demonstrated that aggregates can exhibit a wide range of SSAs (1 m²/g to 1750 m²/g) accessible to the adsorption of nitrogen or methylene blue. The effects of capillary forces, van der Waals interactions and aggregation kinetics on the SSA were explored and an aggregation model was proposed to account for these effects.

In order to minimize aggregation, a new strategy for preparing graphene-based electrodes for EDLCs was developed. Colloidal gels of graphene oxide in a water-ethanol-ionic liquid solution were assembled into graphene-ionic liquid laminated structures. Our process involves evaporating the solvents water and ethanol yielding a graphene oxide/ionic liquid composite, followed by thermal reduction of the graphene oxide to electrically conducting functionalized graphene. This yields an electrode in which the ionic liquid serves not only as the working electrolyte but also as a spacer to
separate the graphene sheets and to increase their electrolyte-accessible surface area. Using this approach, we achieve an outstanding energy density of 17.5 Wh/kg at a gravimetric capacitance of 156 F/g and 3 V operating voltage, due to a high effective density of the active electrode material of 0.46 g/cm². By increasing the ionic liquid content and degree of thermal reduction, we obtain electrodes that retain >90% of their capacity at a scan rate of 500 mV/s, illustrating that we can tailor the electrodes towards higher power density if energy density is not the primary goal. The ease of manufacturing, achieved by combining the steps of electrode assembly and electrolyte infiltration, makes this bottom-up assembly approach scalable and well suited for combinations of potentially any graphene material with ionic liquid electrolytes.
ACKNOWLEDGEMENTS

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Dedicated to my Family
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<tr>
<td>EDLC</td>
<td>Electrochemical double-layer capacitor</td>
</tr>
<tr>
<td>SSA</td>
<td>Mass specific surface area</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>GO</td>
<td>Graphite oxide</td>
</tr>
<tr>
<td>FGS</td>
<td>Functionalized graphene sheet</td>
</tr>
<tr>
<td>EMI$m\text{BF}_4$</td>
<td>1-ethyl 3-methyl imidazolium</td>
</tr>
<tr>
<td>TEABF$_4$</td>
<td>Tetraethylammonium tetrafluoroborate</td>
</tr>
<tr>
<td>AN</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>DCE</td>
<td>1,2-Dichloroethane</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of states</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammogram</td>
</tr>
<tr>
<td>IL</td>
<td>Ionic liquid</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>BAM</td>
<td>Brewster angle microscopy</td>
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<tr>
<td>LB</td>
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1 Introduction

Supercapacitors, also known as ultracapacitors or electrochemical double-layer capacitors (EDLCs), store energy through the formation of an electrostatic double-layer of electronic and ionic charge accumulated on each side of the electrode/electrolyte interface in response to an applied potential.[1, 2] Most batteries undergo chemical changes or phase transitions upon charge/discharge which degrade performance over several hundred to several thousand cycles. In contrast, EDLCs require only the physical re-arrangement of electronic and ionic charge with little to no chemical changes and can typically be cycled over a million times with little performance degradation. They are not limited by reaction kinetics and solid-state mass transport, as is typically the case for batteries, enabling EDLCs to be charged and discharged rapidly with nearly 100% efficiency. As shown in Figure 1.1, current EDLC technologies can achieve power densities approaching that of conventional dielectric capacitors, being several orders of magnitude higher than battery technologies. However, their energy density is currently lower than state-of-the-art battery technologies.

EDLCs are used in numerous applications ranging from portable power for telecommunications to engine starters for trucks and buses.[3] With an improved energy density many additional applications would benefit from the use of EDLCs.[3] Renewable energy generation technologies (ex. wind power) require portable,
rechargeable energy storage buffers which can accept periodic high power bursts.[4] Regenerative breaking to partially recover the kinetic energy lost upon stopping in hybrid or all electric cars and high speed trains also requires energy buffer systems with the high power capabilities of EDLCs. Furthermore, it is thought that EDLCs could assist batteries in all electric vehicles, especially during acceleration when high power is required.[5] The use of hybrid battery/EDLC systems has been shown to extend the life of high energy density Li-ion battery technologies.

Figure 1.1: Ragone plot illustrating typical energy and power densities of portable energy storage devices. (Adapted from ref. [2])

Today, many of these applications rely on overdesigned, over-sized batteries, in order to compensate for their low power. However, these need to be frequently replaced and add unnecessary mass and volume. The use of EDLCs for these and many other applications will increase if their cost to performance ratio is lowered so that they can compete with well-established battery technologies.[6] To this end, major efforts are underway to improve the energy density of EDLCs while maintaining their advantageous attributes such as long cycle-life, high power density and improved safety compared to
batteries. Therefore, the main goal of this thesis work is to develop new materials, processing strategies and identify new mechanisms for improving the energy density of EDLCs.

Before outlining detailed objectives of this thesis work, the following section reviews the general operating principle of an EDLC, the factors which affect their performance and the materials currently used as electrodes.

1.1 Operating Principles of Double-Layer Capacitors

1.1.1 Device Configuration

Figure 1.2a shows the typical configuration of an EDLC.[7] High specific surface area (SSA), porous carbon electrodes are typically cast onto a metallic current collector. Two such electrodes are sandwiched between an ion permeable membrane that prevents the two electrodes from short circuiting. An electrolyte at ~1 M or higher salt concentration is typically imbied into the porous carbon electrode. Upon application of a potential difference between the two electrodes, electrons accumulate near the interface of the negatively polarized electrode. At the same time, holes are generated at the oppositely charged electrode and anions populate the double-layer on the solution side of this interface. To maintain charge neutrality, anions and cations are exchanged across the membrane to balance the charge in each compartment. As schematically illustrated in Figure 1.1b, the ions and electric charge on either side of the interface form what is called a double-layer. The separation distance, \( \delta \), between these two charged regions is typically on the order of a nanometer, corresponding to the radius of a solvated ion. This region of thickness \( \delta \) can be thought of as the dielectric layer separating two plates of a
conventional parallel plate capacitor. The nanometer-scale charge separation and the use of high SSA electrode materials leads to devices with significantly higher specific capacitance than typical dielectric capacitors. A more detailed description of the structure of this double-layer is given in Section 1.2 for various types of electrode materials and electrolytes.

\[ C_{obs} = \frac{1}{C_1} + \frac{1}{C_2} = 2 \frac{1}{C_1} \quad \text{for } C_1 = C_2 \quad (1) \]

Thus the full device capacitance is only half the capacitance of one electrode. It is typical to report the capacitance of a single electrode normalized by the mass of a single electrode. In this case, to estimate the total capacitance expected from a device, the single
electrode capacitance has to be divided by four (a factor of two to account for the two capacitors in series configuration and another factor of two to account for double the mass). Therefore one must be clear about the reported value so that fair comparisons can be made.

1.1.2 Energy Density

![Diagram of charge/discharge relationship between an ideal battery and a capacitor](Adapted from [1])

The specific energy and power density of an EDLC are the most important criteria for evaluating their performance in comparison to other energy storage technologies. Figure 1.3 illustrates the state of charge ($Q$) as a function of the potential difference ($E$) between two electrodes for an EDLC and compares this to the situation observed for a battery. The Gibbs free energy $\Delta G$ of each device can be calculated by integrating this curve and assuming the capacitance is constant with potential:

$$\Delta G = \int E \, dQ = \int \frac{Q}{C} \, dQ = \frac{1}{2} \frac{Q^2}{C} = \frac{1}{2} C \cdot E^2$$  \hspace{1cm} (2)
For an EDLC, $\Delta G$ is half that of a battery charged to the same extent at the same voltage because the potential between the battery anode and cathode does not change significantly with $Q$. The square dependence of $\Delta G$ on $E$ indicates that substantial improvements to device $\Delta G$ can be achieved if an EDLC is operated at higher voltage.

Figure 1.4 illustrates the simple relationship between capacitance, operating voltage and device energy density indicating the typical capacitance and possible reversible operating voltage for several commonly used electrode materials and electrolytes. It is clear from Figure 1.4 that small improvements in the capacitance of carbon electrodes operated in high voltage capable organic electrolytes or ILs have the potential for the largest improvements in device energy density. The main strategy pursued in this thesis work is to improve the capacitance of EDLCs in a way which is compatible with electrolytes capable of stable, high voltage operation.

![Figure 1.4: Estimated energy density of a two electrode cell as a function of operating voltage and single electrode capacitance using $\Delta G \sim \frac{1}{2} CE^2$. Typically the assumption of 30% active material in a device is used to estimate the device energy density. However, this differs for carbon-based and RuO$_2$ systems since in the latter much thicker electrodes can be used due to the metallic conductivity of RuO$_2$. Thus we only compare electrode energy density not device energy density.](image)
The specific capacitance of an electrode material can be reported on a mass or volume specific basis. The mass specific capacitance or gravimetric capacitance, $C_G$, of an electrode is the most commonly used metric to identify promising materials for EDLCs. $C_G$ is the product of the intrinsic capacitance of the interface $C_{\text{int}}$ and the ion-accessible SSA:

$$C_G = C_{\text{int}} \cdot SS\!A$$  \hspace{1cm} (3)

Maximizing each of these parameters will lead to the highest possible $C_G$.

In addition to maximizing $C_G$, the volumetric capacitance, $C_V$, and pore volume must also be considered for two important reasons.[8] (1) If EDLCs are to be used as rechargeable energy storage devices for portable devices their volume must be minimized. (2) $C_G$ is typically reported as the capacitance per mass of active electrode material only and does not account for the mass of electrolyte in the electrodes. Electrodes with low $C_V$ and high pore volume will require a large fraction of electrolyte and will therefore increase the device weight for a given capacitance. This implies that electrode materials with the highest ion-accessible surface area, packed into the densest possible configuration will be the most technologically significant for device applications.[8]

### 1.1.3 Power Density

One of the main advantages that EDLCs possess over other energy storage technologies is the high rate of charge/discharge that can be achieved with little to no impact on device energy density. The metric which describes this is the power density ($P$) which is a function of the operating voltage and the equivalent series resistance (ESR) of
the device. The ESR is the effective resistance of the entire cell which encompasses all
electronic resistances, ionic resistances and the membrane resistance. Unfortunately the
distributed nature of ESR causes it to change with time scale.[1] Therefore, in many cases
an exact treatment of $P$ is complicated. However, an estimate of the ESR and the
operating voltage can be used to approximate the maximum power ($P_{\text{max}}$) of an EDLC if
the charging/discharging is modeled as a simple series RC circuit.[9] From this
assumption, the voltage drop can be calculated from Ohms law as:

$$E = E_i - iR_s$$  \hspace{1cm} (4)

where $R_s$ is the resistance associated with the ESR. Then, $P$ is simply $iE$ and thus:

$$P = iE = iE_i - i^2R_s$$  \hspace{1cm} (5)

The maximum power ($P_{\text{max}}$) is found by taking the derivative of Equation 5 with respect
to the current, $i$, and setting it to zero to find the current and voltage at maximum power.
The product of these parameters leads to an approximation for $P_{\text{max}}$ of an EDLC:

$$P_{\text{max}} = \frac{E_{\text{max}}^2}{4R_s}$$  \hspace{1cm} (6)

This expression is typically used to evaluate the power capabilities of an EDLC. $P_{\text{max}}$ vs.
energy density are typically plotted against each other in what is called a Ragone plot, as
was shown in Figure 1.1, which is commonly used to compare the performance of
various electrodes and energy storage devices.
1.1.3.1 Factors Affecting the ESR

There are three main factors that contribute to the ESR of an EDLC: the ionic resistance, electronic resistance and the membrane resistance (if a membrane is present between the two electrodes). The membrane resistance is typically small and thus the next sections will review the important factors which govern the ionic and electronic conductivity.

1.1.3.1.1 Ionic conductivity

The ionic conductivity is influenced by the number of mobile charge carriers, their mobility in an electric field and the effective number of conductive paths.[1] The number of charge carriers is dictated by the electrolyte concentration and the degree of ion solvation. In water most ions are fully dissociated, but in organic solvents ions can form partially solvated ion-pairs which lower the free charge carrier concentration. The mobility of an ion can be estimated by setting the force on the ion due to an electric field () to the viscous drag or hydrodynamic resistance approximated by Stokes law.[10] This leads to:

\[
\mu = \frac{v_{\text{ion}}}{\xi} = \frac{ze}{6\pi \eta R_{\text{ion},s}},
\]

where \(v\) is the velocity of the ion in a field \(\xi\) of 1 V/cm, \(\eta\) is the viscosity of the solvent, \(R_{\text{ion},s}\) is the radius of the solvated ion and \(\mu = v_{\text{ion}}/\xi\) is the mobility. The ESR of an EDLC will be minimized for an electrolyte with the following properties: high concentration of dissociated ions (facilitated by high dielectric constant solvents), low viscosity and small
solvated ionic radius. The largest ionic conductivities \(O(100 \text{ mS/cm})\) are achieved for aqueous solutions of strong acids or bases while organic electrolytes and room temperature molten salts, which we refer to as ionic liquids, are typically \(O(10 \text{ mS/cm})\). Therefore the increased voltage window of non-aqueous electrolytes comes at the expense of increased ESR due to the lower ionic conductivity compared to aqueous electrolytes.

The typically nanoporous nature of high surface area electrodes used for EDLCs is also a significant factor contributing to their ESR. To achieve high mass and volume specific surface area, electrodes containing a significant fraction of pores < 2nm are used. [7, 11] This pore-size is on the order of a \(R_{\text{ion,s}}\), which can drastically increase the ionic resistance in pores compared to the bulk electrolyte. The size, shape and length of these pores lead to a characteristic pore resistance depend on the time-scale of charging which defines the distance the ions can enter or leave the pore.[1, 12, 13] This distribution of time constants causes the ion-accessible SSA of a porous electrode, and thus the measured capacitance, to depend on the time scale of charging/discharging.

1.1.3.1.2 Electronic conductivity

The electronic conductivity of the electrode also needs to be considered when fabricating electrodes for EDLCs. Typically, a metallic current collector (usually aluminum because it has a low density, is relatively inexpensive and is relatively corrosion resistant due to the native layer of aluminum oxide that forms on its surface) provides the backing to which electrode films are laminated.[1] This distributes the
electronic charge to the thin film electrode. Since the electrode material is typically many orders of magnitude less conductive than a metal (resistivity of $10^{-3}$–$10^{-5}$ $\Omega \cdot m$ vs. $10^{-8}$ $\Omega \cdot m$),[7] electric current only needs to flow through a thickness of typically 100 – 200 $\mu$m so that losses due to ohmic drop are small. However, it is desirable to maximize this thickness to generate a larger ratio of electrode mass to the mass of the total packaged device (including current collector, contacts, membrane and packaging material). Films with increased thickness require electrode materials with higher electronic conductivity.

The two factors that contribute to the electronic conductivity of the electrode film are the inter and intraparticle resistances.[1, 14] The intraparticle resistance is governed by the type of electrode material used. For carbon materials, intraparticle resistance is affected by the heat treatment temperature and the degree and distribution of graphitization within a conductive particle.[14] For non-crystalline carbons conduction is typically by a thermally activated hopping mechanism which is described by:[14]

$$\rho(T) = \rho \exp( E_A / kT),$$

(8)

where the activation energy, $E_A$ depends on the heat treatment temperature and has to do with the distance between conductive domains within the material.

The interparticle resistance is the contact resistance between conducting particles which is controlled by factors like the contact area and surface state of the particles. [14] Electrodes are typically rolled or pressed and devices assembled under pressure to increase the contact area.[1] The oxygen containing functional groups on carbonaceous
materials are thought to significantly affect their contact resistance by increasing the tunneling barrier for electrons to be transferred between particles. [7, 14, 15]

1.2 Theory of the Electrochemical Double-Layer

This section describes the current theory of the electrochemical double-layer, starting from a thermodynamic perspective which allowed for the first measurements of the surface specific double-layer capacitance, $C_{dl}$, on mercury electrodes. This is more restrictive than $C_{int}$ which can include other effects involving charge transfer across the interface, referred to as pseudocapacitance, which will be discussed later Section 1.2.2.2. Measurements of the $C_{dl}$ were used to confirm the applicability of Guoy[16], Chapman[17] and Stern’s[18] theories describing the distribution of ions and the resulting capacitance at a charged surface for dilute electrolytes which was extended to concentrated electrolytes by Graham[19]. This modern view of the double-layer will then be extended to include contributions from the electrode material when the electrode is not a metal, but a semi-metal or semiconductor as is the case for graphite and the carbonaceous electrodes that are commonly used as electrodes in EDLCs. [20, 21] A more detailed review of the thermodynamics and structural models of the electrochemical double-layer than given here can be found in excellent textbooks written by Bard and Falkner[22] and Conway [1].
1.2.1 Thermodynamic Treatment

Double-layer charging is an interfacial phenomenon and information about double-layer structure can be obtained by following the approach of Gibbs.[22, 23] This is achieved by defining a region between the pure electrode phase and pure electrolyte phase as well as the position of a Gibbs dividing surface that can be chosen arbitrarily within this region. In this case it is convenient to define the surface to be coincident with the electrode/electrolyte interface since we do not expect there to be significant changes within the electrodes beyond this point. We consider a reference system (defined with superscript R), which contains only bulk phases and thus the free energy does not depend on area, \( A \):

\[
\overline{G}^R = \overline{G}^R (T, P, n_i^R) \quad (9)
\]

The actual system (defined with superscript S) is defined to be the electrode, electrolyte and interfacial region where:

\[
\overline{G}^S = \overline{G}^S (T, P, A, n_i^R) \quad (10)
\]
The actual system depends on the area, \( A \), of the interface. Expanding the free energy for each of these regions into their total derivatives, subtracting and considering only experiments performed at constant temperature and pressure leads to an expression for the change in excess free energy of the form:

\[
\overline{dG}^\sigma = d\overline{G}^S - d\overline{G}^B = \left( \frac{\partial G^S}{\partial A} \right) dA + \sum_i \left( \frac{\partial G^S}{\partial n_i^S} \right) dn_i^S - \sum_i \left( \frac{\partial G^R}{\partial n_i^R} \right) dn_i^R
\]  

(11)

Here it is recognized that \( \frac{\partial G^S}{\partial A} \) is the surface tension, \( \gamma \) and the \( \frac{\partial G}{\partial n_i} \) terms are the electrochemical potentials, \( \mu_i \) of the various species, \( i \). At equilibrium the electrochemical potentials of each species are constant between the bulk and the interfacial phases.

This leads to the so-called electrocapillary equation[24] which describes how surface tension evolves with changes in potential and chemical potential:

\[
dG^{excess} = \gamma dA + \sum \mu_i dn_i^{excess}
\]  

(12)

After some manipulations (invoking Euler’s theorem and use of the Gibbs-Duhem equation) Equation 13 is obtained:

\[
-d\gamma = \sigma_m dE + \sum \Gamma_i d\mu_i
\]  

(13)

which relates several measurable properties such as the surface charge density \( \sigma_m \) and the surface excess concentrations, \( \Gamma_i \) which accounts for accumulation of ions at the interface between a metal and the solution phase. Holding the composition constant leads to the well-known Lippmann equation.[24]
The excess electronic charge on the electrode side and the excess ionic charge on the electrolyte side must balance each other and therefore:

\[ \sigma_m = -\sigma_s \]  

By differentiating Equation 13 at constant chemical potential leads to the definition of the differential capacitance:

\[ C_{dl} = \frac{\partial \sigma_m}{\partial E} = \frac{\partial^2 \gamma}{\partial E^2} \left|_{\mu=constant} \right. \]  

As shown in Equation 15, the differential capacitance is directly related to the surface tension, a measurable quantity. The current double-layer theory was established in the early to mid-20th century based on surface tension measurements carried out with mercury electrodes and hence the theory is known as the theory of electrocapillarity. Hence, surface tension vs. potential curves are called electrocapillary curves. Using mercury and other liquid metal electrodes provided a convenient means of estimating the surface tension of the electrode/electrolyte interface.[25] However, measuring the surface tension of solid electrodes is difficult and other techniques must be used such as electrochemical impedance spectroscopy (EIS).
1.2.2 Kinetic Theories

1.2.2.1 The metal/electrolyte interface

Figure 1.6: Progression of kinetic models of the double-layer formed at a metallic electrode. $\phi_m$ and $\psi_s$ are the potential of the metal and the potential in solution, respectively. Adapted from [1]

The simplest system to describe is the metal/electrolyte interface, as it is assumed that the potential is constant at any point within the metal. Figure 1.6 schematically shows the progression of theories describing the potential drop ($E = \phi_m - \psi_s$) across the interface between the potential of the metal, $\phi_m$, and the potential of the solution far from the electrode, $\psi_s$, which can be varied experimentally with a device called a potentiostat. Helmholtz assumed that all the potential drop occurred in a single plane of ions which mirrored the electronic charge.[26] Guoy[16] and Chapman[17] accounted for the fact that the ions will not distribute uniformly at the interface due to thermal motion. Their theory was modified by Stern[18] and Grahame[25] to account for the finite size of ions and their adsorption in the so-called Helmholtz layer (Figure 1.6), a fact which is important for predicting the capacitance at high electrolyte concentrations.
I will now give a brief account of the physical description of the double-layer based on the Guoy-Chapman theory used to describe the capacitance of the diffuse layer ($C_{\text{diff}}$), illustrated in Figure 1.6, and the extension of this theory to include the capacitance of the Helmholtz layer ($C_{\text{H}}$). The potential, $\Psi(x)$ and ionic charge distribution, $\rho(x)$, on the solution side can be described by the Poisson equation and Boltzmann distribution, respectively:

$$\frac{\partial}{\partial x} \left( \varepsilon \frac{\partial \Psi}{\partial x} \right) = -4\pi \rho_s,$$  \hspace{1cm} (16)

$$\rho(x) = z_+ e c_+^0 \exp \left( -\frac{z_+ e \Psi}{kT} \right) + z_- e c_-^0 \exp \left( -\frac{z_- e \Psi}{kT} \right),$$  \hspace{1cm} (17)

where the $z \pm$ and $c \pm$ are the valence and concentrations of anions/cations, respectively. Assuming the dielectric constant, $\varepsilon(x) \sim \varepsilon_s$, and thus invariant with distance from the surface and combining 1 and 2 for a 1:1 electrolyte leads to the Poisson-Boltzmann equation which can be solved according to the boundary conditions (BCs) shown below:

$$\frac{\partial^2 \Psi}{\partial x^2} = -\frac{8\pi e c}{\varepsilon} \exp \left( -\frac{e \Psi}{kT} \right),$$ \hspace{1cm} (18)

$$\frac{\partial \Psi}{\partial x} \rightarrow 0 \text{ as } x \rightarrow \infty, \quad \Psi(\infty) \rightarrow \Psi_s \text{ at the potential, } \Psi_{\text{H}} \text{ at the distance of closest approach (the thickness of the Helmholtz layer), } x = d_{\text{H}} \text{ yields:}$$

$$q_s = \left( \frac{2kT e \varepsilon_s}{\pi} \right)^{1/2} \sinh \left( \frac{z e (\Psi_{\text{H}} - \Psi_s)}{2kT} \right),$$ \hspace{1cm} (19)
Taking the derivative of this equation with respect to $\Psi_a - \Psi_s$ leads to the definition of the diffuse double-layer capacitance, $C_{\text{diff}}$:

$$\frac{\partial q_M}{\partial (\psi_H - \psi_s)} = \left( \frac{z^2 e^2 e}{2\pi kT} \right)^{1/2} \cosh \left( \frac{z e (\psi_H - \psi_s)}{2kT} \right) \equiv C_{\text{diff}}$$

Equation 20 describes the differential capacitance of the diffuse layer or region in the electrolyte between $x = d_H$ and $x \to \infty$. The total potential drop is what is experimentally measured, $E = \Phi_m - \Psi_s$; however, this potential drop can be broken into smaller increments by defining a potential at the Helmholtz plane, $\Psi_H$, as shown in Equation 21:

$$\frac{\partial (\phi_m - \psi_s)}{\partial q_M} = \frac{\partial (\phi_m - \psi_H)}{\partial q_M} + \frac{\partial (\psi_H - \psi_s)}{\partial q_M}$$

where:

$$\frac{\partial (\phi_m - \psi_H)}{\partial q_M} = C_H$$

Equation 22 defines the inner layer or Helmholtz capacitance ($C_H$) and demonstrates that the capacitance of each region within the double-layer add like capacitors in series.

$$\frac{1}{C_{\text{obs}}} = \frac{1}{C_H} + \frac{1}{C_{\text{diff}}}$$

$C_H$ can be estimated using the parallel plate capacitor equation and plugging in the solvated ionic radius as the distance and the dielectric constant of the solvent which yields $C_H \approx 20 - 30 \mu F/cm^2$. This same approach can be used to break the total potential drop into even smaller divisions to take other effects into account such as the difference between solvated and unsolvated ions (outer and inner Helmholtz layers respectively) and to include any potential drop within the solid material when semiconductors or semi-
metals are considered. The semi-metal case is important to this thesis work and will be discussed in the next section. The fact that the capacitances add in series is important because it means that the measured capacitance will be influenced most by the smaller of the two capacitance contributions. At low electrolyte concentrations \( C_{\text{diff}} \) is low (\( C_{\text{diff}} \propto c^{1/2} \) – see Equation 20) and thus \( C_{\text{obs}} \sim C_{\text{diff}} \) as the electrolyte concentration approaches zero. At high electrolyte concentrations (0.1 – 1 M) the situation reverses and \( C_{\text{diff}} \) becomes large implying that \( C_{\text{obs}} \sim C_{\text{H}} \). This is demonstrated in Figure 1.7 for the case of mercury in aqueous electrolyte of varying concentration. Phenomena such as the re-orientation of solvent and ions near the electrode at potentials much larger than zero (the potential of zero charge, PZC in this case) cause \( C_{\text{H}} \) to change with applied potential.

![Figure 1.7: Differential capacitance of the Hg/aqueous solution interface at various concentrations of NaF. Adapted from [25].](image)
1.2.2.2 Faradaic Charging and Pseudocapacitance

In addition to double-layer charging, there is another mechanism called pseudocapacitance, $C_\Phi$, which also results in a measurable capacitance (i.e., $dQ/dE$ is non-zero). $C_\Phi$ is caused by charge transfer across the electrode/electrolyte and is thus a faradaic process.[1, 22] These mechanisms all involve a quasi-reversible electrochemical oxidation/reduction (redox) reaction where the extent of reaction is a continuous function of the potential, $E$. This situation can arise when oxidizing/reducing a species in solution[27] or oxidizing/reducing the electrode itself as in the case of RuO$_2$ or MnO$_2$ materials which continuously change oxidation state as a function of potential as demonstrated schematically in Figure 1.8.[1] As discussed in Section 1.1.2, to achieve significant energy densities, this process must be reversible over a wide voltage window. Materials such as RuO$_2$ and MnO$_2$ exhibit a nearly continuous change in oxidation state over a relatively large voltage window of ~1 V and 1.4 V, respectively.[1] For example, Ru changes oxidation state from Ru$^{II}$ to Ru$^{III}$ to Ru$^{IV}$ as the potential is made more positive. The total charge passed is nearly constant with potential, leading to a nearly potential independent capacitance.

![Figure 1.8: Example of pseudocapacitance. Adapted from [1]](image-url)
Redox active polymers like polyaniline and polythiopene[28] as well as transition metal oxides[1, 11] such as MnO₂ and CoO₂ possess similar charging characteristics and are much less expensive than RuO₂ (ruthenium being a precious metal) and are actively being pursued as high capacitance materials for supercapacitors. Carbonaceous materials also typically carry oxygen or nitrogen containing functional groups that display significant \( C_\Phi \) in aqueous electrolytes and lead to very high specific capacitances. [4, 29] Most reactions involving \( C_\Phi \) utilize proton transfer reactions and thus require water or a source of protons. Unfortunately, the use of water is limited by the hydrogen evolution reaction at negative potentials and oxygen evolution at positive potentials leading to a thermodynamically limited potential window of 1.23 V. However, this reaction is kinetically limited at carbon, MnO₂ and RuO₂ electrodes which enables operation of EDLCs in aqueous electrolytes up to ~2 V. Nonetheless, this restricted voltage window limits the attainable energy density from such devices. Furthermore, these reactions are not fully reversible which causes their cycle life to suffer by mechanisms similar to current rechargeable battery technologies.

Both \( C_\Phi \) and \( C_{dl} \) add as capacitances in parallel. (i.e., \( C_{int} = C_{dl} + C_\Phi \)) To understand the mechanism of capacitive charging for a certain electrode/electrolyte system it is necessary to distinguish between these two types of charging. One method which is typically used separate the two is to investigate the frequency dispersion of the \( C_{int} \) over a wide frequency range using techniques based on electrochemical impedance spectroscopy (EIS). Many reactions that lead to \( C_\Phi \) can only charge on the timescale of ~1 Hz due to limitations in reaction kinetics.[1] On the other hand, \( C_{dl} \) is constant with
frequency and can be measured at frequencies of ~1 kHz, limited only by the RC time constant of the electrochemical cell. Therefore $C_{dl}$ can often be distinguished from $C_\Phi$ according to the frequency dependence of the measured capacitance. However, as was discussed in Section 1.1.3.1.1, when experiments are carried out using porous electrodes, the distributive nature of charging, due to varying electrolyte resistance in pores of different lengths and shapes, also yield a frequency dependent capacitance. Such a process can be modelled as transmission line of resistors which yields a Warburg-like impedance response, exhibiting a 45° phase angle.[12] This makes $C_\Phi$ and $C_{dl}$ practically indistinguishable in porous systems.[1] In the case of porous electrodes, $C_\Phi$ can often be eliminated or ignored by testing capacitors in a non-aqueous aprotic electrolyte as most of these Faradaic charge transfer processes involving proton transfer reactions cannot occur.

1.2.2.3 The graphite/electrolyte interface

Now that the mechanisms of charging have been discussed for the most simple systems I will briefly discuss the applicability of these models to carbon materials which are the materials typically used as EDLC electrodes as will be discussed in Section 1.3.

Randin and Yeager were the first to develop a well-controlled method for isolating the two principle surfaces of high quality single crystal of pyrolytic graphite.[20] [21, 30] These are generally referred to as the basal-plane and the edge-plane of graphite as shown in Figure 1.9. The c-axis is normal to the basal-plane and the a-axis is normal to edge-plane. When referring to the dimensions of a graphite crystal we will use the
characteristic lengths $L_a$ and $L_c$ to indicate the size of graphitic domains and stacking order, respectively.

![Diagram of graphite crystals](image)

**Figure 1.9:** Naming conventions for describing graphite crystals

### 1.2.2.3.1 Basal-Plane of Graphite

Randin and Yeager observed an anomalously low capacitance (3-4 µF/cm²) for the basal-plane of graphite in a non-adsorbing aqueous electrolyte at high concentration even at high electrolyte concentrations up to 0.9 M. Their results could not be explained by the Guoy-Chapman-Stern theory. They suggested that the basal-plane of graphite behaves like an intrinsic semiconductor. At the semiconductor/electrolyte interface, there can be a significant potential drop within the solid side of the interface. This creates what is called a space charge layer within the electrode material. Analogous to Equation 23, the total potential drop measured between the electrode bulk and the electrolyte bulk can now be broken down into three distinct regions as opposed to two, including the capacitance of the space charge layer ($C_{sc}$):

$$\frac{1}{C_{obs}} = \frac{1}{C_{sc}} + \frac{1}{C_H} + \frac{1}{C_{diff}}$$

(24)
They estimated the characteristic decay length of the electric field within the graphite to be on the order of a nanometer which would explain the low measured capacitance of 3-4 µF/cm².[21]

This explanation was revisited by Gerischer[31] a decade later and corrected for the fact that graphite is not a semiconductor but a semi-metal, a material with a low density of electronic states (DOS) near the Fermi level. In contrast to the semiconductor view, in which electrons have a finite probability of jumping from the valence band into the conduction band depending on temperature, a semi-metal like graphite has a populated conduction band, however, there are a limited number of quantum states in which these electrons are allowed to sit.[31] Assuming a constant DOS with distance into the material, Gerischer estimated the extent of the space-charge layer to be ~0.85 nm indicating that a non-uniform charge distribution exists in graphite nearly 3 graphene sheets thick. He derived a simple relation to estimate $C_{sc}$ near the Fermi level:[31, 32]

$$C_{sc}^2 \approx \varepsilon N_0 e$$

(25)

where $N_0$ is an estimate for the DOS near the Fermi level ($N_0 \sim 10^{20} \text{cm}^3\text{eV}^{-1}$) and $\varepsilon$ is the dielectric constant of graphite (~3.28 for pyrolytic graphite). In a later review on the electrochemistry of semiconductors, Gerischer provides a useful schematic illustrating the charge density on either side the graphite/electrolyte interface compared to a metal/electrolyte interface (reproduced as Figure 1.10).[33]

In an analogous fashion to the doping of semiconductors, it has been shown that the basal-plane of graphite can also be doped with boron[34] and, more recently, with nitrogen[35, 36] to yield p and n-doped electrodes, respectively.
1.2.2.3.2 The Edge-Plane and Glassy Carbon

In subsequent work, Randin and Yeager also showed that edge-plane carbon electrodes possessed an anomalously high capacitance ($50 - 100 \ \mu F/cm^2$).[30] They attributed this to functional groups, defects and dangling bonds associated with the terminal edges of the carbon. However, surface roughness, porosity and the possibility of $C_\Phi$ precluded a direct observation of $C_{dl}$. According to the double-layer theory described in the previous sections, $C_{obs}$ cannot be larger than $C_H$ and thus it is likely that any additional capacitance above $C_H \sim 16-24 \ \mu F/cm^2$ (typical values for $C_H$ measured experimentally by Grahame for a range of electrolytes) [1, 25] is due to such effects. In addition to edge-plane electrodes, these researchers also measured the capacitance of polished glassy carbon (GC) electrodes in aqueous electrolyte. The capacitance was also found to be high ($\sim 10 - 60 \ \mu F/cm^2$) and depended on electrolyte pH, measurement frequency and scan direction in a similar way as the edge-plane graphite electrodes.[30]
Several recent works have determined $C_{dl}$ of GC electrodes in the absence of $C_\Phi$ by measuring capacitance in non-aqueous electrolytes. The $C_{dl}$ of GC was found to be governed by the electrolyte and $C_H$ indicating that the GC/electrolyte interface behaves like a metal/electrolyte interface, possessing a $C_{dl}$ as high as 20 $\mu$F/cm$^2$.[37-39]

1.2.2.4 The graphene/electrolyte interface

The capacitance of graphene, an atomically thin, single-layer of graphite was also measured recently. Xia et al. used the “Scotch-tape method” to generate single sheet graphene which were contacted by micropatterning techniques and supported by a silicon substrate on one side of the sheet.[40] They found the capacitance to be similar to the basal-plane of graphite. This was also verified by Stoller et al. for graphene produced by a carbon vapor deposition (CVD) method.[41]

Prior to these studies, graphene-like domains were known to make up the pore walls of conducting activated carbons.[42] It was expected that this material would also be limited by the low $C_{sc}$, as it is for basal-plane graphite.[43, 44] Barbieri et al. were the first to discuss the possible implications of this space-charge layer on the capacitance as the pore wall thickness approaches that of a single sheet of graphite (i.e., graphene).[42] They suggested that the low DOS would have to support double-layer charging on either side of the pore wall and that this phenomenon may lower $C_{dl}$ as it effectively decreases the approximated carrier density near the Fermi level by a factor of two. They used this idea to explain the leveling off of the mass specific capacitance when electrodes with higher surface area are used (see Figure 1.11). Evidence for this phenomena was recently
given by Stoller et al. who used large single sheets of CVD grown graphene in an electrode designed such that the electrolyte was exposed to both sides of a single sheet.[41]

Figure 1.11: Saturation of specific capacitance with increasing specific surface area. (Reproduced from [42])

1.3 Porous Carbonaceous Electrodes

Compared to most metals, conductive carbonaceous materials are typically more corrosion resistant, electrochemically stable, less expensive and lower in density.[7, 14] Despite the fact that their $C_{dl}$ is thought to be lower than a metallic electrode,[21, 41, 42] these properties lead to the highest SSAs, implying the potential for high specific capacitance and thus energy density. The inherent corrosion resistance of carbonaceous materials allows them to be stably operated for millions of cycles with little performance degradation.[7] In the following sections, four major classes of electrically conductive, high SSA carbonaceous materials commonly used as EDLC electrodes are reviewed. Their advantages and disadvantages are highlighted. A more detailed review of graphene-
based materials is given in Section 1.3.4 as this material and its use in EDLCs is the focus of this thesis work.

1.3.1 Activated Carbons

Activated carbons are typically formed by carbonizing a solid or liquid carbon precursor to what is called a char in an oxygen-free environment.[14] There are many carbon precursors, such as saw dust, coconut shell, black ash, bituminous coal, petroleum coke, etc. which can lead to activated carbons with varying material properties. The char is then annealed at high temperature to graphitize the material and achieve a percolated sp² phase. The conductive sp² hybridized phase is then exposed by activation or etching away of the surrounding sp³ hybridized carbon by either thermal or chemical means – typically by hot, concentrated KOH, superheated steam or H₂SO₄. This results in a porous, conductive matrix of more or less disordered sp² hybridized carbon.

The resulting material can be prepared either by grinding the solid into a fine powder (diameters typically > 2 µm) or activation can be carried out on carbon fibers produced as interwoven fibers or felts.[14] The nitrogen accessible SSA of activated carbons can be more than 1000 m²/g and this surface area is typically in nanometer to sub-nanometer sized pores.[45]

Most commercially available EDLCs use activated carbons as their electrode material.[7, 46] This is likely because they were the first to arrive on the scene and are relatively inexpensive. However, activated carbons have several major disadvantages. Solvated ions can typically only access pores larger than ~1 nm and thus a large fraction
of the nitrogen accessible surface area cannot be accessed by the electrolyte. This can considerably lower the specific capacitance. Activated carbons also have a low electrical conductivity and the nanopores within the micron sized particles/fibers can significantly increase the electrolyte resistance. These limitations have prevented EDLCs from entering what could be a potentially large market for portable, nearly limitless cycle life, rechargeable energy storage devices.

1.3.2 Templated Carbons

Another major family of electrode materials is comprised of templated carbons. The need to control pore-size to maximize ion-accessibility was recognized and methods to create materials with narrow pore-size distributions were developed. [47, 48] This is carried out using two typical procedures: (1) Using a molecular template, typically an ionic or non-ionic surfactant which is added to a medium such that it self-assembles into a hexagonal or cubic phase.[47, 49] This was first achieved using so-called SBA-15 type materials where silica is template around the block copolymer phase. The block copolymer is extracted and a carbon precursor (ex., sucrose, furfuryl alcohol etc.) is infiltrated around the silica, heat treated to graphitize the carbon and the silica is extracted by KOH or HF. This procedure yields carbon materials with a narrow pore-size distribution. (2) Another approach to controlled pore size is to use silicon carbide or transition metal carbides to form an ordered crystalline phase.[11, 48] The silicon or transition metal is leached out, typically with hot chlorine gas to form what are known as carbide-derived carbons:
TiC + 2Cl₂ → TiCl₄ + C

These materials also possess a narrow pore-size distribution that depends on the chlorination temperature.[50, 51] Figure 1.12 below shows cross-sectional TEM images of electrode materials generated by this technique.

![Figure 1.12: Transmission electron micrograph of TiC treated by chlorination at various temperatures. Graphitic fringes can be seen as dark contrast. Reproduced from [50]](image)

These materials provide an advantage that the pore-size can be finely adjusted to optimize the ion-accessible SSA and can be made as a monolithic block which leads to increased bulk density and thus devices with a smaller volume (i.e., higher volume specific capacitance). Nitrogen accessible SSAs can be as high as 1500 m²/g leading to specific capacitances of 100 – 140 F/g in organic electrolytes[50, 51] and ILs[51].
However, the ionic conductivity of these materials is typically low, due to the tortuous, resistive path an ion has to take to enter or leave the dense monolith.

### 1.3.3 Single-Walled Carbon Nanotubes

Single-Walled Carbon Nanotubes (SWCNTs) have also been extensively studied as electrodes for supercapacitors.[7] These materials have a maximum theoretical surface area of 1315 m$^2$/g (half that of a graphene sheet). I will not discuss multi-walled carbon nanotubes (MWCNTs) because of their even lower SSA. SWCNTs have a high conductivity and can be fabricated into electrodes with nitrogen accessible SSAs approaching ~9000-1000 m$^2$/g.[52] This high surface area can only be achieved if the tubes are effectively debundled and filtered into mats or so-called “bucky-gels” where they lie in a randomly oriented crossed cylinder aggregate morphology. When aggregated and aligned in what is called a bundle, the SWCNTs can be compressed by intertube van der Waals (vdWs) forces which severely limit their accessible surface area.[53-55] In crossed cylinder form they only form point contact which enables SSAs closely approaching theoretical.[52] The porous network is also continuous and mesoporous which enables high ionic conductivity.[56] The combination of high electronic and ionic conductivity leads to devices with high charge-discharge rates and moderately high capacitance (~80 – 100 F/g in organic electrolytes).[7, 52] Despite the high charge/discharge rates, the capacitances attained with SWCNTs are less than or similar to the capacitances typically achieved with the best activated carbons.[7, 52]
The capacitance of SWCNTs is also thought to be limited by the same $C_{sc}$ phenomenon as with HOPG and graphene.[57] It has been suggested that only the semiconducting tubes are limited by the $C_{sc}$ and not metallic tubes which differ only in terms of chirality. Unfortunately, I have not come across a study which compares purified semiconducting tubes to metallic ones. If metallic tubes are limited by the electrolyte and not the electrode side of the interface it could be possible to achieve ~200 F/g (assuming $C_I \sim 20 \mu F/cm^2$ and a SSA $\sim 1000 m^2/g$) if electrodes were prepared from purified metallic tubes. However, the production and/or separation of these tubes would likely make such an electrode material prohibitively expensive. Studies have also showed that it is possible to nitrogen dope SWCNTs which increases their capacitance from $\sim 3 - 7 \mu F/cm^2$ to $\sim 8 - 9 \mu F/cm^2$ over the voltage window tested.[35]

1.3.4 Graphene-based materials

A graphene sheet has double the SSA of a SWCNT (2630 m$^2$/g) while possessing a similar electrical conductivity and thus has the potential to outperform SWCNTs and activated carbons as EDLC electrodes. Graphene networks may also facilitate higher ionic conduction due to their quasi 2 D nature and the interconnectivity of the pore-space in contrast to 1 D transport in nanoporous activated and templated carbons. There are many types of graphene-based materials that have been developed over only a short period of time (all during my thesis work at Princeton). We define pristine graphene to be single sheet of graphene with no functional groups on its surface or lattice defects (a small number of defects are expected to occur in all materials processed at a finite
temperature due to entropy)[58]. This material was first generated by successively cleaving a block of highly ordered pyrolytic graphite (HOPG) with Scotch tape until a single layer was isolated and observed.[59, 60] Other methods have now been developed to generate pristine graphene such as chemical vapor deposition (CVD)[61] or exfoliation of graphite by ultrasonication in appropriate solvents.[62] However these methods cannot yet efficiently and economically yield bulk quantities of graphene for use as thick, porous electrode films. Most production strategies are aimed towards high performance electronics where graphene holds promise as a material for high speed transistors.[59]

Alternatively, a form of “defective” graphene that contains a significant number of functional groups and lattice defects can be generated economically and in large quantities.[63-66] This route is based on the exfoliation and decomposition of graphite oxide (GO) into a material typically referred to as reduced graphene oxide or functionalized graphene sheets (FGSs). Since I will be focusing mainly on EDLC electrodes based on FGSs throughout my thesis, I provide a more detailed review of its production and properties in the sections to follow.

1.3.4.1 Oxidation of Graphite

Graphite oxidation was first achieved in 1859 by Brodie using the method of graphite intercalation developed earlier by the German scientist Schafhautl.[67, 68] A minor improvement to this process was later suggested by Staudenmaier.[69] Their methods involve a mixture of graphite, HNO$_3$ and KClO$_3$ dissolved in concentrated sulfuric acid as a solvent. However, the use of KClO$_3$ and its addition to the acid mixture poses a
constant explosion hazard and requires oxidation for several days to weeks. Therefore an improved method was developed by Hummers and Offeman in 1958 where KClO₃ was replaced with KMnO₄ and NaNO₃.[70] Their reaction took only 2 h and was carried out at low temperature (45 °C) yielding GO with an atomic ratio of carbon-to-oxygen (C/O) of between 2.1 and 2.9. More recently, the Hummers method was improved upon by Marcano et al. by increasing the ratio of KMnO₄ to graphite and substituting H₃PO₄ for the nitrate salt.[71] This improved the product yield and resulted in GO with a C/O typically below 2.

**Oxidation mechanisms**

In all of the proposed reactions sulfuric acid is used for two reasons: (a) the reaction is facilitated using anhydrous conditions and sulfuric acid can be more easily purified than many other acids (i.e., HCl, H₃PO₄)[70] and (b) because sulfuric acid readily intercalates into graphite which facilitates transport of the oxidizing agents between graphene sheets.[72] In the Brodie and Staudenmaier methods, HNO₃ oxidizes the surface of graphite while KClO₃ is thought to provide a source of dioxygen for the reaction.[68] In the Hummers and Marcano methods, the active species is thought to be dimanganese heptoxide.[68] This strong oxidizer is thought to form when KMnO₄ is added to strong acid according to the following mechanism:

\[
\text{KMnO}_4 + 3 \text{H}_2\text{SO}_4 \rightarrow \text{K}^+ + \text{MnO}_3^+ + \text{H}_3\text{O}^+ + 3\text{HSO}_4^- \\
\text{MnO}_3^+ + \text{MnO}_4^- \rightarrow \text{Mn}_2\text{O}_7
\]
In the early part of the reaction, a 2\textsuperscript{nd} stage graphite intercalation compound (GIC) is formed. The term “stage” is used to describe the number of graphite layers or graphene sheets between each layer of intercalant. As intercalation proceeds the material converts to a 1\textsuperscript{st} stage GIC. Upon the addition of the oxidizer, a peak corresponding to the GO d\textsubscript{0002} spacing emerges. Complete oxidation is achieved when there is no detectible graphite peak in the profile or qualitatively observed by the color of the suspension formed when the material is added to water.[70] The GO should appear bright yellow or even white[73] if well oxidized. Tinting from unoxidized graphite can make the resulting material look darker brown, green or even grey.

**Proposed structure of graphite oxide**

The structure and chemistry of GO or singles sheets of graphite oxide (which we refer to as graphene oxide) was recently discussed in several reviews.[68, 74] The various structural models proposed over the last ~80 years are schematically illustrated in Figure 1.13. Primitive models based only on elemental analysis, XRD and inferences based on chemical reactivity were used to build the first models of GO. Hofmann and Holst proposed that GO contained only epoxides to give a stochiometry of C\textsubscript{2}O.[75] Due to the presence of hydrogen in the material Ruess suggested that hydroxides also existed on the surface. Scholtz and Boehm were the first to suggest that quinoidal species may also exist.[76]
The first detailed model based on nuclear magnetic resonance (NMR) and complemented by chemical reactivity was set forth by Lerf and Klinowski.[77, 78] They made several important conclusions from their detailed analysis. They confirmed the presence of tertiary hydroxyls on the basal-plane. The NMR spectra before and after various partial deoxygenation reactions suggested that epoxides are in the form of 1,2-ethers and not 1,3-ethers and that these epoxides must be located in close proximity to hydroxyls. Their evidence also suggested that alkenes are present in the form of stable aromatic rings or conjugated clusters and not significantly present as isolated structures due to the lack of chemical reactivity. This suggested that GO is composed of two types of regions, mainly aliphatic, 6-member rings bound to oxygen and clusters of aromatic networks whose size and number depend on the extent of oxidation. Furthermore they suggested that the structure is not periodic in nature but functional groups and sp²
domains are distributed randomly. This is currently the most widely accepted model for GO and has only been slightly improved upon. To explain FTIR spectroscopic evidence for the presence of ketones and/or quinines in the GO structure, Szabo et al.[79] proposed that phenol-quinone structures are likely associated with aromatic regions. This model could explain these features and also the observed acidity of GO when dispersed in water that could not be fully explained by the presence of carboxylic acids and phenolic hydroxyls existing only at the edges.[79] Therefore this updated model includes the features suggested by Sholtz and Boehm.

Cai et al. also used solid state NMR with $^{13}$C labeled GO to investigate the types of functional groups and their 2D distribution on the graphene oxide surface. [80] Their results indicated the presence of mostly epoxides and hydroxides with a smaller fraction of phenolic hydroxyls than predicted by Szabo et al.[79]. They also found that a significant number of carbons bound to hydroxides or epoxides were also bound to $sp^2$ hybridized carbons. Also, a significant number of hydroxides were located on carbons bonded to a neighboring carbon of an epoxide. Their work supported elements described by both the Lerf-Klinowski and Szabo-Dekany models.

Although these models describe the general structures that have been observed on some types of GO, the final structure is thought to differ depending on the oxidation method and extent of reaction.[68, 81] To complicate things further, the washing procedure and storage conditions are also thought to change its chemical nature. Dimiev et al. showed that if GO was washed with anhydrous solvents it remained white.[73] Exposing this material to moisture caused its absorbance to slowly increase with time as
water reacted with the GO, removing some of the oxygen containing functional groups and creating $sp^2$ hybridized pairs.

1.3.4.2 Exfoliation and Reduction of Graphene Oxide

The GO produced after the oxidation of graphite is an electrical insulator and is typically in the form of large crystals of stacked single sheets of graphene oxide typically ranging in size from 1 to 100 $\mu$m.[65, 82] These lamellar aggregates must be exfoliated into single sheets and reduced through deoxygenation to a conductive state before we consider them FGSs. This can be achieved by two different routes. (1) GO was known to be thermally unstable since the early work of Brodie.[67] Deflagration was observed when heated to temperatures above 200 °C forming a low density graphite-like material.[63, 67] Our group recently demonstrated that single sheets of disordered and functionalized graphene could be produced by ultrasonating this “deflagration product” in an appropriate solvent.[64, 65] During this process it was shown by simultaneous TGA/DSC and FTIR that water vapor and CO/CO$_2$ are liberated during thermal reduction. McAllister et al. suggested that the buildup of these gases between the sheets is responsible for exfoliation.[65] Therefore for complete exfoliation it is necessary that the rate of decomposition exceed the rate at which gas diffuses out of the galleries between each sheet. If heated slowly enough it was possible to prevent exfoliation altogether. (~0.1-1 °C/min). Thermal decomposition leads to partial restoration of the conductive graphene lattice but the removal of CO and CO$_2$ implies that many vacancy defects are also produced.[64, 83] (2) Alternatively, GO can be exfoliated as single sheets in water or
other polar solvents, a process which is also facilitated by ultrasonication. This material can then be chemically reduced using strong reducing agents like hydrazine hydrate[63, 66] and sodium borohydride[84] to remove a significant amount of functional groups and partially restore the conductive graphene lattice. Solvothermal reduction of dispersions of graphene oxide in water and other solvents has also been carried out.[85, 86] Reduction can also be achieved electrochemically by cycling graphene oxide electrodes in electrolytes to large negative potentials.[87, 88]

**Structure of reduced graphene oxide**

Brodie[67] observed that thermal decomposition of GO produced H₂O and CO₂ and it was later suggested by Boehm *et al.*[63] that holes are formed in the graphene lattice due to the removal of carbon. Schniepp *et al.* suggested that these holes or vacancies likely form or reconstruct into stable structural defects like the 5-8-5 divancy defect.[64] The possible defect structures that form in graphite and graphene were recently reviewed by Banhart *et al.* [89] and several theoretically and experimentally observed structures are shown in Figure 1.14. These defects introduce 5, 7 and 8 member rings which are non-planar and are thought to contribute to the increased thickness of FGSs produced by thermal reduction when measured by atomic force microscopy (AFM).[64, 65]
Gas evolution is not observed to occur during chemical reduction which suggests that fewer vacancy defects are formed compared to the thermal reduction approach.[63] Chemical reduction is limited by a smaller extent of deoxygenation and typically yields materials with lower C/O, typically less than 10 - 14.[90] We will show in the chapters to follow that the C/O of thermally reduced FGSs can be increased to as high as 400.

There has already been an extensive body of works which attempt to explain the chemical and structural changes in FGSs at various stages of reduction.[83, 91] [92-94] [95-97] Jung et al [97]. used temperature programmed desorption (TPD) in an attempt to quantify the reaction products evolved when graphene oxide is thermally reduced at temperatures up to 300 °C.[97] The relative amounts of the major products are summarized in Table 1.1. Trace amounts of some other species such as OH⁻ and CH₄ may have also been detected. Over 40% of the gaseous by-products consist of CO and CO₂ suggesting that a significant number of lattice defects are introduced.

Figure 1.14: Reconstructed double-vacancy defects in graphene : (a-c) Atomic structures calculated by density functional theory (DFT) calculations; (d-f) experimental TEM images of the same structures. Reproduced from [89]
Table 1.1: Relative partial pressures of reaction products generated by thermal reduction of graphite oxide measured by TPD (Calculated from [97])

<table>
<thead>
<tr>
<th>Reaction product</th>
<th>Relative amounts</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>0.6</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.26</td>
</tr>
<tr>
<td>CO</td>
<td>0.14</td>
</tr>
</tbody>
</table>

Acik et al. showed that the presence of interlayer water can significantly influence the final structure/chemistry of FGSs by facilitating both the formation of lattice defects and conversion of some functional groups to carbonyl functionalities. Acik et al. showed that the presence of interlayer water can significantly influence the final structure/chemistry of FGSs by facilitating both the formation of lattice defects and conversion of some functional groups to carbonyl functionalities. Another detailed analysis by the same authors highlighted the role of evolved O₂ on the formation of CO and CO₂ and the evolution of the residual functional groups left after thermal annealing at temperatures up to 850 °C. Gao et al. used a density functional theory (DFT) method to study the possible reaction mechanisms for reducing graphene oxide using hydrazine and thermal methods. However, their calculations were performed on small domains of pristine graphene with isolated functional groups and may be more representative of the mechanisms involved when most of the oxygen has already been removed. Bagri et al. carried out molecular dynamics (MD) simulations coupled with FTIR to determine the structural changes in the graphene oxide lattice at various annealing temperatures by assuming various initial O contents and fractions of epoxy to hydroxyl groups present in the starting material. They also position their epoxy and hydroxyls beside each other to consider the experimental results of Cai et al. who showed hydroxyls and epoxides are often located on neighboring carbon atoms. It was shown that CO and CO₂ were produced only where hydroxyl and epoxide groups are located in such close proximity. In conjunction with this observation, vacancy defects...
increased at larger initial epoxide/hydroxide ratios. Otherwise, O\textsubscript{2} was shown to desorb from isolated epoxides and water from hydroxides which are processes that do not create vacancies defects. They also investigated that the remaining functional groups on the FGSs after annealing at various temperatures and demonstrated that carbonyls typically form at low temperatures while C-O-C ether rings were formed at higher temperatures. These stable functional groups were shown to persist even after high temperature annealing.

1.3.5 Review of Graphene-Based EDLCs

Over the course of this thesis the first papers describing the use of graphene-based materials as an electrode material in EDLCs were published.[99, 100] Since 2008, the number of papers on this topic has exploded due to the vast potential of graphene in this application. The following paragraphs review the progress made in this area focusing on the main ideas and themes.

Vivekchand \textit{et al.} were the first to report EDLCs based on FGSs. Their material was prepared by the rapid thermal expansion of GO.[99] They compressed the low density FGS powder obtained directly after thermal exfoliation into electrodes and tested them with an aqueous sulfuric acid electrolyte and also an IL electrolyte, reporting capacitances of 117 F/g and 75 F/g respectively. These values are similar to what can be achieved with activated carbons. Subsequently, Stoller \textit{et al.} prepared electrodes based on FGSs produced by hydrazine reduction of graphene oxide.[100] They reported capacitances in aqueous electrolyte and organic electrolyte of \textasciitilde{}100 F/g. In aqueous
electrolyte, this capacitance remained nearly constant over a large range of scan rates between 20 and 400 mV/s when 5.5 M KOH was used as the electrolyte. The SSA of their electrodes was estimated by nitrogen adsorption to be 700 m²/g, significantly lower than the theoretical limit of 2630 m²/g. They suggested their material had significantly agglomerated and that electrolyte ions may not be able to access the surface area inside these agglomerates.

To prevent aggregation and restacking Si and Samulski[101] demonstrated a means to use spacer particles to control the separation distance between graphene sheets in order to enhance the ion-accessible SSA. They coated FGSs with Pt nanoparticles which showed a higher nitrogen accessible and electrochemically accessible surface area. Shortly after, our groups in collaboration with Pacific Northwest National Labs (PNNL) demonstrated a similar approach using surfactant templated silica as shown in Figure 1.15.[102] We demonstrated that the capacitance could be improved compared to drop cast controls even when the dead weight of the electrochemically inactive silica was included. The specific capacitance (on a per gram of FGS basis) increased with increasing silica content as the material became better dispersed in the porous silica matrix.
Figure 1.15: Self-assembly approach to yield ordered metal oxide-graphene nanocomposites. (Left) Surfactants are used to disperse and coat FGSs forming hemicylindrical micelles. The surfactant is used to template a silica precursor which forms a mesoporous coating on the sheets and prevents them from aggregating. (Middle) Specific capacitance (normalized to FGS and silica mass) of composites formed with varying wt% silica. (Right) Specific capacitance (normalized to FGS mass only) as a function of scan rate for composites with varying silica content.

Over the last few years many other approaches have been developed to keep the sheets from aggregating. I have categorized these into two general ideas: (a) Keeping sheets apart using spacers such as metal nanoparticles,[103, 104] mesoporous metal oxides,[102, 105] carbon nanotubes,[106] activated carbons,[107] or polymers[108, 109] and (b) by changing the structure or morphology of FGSs, without the use of additives, through approaches based on templating or growing graphene sheets on high surface area porous supports,[110] chemical or thermal activation,[111] or crumpling individual sheets.[112, 113]

Using these approaches gravimetric capacitances ranging from 75 to 180 F/g[99, 100, 109, 111] with several unconfirmed reports even exceeding 250 F/g have been achieved in organic or IL electrolytes where double-layer charging is expected to be the dominant charging mechanism.[114, 115] In terms of gravimetric capacitance, FGSs out-perform other carbonaceous electrodes which typically achieve less than 120-140 F/g in the non-aqueous electrolytes.[51, 116, 117] However, as discussed in Section 1.1.2., the
volumetric capacitance, $C_V$ is also important because it includes the volume of both electrode and electrolyte. Since the electrolyte is often the largest fractional mass in the system, it often dictates the device mass and volume. As shown in Table 1, $C_V$ can be quite low due to the low bulk density, $\rho_B$ of FGSs in the electrode material. For comparison, carbonaceous electrodes prepared from carbide-derived carbons or carbon aerogels can achieve $\rho_B$ of 0.5 - 1 g/cm$^3$ which can lead to higher $C_V$.[118] Therefore to achieve significant device capacitances, the mass and volume of all device components (FGSs, electrolyte, spacer material etc.) must be minimized.

<table>
<thead>
<tr>
<th>Approach</th>
<th>$C_G$ (F/g)</th>
<th>$C_V$ (F/cm$^3$)</th>
<th>$\rho_B$ (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation of FGSs$^{29}$</td>
<td>166</td>
<td>60</td>
<td>0.36</td>
</tr>
<tr>
<td>FGSs separated by poly-ILs$^{32,28}$</td>
<td>164</td>
<td>&lt; 20</td>
<td>0.12</td>
</tr>
<tr>
<td>Hydrated FGSs$^{30}$</td>
<td>273</td>
<td>25</td>
<td>0.09</td>
</tr>
</tbody>
</table>

*Estimates for $C_V$ assume a carbon electrode density of 2.2 g/cm$^3$ and IL density of 1.3 g/cm$^3$

To date, there have only been a few fundamental studies on the $C_{dl}$ of the graphene-electrolyte interface.[40, 41] As discussed in Section 1.2.2.4., these studies, carried out on pristine graphene, indicate that the maximum realizable $C_{dl}$ should be low. The maximum $C_G$, calculated by assuming all graphene’s theoretical surface area can be exposed to the electrolyte, should not exceed 200 F/g. However, very few studies actually use EDLC electrodes composed of pristine graphene. Most use FGSs derived by the chemical or thermal reduction of graphene oxide which differ significantly from pristine graphene in terms of structure and chemistry. The $C_{dl}$ of this family of materials is currently unknown and therefore we cannot even predict what the theoretical limits are for this material.
CHAPTER 1: INTRODUCTION                  63

1.4 Goals and Layout of Thesis Work

The main goal of this thesis work is to develop new methods and a deeper understanding of how to increase the energy density of EDLCs while maintaining their other useful characteristics such as high power density and nearly unlimited cycle-life compared to current secondary battery technologies. To achieve this, I focus on mechanisms to increase the specific capacitance of graphene-based electrode materials in a way that is compatible with the use of non-aqueous electrolytes capable of operating over large potential windows. As discussed in Section 1.1.2 even small improvements to such systems can lead to substantial improvements to device energy density.

The specific capacitance is a function of the intrinsic double-layer capacitance, $C_{dl}$ and the ion-accessible SSA of graphene-based electrodes and therefore I attempt to separate these two variables to study them independently. The use of functionalized graphene sheets (FGSs) provides the unique possibility of effectively decoupling the SSA from its chemistry/structure which I hypothesized might control the $C_{dl}$ of the electrode/electrolyte interface. To this end, my thesis was broken into two major sections. The first two chapters focus on a means for studying the $C_{dl}$ of the FGS/electrolyte interface while holding the SSA constant and using this to study how thermal processing affects the structure and resulting $C_{dl}$ of FGSs. The last two chapters focus on the ion-accessible SSA of FGS-based electrodes. These ideas are summarized in the following specific aims and detailed in the paragraphs to follow:

Towards maximizing $C_{dl}$:
• Development of a model system for accurately determining the intrinsic capacitance of the FGS/electrolyte interface. (Chapter 2)

• Investigating how the $C_{dl}$ evolves when the structure/chemistry of FGSs are systematically tuned by thermal treatment. (Chapter 3)

Towards maximizing ion accessible SSA:

• Determining the factors that control the SSA of FGSs when many sheets are processed into a dense electrode film. (Chapter 4)

• Development of an approach that maximizes the ion-accessible SSA of FGS-based electrodes. (Chapter 5)

Chapter 2 focuses on developing a model system for measuring $C_{int}$ of FGS in the absence of artifacts and uncertainties inherent to measurements carried out on porous electrodes. A method was developed to disperse FGSs as a monolayer at the air-water interface using a Langmuir-Blodgett technique. The ability to transfer these monolayers onto gold and HOPG electrodes was demonstrated and that it was also shown possible to measure the $C_{int}$ of various types of FGSs with negligible contributions from the underlying substrates (HOPG and gold – after passivation with alkane thiols). This approach was recently published in the *Journal of Physical Chemistry C*. [119] Thus Chapter 2 includes the results from this manuscript and its supporting information. Section 2.3.4 provides some additional observations and analysis of the behavior of FGSs at the air-water interface that was beyond the scope of the published manuscript.

In Chapter 3, I use the model system described in the previous chapter to carry out a systematic study of how the chemical and structural changes elicited by various heat
treatments and reduction strategies affect the $C_{dl}$ of FGSs in an organic electrolyte commonly used in EDLCs. The non-porous nature of our monolayer electrodes and the use of a non-aqueous electrolyte enabled measurements of the intrinsic $C_{dl}$ with negligible contributions from $C_\Phi$. This work demonstrated that under certain reduction/annealing conditions, it is possible to increase $C_{sc}$ of FGSs such that it approaches the metallic limit (i.e., $C_{dl} \rightarrow C_H$). The capacitive behavior of FGSs is compared to the behavior observed for glassy carbon (GC) and HOPG electrodes. This work defines the theoretically attainable capacitance of FGSs in non-aqueous EDLCs and highlights the importance of disorder, in terms of defects, functional groups and their distribution, for maximizing the theoretically attainable gravimetric capacitance of FGS-based EDLCs.

In order to generate the high theoretical gravimetric capacitances predicted in Chapter 3, it is necessary to engineer electrodes which possess high ion-accessible SSA. Therefore in Chapter 4, I discuss the processing factors that influence the SSA of aggregated FGSs. By measuring the nitrogen and methylene blue accessible SSA before, after and during several commonly used processing procedures I identify important parameters which strongly affect the measured SSA. I attempt to explain these changes by extending the well-known ideas of colloidal aggregation of rigid particles to FGSs which can be considered as flexible colloidal sheets or membranes. A simple scaling analysis is used to demonstrate the magnitude of inter-sheet van der Waals forces and the capillary forces that typically act on the FGSs as they aggregate and are consolidated into dense electrodes for EDLCs.
The final chapter describes a new strategy for fabricating EDLCs based on graphene to minimize aggregation by van der Waals and capillary forces. Instead of preparing a graphene-based electrode first and then imbibing an electrolyte, I explore the idea of co-assembling the electrode with the electrolyte. In this way, the electrolyte (a non-volatile IL capable of high voltage operation) is used both as the active electrolyte and a physical spacer which keeps the sheets from aggregating. By optimizing the amount of ionic liquid and the degree of graphene oxide reduction, specific capacitances of up to 154 F/g of graphene were achieved at a discharge current of 0.2 A/g. At a low ionic liquid content of 60 wt%, a high volumetric capacitance of approximately ~65 F/cm³ was attained. Tuning the degree of thermal reduction of the graphene oxide and increasing the ionic liquid content to ~86 wt% lead to equal mass-specific capacitance but showed improved high-discharge rate capacitance, maintaining 90 % of its value at 500 mV/s. This bottom-up approach to electrode design is simple, scalable and ideally suited for combining potentially any graphene-based material with any ionic liquid electrolyte.
2 A Model System for Measuring the Intrinsic Capacitance and Redox Activity of Functionalized Graphene Sheets

In this section, a general method is developed for characterizing the intrinsic electrochemical properties of graphene sheets, such as the specific double-layer capacitance, in the absence of porosity-related artifacts and uncertainties. By assembling densely tiled monolayers of electrically insulating or conductive functionalized graphene sheets onto electrode substrates (gold and highly oriented pyrolytic graphite), we demonstrate our ability to isolate their intrinsic electrochemical response in terms of surface specific double-layer capacitance and redox behavior. Using this system, the electrochemical properties of various types of graphene can be directly compared without the need to take into account changes in electrode morphology and electrolyte accessibility arising due to varying material properties.

2.1 Introduction

A major difficulty in measuring the intrinsic electrochemical properties of FGSs is the lack of a well-defined electrode system: A meaningful interpretation of electrochemical measurements relies on the precise knowledge of the electrochemically active surface area, electrode geometry and porosity.[120, 121] These properties are difficult to control with electrode materials such as FGSs or CNTs, because preparing
electrodes from these materials typically results in porous films when fabricated by methods such as drop-casting or filtration of dispersed suspensions or slurries.[121] For FGSs, the surface area of dried electrode films made from suspensions or slurries varies between 44 to 700 m²/g depending on the type of FGSs and on the processing conditions.[100, 101, 121, 122] The inability to control the accessible surface area and the porosity of the FGS aggregates when they are produced as thick films leads to difficulties in measuring the intrinsic electrochemical properties of the material such as the \( C_{dl} \) (a key parameter for energy storage applications) or the electron transfer rates and redox potentials important for electrocatalysis and sensing.[121, 123]

In a recent case study on the role of process-specific aggregation, we demonstrated that the evaporative coating of substrates with FGS suspensions in different solvents causes the dried films of FGSs to exhibit largely different porosities.[121] The film porosity was correlated with changes in the oxidation overpotential for nicotinamide adenine dinucleotide (NADH) which severely complicated a direct comparison between different types of FGSs and also prevented a direct observation of the intrinsic electrocatalytic capabilities of FGSs. Similarly, Menshykau and Compton showed in recent theoretical studies that electrode roughness and porosity can lead to the observation of effective electrocatalytic behavior of an electrode.[120] The measurement of the surface specific double layer capacitance \( C_{dl} \) of an electrode, an important metric for comparing the charge storage capabilities of materials used for EDLCs is severely affected by electrode morphology. For example, Goh and Pumera have shown that the
mass specific capacitance of multisheet graphene nanoribbons is larger than single sheets. This was attributed to overlap between single sheets especially at edge-plane sites which are known to have higher capacitance than the basal-plane. Brownson and Banks also showed that processing of electrodes with or without surfactant and binder can also significantly impact the measured capacitance of porous graphene-based electrodes. Furthermore, in a porous system, the measurement of a material’s intrinsic $C_{dl}$ involves estimating the ion accessible surface areas by gas adsorption measurements. However, it is still not well understood which pore sizes contribute to double-layer charging and it has also been claimed that pore-size may have an effect on the measured $C_{dl}$ of an electrode and therefore may introduce substantial errors in the estimation of this important parameter.

To circumvent morphology-related measurement artifacts, fundamental studies of double-layer charging or other electrochemical properties are – whenever possible – carried out on well-polished flat electrodes. For instance, the intrinsic capacitance of carbon surfaces such as glassy carbon, boron-doped diamond and single-crystal graphite electrodes has been measured with this approach. More recently, microfabrication techniques have been employed to isolate electrodes of single pristine graphene sheets ranging in size from tens of microns to millimeters in diameter produced by both mechanical exfoliation of graphite (“Scotch-tape” method) and by CVD processing in order to measure their electrochemical properties. These studies suggested that pristine graphene behaves similarly to the basal-plane of highly-oriented...
pyrolytic graphite (HOPG) which has a low $C_{dl}$ and poor electron transfer kinetics.[21, 129]

FGSs, however, are expected to exhibit a rich and diverse electrochemistry due to the presence of lattice defects and functional groups. To support this conjecture, a suitable method for measuring the intrinsic electrochemical properties of such a material needs to be developed. The micropatterning techniques developed for pristine graphene would be difficult to apply to FGSs as the majority of FGSs are below 1 µm in size.[64, 65] Contacting such sub-micron sheets and masking these contacts would require tedious nanopatterning techniques. Also, electrical contacts cover the edges of graphene sheets and limit electrochemical measurements to the basal-plane of graphene only. It is also likely that patterning in general may alter the electrochemical properties of FGSs, and the performance of individual sheets may not be representative of the entire distribution of material.

To avoid these problems, the approach taken in our work involves the dense packing of a large ensemble of single sheets lying flat on a planar electrode substrate. A convenient and controllable method for preparing such a monolayer is to first assemble FGSs at the air-water interface in a Langmuir-Blodgett (LB) trough. This has been demonstrated previously both for FGS$_2$[130] and for pristine graphene produced by the direct exfoliation of expanded graphite.[131] We use a modified version of these approaches in this study to coat electrode surfaces with FGS$_2$ and other types of FGSs. Basal-plane HOPG and passivated gold are used as substrates for the monolayer coatings
and to demonstrate our ability to measure $C_{\text{int}}$ and redox capabilities of FGSs with minimal contribution from the underlying substrates.

### 2.2 Experimental

#### 2.2.1 Production of FGSs

FGSs with different C/O were prepared for this study by systematically varying the reduction and/or annealing treatments. To synthesize FGS$_2$ used for LB coatings, a modified Hummer’s method[70] was carried out according to the procedure of Cote et al.[130] While continuously stirring in an ice bath, a slurry of 0.5 g of graphite, 0.5 g of NaNO$_3$, and 23 mL of H$_2$SO$_4$ was prepared. After adding 3 g of KMnO$_4$, the slurry was heated to 35 °C and stirred at that temperature for 1 h. Subsequently, we added 400 mL of water and stirred the resulting suspension for 30 min while raising the reaction temperature to about 90 °C. The suspension was then diluted with another 100 mL of water followed by 3 mL of H$_2$O$_2$ (30%). Subsequently, centrifugation was used to separate FGS$_2$ from the soluble components of the reaction mixture and also to select for large sheets that float at the air water interface more easily.[130, 132]

Thermally reduced FGSs prepared by the rapid thermal expansion of graphite oxide (GO preparation proprietary) were provided by Vorbeck Materials Corporation (Batch BK86X) and had a C/O of 13. For measurements on FGSs with C/O greater than 13, we reduced this material further by heat-treatment in a nitrogen atmosphere at 1500 °C for 2 h using a resistively-heated graphite furnace (Astro-1000, Thermal Technologies).


2.2.2 FGS Characterization

The C/O of FGSs was determined by combustion analysis (Atlantic Microlabs Inc., GA). Before and after heat treatment, FGS powder was analyzed by X-ray diffraction (XRD) using a Miniflex II (Rigaku Americas Corp., CuK$_\alpha$ radiation) and Raman spectroscopy (Kaiser Optics, $\lambda$=532 nm). The nitrogen accessible surface area was determined according to the Brunauer, Emmett, and Teller (BET)[133] method using a Gemini V unit (Micromeritics Instruments Corp.).

2.2.3 Preparation of Monolayer Electrodes

Aqueous suspensions of FGS$_2$ were mixed with methanol at a volume ratio of 1:5 water to methanol.[130] FGSs with C/O of 13 and above were suspended in residue-free 1,2-dichloroethane (DCE) at a concentration of 5 mg per 15 mL, and the resulting suspensions were tip-ultrasonicated in an ice bath for 30 min at 60 % amplitude (150 W, Branson Ultrasonics Corp.). Aggregates were removed by centrifugation at 3000 RPM for 60 min and the supernatant was diluted 3:1 with pure DCE.

The suspensions were spread out on the air-water interface of an LB trough (Nima Technology, maximum area of 280 cm$^2$) using a syringe pump set at a flow rate of 0.1 mL/min. A sufficient coverage of FGS$_2$ was attained after adding only 1 mL of suspension while other FGS suspensions required 3-5 mL. The FGS$_2$ coverage was observed with a Brewster angle microscope (BAM, BAM2plus, Nanofilm Technologie GmbH) and the surface tension was monitored using a Wilhelmy plate cut from filter paper. LB films of reduced FGSs could be observed as a faint dark film with the naked
eye, and thus the BAM was unnecessary. Movable Teflon barriers were used to adjust the surface pressure at a speed of 30 cm²/min.

The LB films were transferred to various substrates by the horizontal deposition method.[134] Dip coating was not performed because the adhesion of FGS films to the HOPG surface was insufficient. Multiple substrates were placed in the cleaned deionized water sub-phase in the absence of the LB film. Once the LB film was under compression, it was lowered onto the various surfaces by slowly pumping water out of the trough. Coated samples were air dried for 15 min and then transferred to an Ar-filled glove box and placed on a hotplate at 80 °C to dry overnight.

2.2.4 Electrochemical Setup

![Figure 2.1: Overview of experimental approach. (a) Schematic of electrochemical cell where electrodes are spring loaded against a silicon o-ring to define the electrochemically active surface area. (b) Schematic of monolayer electrodes on HOPG and silicon coated with Au. (c) Scanning electron micrograph of a continuous FGS monolayer film on gold after electrochemical cycling. The o-ring removes some of the FGSs allowing us to estimate the active surface area (indicated by the dashed white ring).]
A home-made electrochemical cell was designed as shown schematically in Figure 2.1 to hold block-type electrodes of HOPG and gold evaporated onto pieces of silicon wafer. This design is a slightly modified version of the electrode holder described by Randin and Yeager[21] and later modified by Compton’s group.[135] The electrodes are spring loaded against a silicone O-ring that is used to isolate the electrochemically active surface area. In this design, the electrolyte reservoir is built into the electrode holder and the electrode faces upwards which prevents any gases (from purging or electrolysis) to accumulate in the divot formed by the holder. The screw-on Teflon lid features ports for a Pt counter electrode, a double-junction Ag/AgCl reference electrode (inner and outer compartment filled with 1 M KCl and 0.5 M NaF, respectively)\(^1\) and a Teflon hose for nitrogen purging. All potentials are reported vs. the Ag/AgCl reference electrode (1 M).

As shown in Figure 2.1, we used either HOPG blocks or gold films evaporated onto silicon wafers as substrates for the FGS films. The gold substrates were prepared by evaporating a 10 nm adhesion layer of Ti followed by 50 nm of a Pt diffusion barrier and a final 300 nm gold coating using an e-beam evaporator (Angstrom Engineering). Electrodes were cut into 1 cm × 1 cm pieces and annealed for 4 s in a H\(_2\) flame to clean the surface and to create large gold domains with near atomic smoothness.[136] HOPG working electrodes (Grade 2) were obtained from Structure Probe, Inc. Prior to each experiment, the top layer was peeled off with a piece of adhesive tape in order to expose a fresh basal-plane HOPG surface (below, the term HOPG is used to denote the basal-

\(^1\) A double-junction reference electrode was used because trace amounts of chloride complex with gold at high potentials which was found to significantly alter the electrochemical response of the gold electrodes used.
CHAPTER 2: A MODEL SYSTEM FOR MEASURING THE INTRINSIC CAPACITANCE AND REDOX ACTIVITY OF FUNCTIONALIZED GRAPHENE

plane of HOPG). Gold and HOPG cleaning procedures were performed within 15 min prior to LB coating or electrochemical measurements to minimize the adsorption of contaminants from the environment. The gold surfaces were modified with hexadecanethiol (HDT) or 16-mercaptohexadecanoic acid (MHDA) by soaking them in 1 mM solutions of HDT or MHDA in ethanol for at least 4 h.

2.2.5 Characterization of Electrodes

Electrodes were characterized by scanning electron microscopy (SEM, VEGA1, Tescan USA Inc.) at 20 kV acceleration voltage using the secondary electron detector. The O-ring seal of the cell leaves a mark on the electrode surfaces (Figure 2.1c) which we used to determine the geometric surface area of the part of the electrode that was exposed to the electrolyte. The relative coverage \( A_{rel} \) of the electrodes with FGSs was determined by SEM image analysis (MatLab): Images were taken at five different randomly chosen locations within an area of 1 cm\(^2\). Morphology and height of various FGSs on the gold and HOPG surfaces were determined using tapping-mode and contact-mode AFM, carried out with a MultiMode/Digital Nanoscope IIIa system (Veeco Instruments Inc.) using RTESP and NPS-type tips to confirm if single sheet monolayers indeed formed.

Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were performed using a computer-controlled digital potentiostat (VSP, Bio-Logic USA Inc.). An aqueous electrolyte of 0.5 M NaF was used as a supporting electrolytes since it is not electrochemically active on gold or HOPG and minimizes specific adsorption.[137] A
5 mM solution of potassium ferrocyanide was used as a redox probe with 0.5 M NaF as the supporting electrolyte. Cyclic voltammetry on bare Au was first performed in 10 mM HClO₄, which is known to clean the Au surface,[137] prior to electrochemical testing in 0.5 M NaF. The solution resistance was measured before cyclic voltammetry tests and compensated during the measurements.

### 2.3 Results and Discussion

In order to prove the validity of the results obtained with our setup, we first present the capacitance and redox activity of highly reduced and annealed FGSs which we expect to be similar to those of HOPG and pristine graphene and which can be compared to data published in the literature.[21, 40] We then analyze the other extreme, fully oxidized graphene, FGS₂, which is expected to act as a blocking layer since it is an insulator. After confirming that measurements carried out on these reference systems give the expected results on both gold and HOPG substrates, we demonstrate the vastly different properties of FGSs with intermediate C/O.

#### 2.3.1 Reduction and Annealing of FGS Powder

FGS₁₃ had a specific surface area of 580 m²/g, and there was no noticeable graphite or graphite oxide peak in its XRD spectrum (see Figure 2.2) which is indicative of completely exfoliated FGSs.[64, 65] When the 1500 °C heat treatment was applied to FGS₁₃, the C/O increased to 385, the surface area decreased to 380 m²/g, and a broad graphite d₀₀₀₂ peak became apparent in the XRD profile. The increase in the C/O from 13
to 385 indicates that many of the oxygen-containing functional groups were removed by the thermal post-treatment. Since we expect functional groups to desorb as CO or CO₂, such a reduction without annealing,[138] increases the defect density of the FGSs by producing vacancies in the lattice.[64] However, the decrease in surface area and the emergence of a d₀₀₀₂ reflection in the XRD profile suggests that the heat treatment at 1500 °C is also sufficient to anneal the FGSs into small graphitic domains which likely form at overlapping regions. These claims are further substantiated by comparing the Raman spectra for FGS₁₃ before and after heat treatment (Fig. 3b).

Figure 2.2: Structure of FGS₁₃ before and after 1500 °C heat treatment. (a) XRD profiles and (b) Raman shift.

The ratio of the intensities of the D band to the G band (I₆/I₃) decreased from 1.1 to 0.4 after the 1500 °C treatment. This ratio is related to the number of defects in the carbon lattice[139] and the observed decrease in I₆/I₃ after heat treatment demonstrates that the defect density was reduced with respect to FGS₁₃. A recent transmission electron microscope (TEM) and Raman study on graphene nanoribbons heated to 1500 °C has also demonstrated that lattice defects begin to anneal out at this temperature.[140]
Annealing at higher temperatures (>2000 °C) is known to be necessary for nearly complete removal of the defects.[141] Thus, FGS₁₃ was also annealed using a higher temperature treatment (2250 °C). However, this material could no longer be dispersed as individual sheets, likely because the extent of graphitization between FGSs within the powder was so extreme that the ultrasonication procedure used could no longer provide enough energy to separate the graphene sheets. Although we may not have removed all the defects at 1500 °C, we will show that this material has a capacitance-potential \((C/E)\) behavior that is similar to pristine graphene or HOPG.

### 2.3.2 Morphological Characterization of LB Films Transferred to Gold and HOPG

The secondary electron contrast of the SEM images of Figure 2.3 between the gold (bright) and LB film (dark) indicate that the film is composed of a monolayer of discretely tiled but densely packed FGSs. Although the exposed gold or underlying HOPG could be completely covered with FGSs, either by increasing the surface pressure or by applying multiple coatings, this inherently caused the formation of multilayers or overlapped regions between FGSs. The overlapping of sheets was avoided in order to prevent the formation of pores and related uncertainties in the accessible surface area of the FGS electrode. For FGS₂, a densely packed but discretely tiled coating was obtained at a surface pressure of 8 mN/m while FGS₁₃ and FGS₃₈₅ required 20 and 30 mN/m, respectively. For FGS₁₃ a relative area coverage of \(A_{rel} = 84\%\) with a standard deviation of only 3% was obtained confirming a large degree of film homogeneity.
Figure 2.3: Morphology of FGSs on gold and HOPG substrates. (a) SEM image of FGS2 coated on gold and tapping-mode (b) AFM image of FGS2 on HOPG; (c) SEM image of FGS13 on gold and tapping-mode (d) AFM image of FGS13 on HOPG; (e) SEM images of FGS385 on gold and tapping-mode (f) AFM images of FGS385 on HOPG.

The AFM images in Figure 2.3(b,d,f) demonstrate that the sheets conform to the topographical features of the substrates (e.g., edge-plane steps of the HOPG) and show wrinkles and folds. FGS2 exhibits a thickness of about 1 nm and diameters of several tens of microns. FGS13 has a typical thickness of ~2 nm and a diameter of 1 µm or less. The distribution of sheet thickness was similar to our previous studies and indicates that the FGS13 system consists of a mixture of single and few-layer FGSs. (Figure 2.4)
We attribute the increased thickness of FGS\textsubscript{13} compared to FGS\textsubscript{2} to functional groups and defects as discussed by Schniepp \textit{et al.}\[64\]. As shown in Figure 3f, FGS\textsubscript{385} appears much more wrinkled than FGS\textsubscript{13}. A thickness distribution for FGS\textsubscript{385} was not generated because the wrinkled nature of many of the sheets prohibited a reliable height measurement. However, the FGS\textsubscript{385} typically appeared thicker than FGS\textsubscript{13}. We expect the thickness of an FGS to decrease as functional groups and lattice defects are removed. The appearance of thicker sheets with a higher degree of wrinkling is likely due to the formation of graphitic domains between adjacent sheets during the 1500 °C treatment as evidenced by the appearance of a d\textsubscript{0002} reflection in the XRD profiles (Figure 2.2a) and indicates that FGS\textsubscript{385} may be composed of a larger proportion of few-layer FGSs. Since in this study we are interested in the surface specific capacitance and not the mass specific capacitance, the presence of a population of multistacked sheets will not significantly affect our measurements.
2.3.3 Capacitance and Redox Activity

2.3.3.1 Reduced and annealed FGS monolayers

We first focus on the capacitance and redox activity of FGS\(_{385}\) monolayers since we expect their electrochemical properties to be similar to what is observed with pristine graphene\[40\] and HOPG.\[21\] As shown in Figure 2.5, the capacitance of the HOPG-FGS\(_{385}\) electrode ranged from 7 to 9 \(\mu\)F/cm\(^2\) between \(-0.7\) and 0.6 V. The \(C/E\) curve has a smoothed V-shape with a small local maximum at \(-0.23\) V and which was similar to what was reported by Randin and Yeager for a high quality single crystal (X-ray rocking angle < 0.4°) HOPG surface with few edge-plane defects.\[21\]

![Figure 2.5: Capacitance of FGS\(_{385}\) monolayers on gold and HOPG. (a) \(C/E\) curves of various electrodes in 0.5 M NaF measured at 1000 Hz. (b) Frequency dependence of the capacitance of various electrodes measured in 0.5 M NaF.](image)

However, their curve does not show a local maximum, and we find that measurements made on a lower quality HOPG (8° rocking angle) which exhibited a larger density of
edge-plane defects resemble our result more closely. The capacitance is fairly constant with frequency changing less than 10 % between 10 and 1000 Hz (Figure 2.5b). Figure 2.5a also shows the capacitance measured for the underlying bare HOPG electrode. The shape of $C/E$ is similar to the HOPG-FGS\textsubscript{385} electrode but ranges between 4 and 6 $\mu$F/cm\textsuperscript{2} and also displays a small local maximum near $-0.23$ V vs. Ag/AgCl. The frequency dispersion of the capacitance was nearly identical to HOPG-FGS\textsubscript{385} (Figure 2.5b). Since frequency dispersion is associated with surface roughness\cite{142} or frequency dependent Faradaic charging events\cite{1} the similar behavior between the atomically smooth, bare HOPG surface and HOPG-FGS\textsubscript{385} suggests that the FGS\textsubscript{385} monolayer coating introduces negligible surface roughness or porosity. The small but finite frequency dispersion for HOPG is likely associated with a high density of exposed edge-plane sites which may lead to the small local maximum observed at $-0.23$ V vs. Ag/AgCl. AFM measurements indicated that edge-plane steps in our HOPG can be found every few microns. The edges and residual lattice defects within the FGS\textsubscript{385} monolayers may also contribute to a larger capacitance of FGS\textsubscript{385} compared to the HOPG. Since AFM images (Figure 2.3) indicate that many of the FGS\textsubscript{385} are wrinkled, it is also possible that some of the electrolyte penetrates beneath the wrinkled regions. This extra surface area could contribute to a higher measured capacitance compared to HOPG.

In order to ensure that the underlying HOPG electrode does not significantly influence the measured capacitance of the FGS\textsubscript{385} monolayers, we also tested the capacitance of FGS\textsubscript{385} monolayers on gold. The electrochemical properties of the bare
gold electrodes were also characterized by cyclic voltammetry and EIS. Figure 2.6a shows a cyclic voltammogram (CV) of an annealed gold electrode in 10 mM HClO₄. The characteristic gold oxidation and reduction peaks were stable with cycling over a wide potential window, indicating that flame annealing was sufficient to clean the surface.[137] CVs in 5 mM ferrocyanide solution (Figure 2.6b) exhibit a peak-to-peak separation ($E_{pp}$) between the oxidation and reduction waves of about 60 mV over a wide range of scan rates. Such behavior is typical for a reversible, diffusion-limited one-electron transfer reaction and is expected for a clean gold surface since the kinetics of the oxidation and reduction of ferro/ferricyanide are fast.[22]

Figure 2.6: Electrochemical characterization of bare and thiolated gold electrodes. (a) CV of bare gold in 10 mM HClO₄ at 100 mV/s. (b) CVs of bare gold and thiolated gold in 5 mM potassium ferrocyanide with 0.5 M NaF supporting electrolyte. (c) $C/E$ of bare gold before coating with FGSs or SAMs in 0.5 M NaF at various frequencies. (d) CVs of bare gold and thiolated gold in 0.5 M NaF at 100 mV/s.

The capacitance of gold in 0.5 M NaF, measured by EIS, was found to be $\sim 20 \mu F/cm^2$ between $-0.7$ and 0 V and shows a frequency-dependant maximum around
0.4 V as shown in Figure 2.6c. The frequency-independent capacitance of 20 μF/cm² is a typical value for the Helmholtz capacitance at a metal-aqueous electrolyte interface.[21] The observed maximum is due to the specific adsorption of fluoride ions which occurs on gold electrodes at large fluoride concentrations.[143]

The observation of the redox activity of gold electrodes and their large $C_{dl}$ (>20 μF/cm²) compared to what is expected for graphene (>7 μF/cm²) demonstrates that without passivation, the electrochemical response of FGS-coated gold substrates would be in large parts due to the exposed gold and not the FGSs alone.

Figure 2.6b shows CVs carried out in 5 mM ferrocyanide solution after application of hexadecanethol (HDT) and mercaptohexadecanoic acid (MHDA) self-assembled monolayers (SAMs) to the gold electrodes. The redox current associated with oxidation and reduction of the ferro/ferricyanide redox couple was reduced by more than a factor of 20 by the coatings. Thus, both HDTs and MHDAs effectively block electron transfer across the electrode-electrolyte interface. This can be understood by considering that the insulating thiol coatings are about 2 nm thick which render the probability of electron tunneling (necessary for this redox reaction to take place despite the insulating coating) small.

Coating the gold surfaces with HDT and MHDA also strongly reduces $C_{dl}$ (Figure 2.6c). For the Au-HDT electrode and the Au-MHDA electrode we measure capacitances of ~1 μF/cm² and ~1.9 μF/cm², respectively. Both coatings result in a $C_{dl}$ close to the theoretically estimated capacitance of a dielectric hydrocarbon film of ~2 nm in thickness.
However, the smaller capacitance for the HDT-coated electrode indicates that HDTs form a less permeable coating than MHDAs which cannot pack as closely due to the bulkier carboxylic acid groups at the ends of their hydrocarbon chains.

The electrochemical stability of the films was probed by repeated cycling to different potentials, followed by measuring $C_{dl}$ using EIS. The capacitance remained constant after repeated cycling between $-0.9$ and $+0.6$ V. Outside of this potential window, the capacitance slowly increased during cycling and the characteristic redox peaks of bare gold began to emerge indicating that the coating was slowly degrading, thereby exposing the underlying gold surface. Figure 2.5a shows the capacitance of Au-FGS385-HDT. The C/E is found to lie nearly on top of the HOPG-FGS385 curve and the frequency dispersion (Figure 2.5b) is also nearly identical. The Au-HDT response, in the absence of FGS385, is also shown in Figure 2.7. The capacitance is constant ($\sim 1 \mu F/cm^2$) within the potential limits and shows a frequency dispersion similar to that observed for HOPG and HOPG-FGS385. Since the Au-FGS385-HDT monolayer shows no evidence of the underlying gold capacitance and the shape of the Au-HDT capacitance is nearly constant with potential, we conclude that we are indeed measuring the capacitance of the FGS385 monolayer only. The similarity between the behavior on HOPG and passivated gold also demonstrates that the thiol coating process has no measurable effect on the electrochemical behavior of the FGS385 monolayers.
The redox activity of monolayer-coated electrodes was determined by recording cyclic voltammograms (CVs) in 5 mM potassium ferrocyanide solution as shown in Figure 2.7. In the case of potassium ferrocyanide in an inert supporting electrolyte, the separation between oxidation and reduction peaks ($E_{pp}$) is an indicator of whether the charge transfer reaction is limited by diffusion or by the kinetics of heterogeneous charge transfer across the electrode/electrolyte interface.[146] CVs for FGS385 on HOPG and gold at a scan rate of 100 mV/s are shown in Figure 2.7a. Both electrodes are capable of oxidizing and reducing the redox couple, and the CVs lie nearly on top of one another. Figure 2.7b shows that, between 20 and 2000 mV/s, $E_{pp}$ depends only weakly on the scan rate, which is indicative of a solely diffusion limited reaction.[146] The small increase of $E_{pp}$ with scan rate is likely due to uncompensated solution resistance although kinetic limitations cannot be fully excluded.

Figure 2.7: Redox response of FGS385 monolayers analyzed by cyclic voltammetry. (a) CVs of monolayer electrodes carried out in 5 mM potassium ferrocyanide in 0.5 M NaF carried out at 100 mV/s. (b) The dependence of $E_{pp}$ on scan rate for various electrodes. (HOPG used had only been cleaved once before)
Conversely, electron transfer across a pristine HOPG electrode/electrolyte interface is slow and therefore CVs exhibit characteristics of a kinetically limited rather than diffusion limited reaction.\cite{129} Figure 2.7b shows a strong dependence of $E_{pp}$ with scan rate when bare HOPG electrodes are used. However, this behavior was only observed during the first few uses of an HOPG block. After several experiments with the same HOPG block (involving repeated peeling of the HOPG), the reaction at the electrode surface became diffusion limited as indicated by a nearly constant $E_{pp}$ near the theoretical value of 56 mV. After repeated use, the HOPG developed edge-plane defects every few microns. These edge-plane defects are known to display anomalously fast kinetics and their close spacing caused the electrode to behave as an array of closely spaced microelectrodes leading to a reversible kinetics.\cite{129} Although the basal-plane of the FGS$_{385}$ can be expected to show kinetic limitations, the micron and submicron-sized sheets also have many closely spaced edges which may cause the observed diffusion limitations for FGS$_{385}$ monolayers.

2.3.3.2 Insulating graphene oxide

Now that we have demonstrated our ability to isolate the electrochemical properties of FGS$_{385}$ monolayers which showed a similar capacitance behavior to HOPG or pristine graphene, we now analyze the most highly oxidized form of graphene, FGS$_2$. Since FGS$_2$ is known to be an electrical insulator, we expected that monolayers of FGS$_2$ would at least partially block the electrochemical behavior of the underlying HOPG or gold electrodes. When FGS$_2$ monolayers are present on the HOPG surface, the CVs obtained
with the redox probe change considerably (see Figure 2.8a). At 100 mV/s, $E_{pp}$ increased from 56 mV to more than 500 mV which indicates that the Figure 2.7 FGS$_2$ film is indeed insulating and blocks many of the electroactive edge-plane sites on the bare HOPG surface. Figure 2.8b shows that the presence of the FGS$_2$ monolayer decreases the capacitance by $\sim$1 µF/cm$^2$. (The applied potential was kept above $-0.5$ V to prevent electrochemical reduction of the FGS$_2$.) Since FGS$_2$ is a dielectric, a decrease in the capacitance is expected: Its presence increases the distance between the electrically conducting electrode and ionic species in solution.

**Figure 2.8**: Electrochemical behavior of gold and HOPG coated FGS$_2$ monolayers. (a) CVs in 5 mM potassium ferrocyanide and 0.5 M NaF measured at 100 mV/s compared to bare gold. (b) $C/E$ curves of in 0.5 M NaF measured at 100 Hz.

When the HDT coating was applied to Au-FGS$_2$ electrodes, FGS$_2$ were found to roll and crumple forming a sparse needle-like morphology on the gold surface. (Figure 2.9) This problem was ameliorated by using a hydrophilic MHDA coating which allowed the sheets to retain their densely tiled, flat conformation.
Figure 2.9: Impact of thiol coating on FGS morphology. (a) SEM and (b) tapping-mode AFM images of FGS$_2$ on gold after soaking in a 1 mM ethanol solution of HDT. (c-d) Tapping-mode AFM images of (c) FGS$_2$ and (d) FGS$_{13}$ on gold after exposure to MHDA in ethanol. The wrinkled nature of FGS$_{13}$ and the roughness of the gold make it difficult to identify FGS$_{13}$ in a height contrast image. Thus, the same area is also shown in phase contrast where the FGSs can be clearly distinguished from the substrate.

Figure 2.8a shows that the oxidation peak current for the redox probe at a Au-FGS$_2$-MHDA electrode was reduced by more than a factor of 50 with respect to bare gold and was similar to the response of gold passivated with only MHDA. The capacitance of Au-MHDA and Au-FGS$_2$-MHDA is shown in Figure 2.8. The FGS$_2$ coating decreases the capacitance by $\sim 0.5 \ \mu$F/cm$^2$. As with the HOPG-FGS$_2$ electrodes, these results indicate that FGS$_2$ is not electroactive but acts as a blocking layer.
2.3.3.3 Thermally exfoliated and electrochemically reduced FGSs

We now investigate the electrochemical behavior of FGSs that are electrically conducting but have not been annealed at high temperatures and thus contain a larger number of lattice defects and functional groups compared to FGS\textsubscript{385}. We first contrast the behavior of FGS\textsubscript{385} with FGS\textsubscript{13}, the material obtained by the rapid thermal expansion of GO without any thermal post treatment. Figure 2.10a shows the $C/E$ behavior of HOPG-FGS\textsubscript{13} and the corresponding CVs within three different potential windows in the range between $-0.8$ V and $1.2$ V. Over all potential limits explored, the capacitance is significantly larger compared to our observations with FGS\textsubscript{385} and increases further as the potential window is expanded. This increase in capacitance is irreversible since the $C/E$ curves obtained within the intermediate potential window cannot be reproduced after the electrodes have been subjected to more extreme potentials. CVs recorded in the supporting electrolyte are symmetric and indicative of double-layer charging with the capacitive charging current also increasing as the potential window is made larger. The small peak observed at $-0.5$ V decreased in magnitude with inert gas purging and is attributed to the reduction of residual oxygen in the electrolyte.
The capacitance of the FGS$_{13}$ electrode depends largely on the measurement frequency (Figure 2.10b) and shows hysteresis upon reversal of the direction of the potential scan (Figure 2.10c). This is indicative of Faradaic charging and is typically observed also at other carbonaceous electrodes such as glassy carbon and edge-plane HOPG: Surface functional groups on these materials cause a charging behavior that changes depending on frequency, electrolyte pH, potential range, and scan direction. Randin and Yeager have shown that the capacitance of such surfaces ranges from 10 to 70 µF/cm$^2$.[21, 30] Our results lie within this range and suggest that FGS$_{13}$ prior to annealing behaves more like glassy carbon or the edge-plane of HOPG rather than the
basal-plane of HOPG. Our results for Au-FGS$_{13}$-HDT were confirmed by measurements with FGS$_{13}$ monolayers on HOPG.

The FGS$_{13}$ monolayers were also redox-active and displayed the same diffusion limited redox behavior as FGS$_{385}$ (Figure 2.11). We expect the basal-plane of FGS$_{13}$ to facilitate electron transport because compared to FGS$_{385}$ it is more defective and decorated with functional groups, but we currently cannot distinguish between the reactivity of electroactive edge-plane sites and the basal-plane using cyclic voltammetry in this system.

Besides starting with monolayers of FGSs reduced/annealed in bulk, our system is also capable of measuring FGSs produced by reducing monolayers of FGS$_{2}$ to an undefined C/O. As an example, FGS$_{2}$ can be electrochemically reduced to electrically conducting FGSs (referred to as erFGS).[87, 88] Using our monolayer system, we performed such a reduction and subsequently determined the impact on the electrochemical properties of the resulting FGSs. The electrochemical reduction of FGS$_{2}$
monolayers was carried out by cycling the Au-FGS2-MHDA electrodes repeatedly to 
−0.9 V. As shown in Figure 2.12 a, the capacitive charging current increased with cycling 
and equilibrated after about 20 cycles. This indicated that the FGS2 monolayers were 
reduced to conducting erFGS. The electrodes were then further characterized with the 
errocyanide redox probe and by EIS to determine their capacitance.

As shown in Figure 2.12b, monolayers of erFGS are capable of oxidation and 
reduction of the ferro/ferricyanide redox couple. The capacitance of the electrode (Figure 
2.12c) lies between 8 and 14 μF/cm² depending on the electrode potential and thus is 
significantly smaller than the capacitance of FGS13 monolayers. The shape of the C/E 
curve is similar to that of FGS13, but exhibits a smaller asymmetry between negative and
positive potentials. There are no indications of exposed gold in the CVs or the \( C/E \) data, confirming that the thiol coating remains stable during the electrochemical reduction of FGS\(_2\).

FGS\(_{13}\) and erFGS can be expected to exhibit different atomic structure and composition which may result in different electrochemical properties.\(^{[147]}\) The number and type of functional groups after electrochemical reduction compared to rapid thermal reduction may be different. It has, for example, been shown that the \( C/O \) of erFGS reduced at a similar potential as used by us was 24.\(^{[148]}\) A smaller density of functional groups may lead to less pseudocapacitance, which might explain the difference we observe between erFGS (8-14 \( \mu \)F/cm\(^2\)) and FGS\(_{13}\) (15-35 \( \mu \)F/cm\(^2\)). Also, a comparably large number of lattice defects may be introduced during thermal reduction of GO which may lead to increases in capacitance. Furthermore, the FGS\(_{13}\) used in this study are typically smaller in diameter (~1 \( \mu \)m) compared to erFGS (~10 \( \mu \)m). Thus, a larger number of edge-plane sites exist for FGS\(_{13}\). Since the edge-plane of graphite is known to exhibit a larger capacitance than the basal-plane,\(^{[30]}\) the smaller diameter of FGS\(_{13}\) may contribute to the observed capacitance of the material.

Monolayers of FGS\(_2\) can be reduced not only by electrochemical methods; But, it is also possible to use our system together with other techniques such as chemical (hydrazine, sodium borohydride)\(^{[68]}\) and thermal\(^{[64, 65]}\) reduction and to study and systematically compare their impact on the electrochemical properties of the resulting FGSs.
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A comparison of the properties of the various types of FGSs used in this study is given in Table 2.1. The capacitance tends to increase with decreasing C/O (down to 13) and increasing defect density. However, it is currently unknown whether or not this capacitance increase is due to pseudocapacitance contributions or changes in the $C_{dl}$ of the FGS/electrolyte interface. We are currently working on extending this model system to use non-aqueous electrolytes such that pseudocapacitance is suppressed and a direct comparison of the $C_{dl}$ of various types of FGSs can be made.

Table 2.1 Summary of the physical and electrochemical properties of various FGSs. Capacitance reported for 100 Hz and $E_{pp}$ reported for 100 mV/s using monolayers on HOPG. The C/O of erFGS was not measured but taken from the literature [148]

<table>
<thead>
<tr>
<th>Sample</th>
<th>C/O ratio</th>
<th>$I_d/I_o$ ratio</th>
<th>Min. capacitance (μF/cm$^2$)</th>
<th>Max. capacitance (μF/cm$^2$)</th>
<th>$E_{pp}$</th>
</tr>
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<td>FGS$_2$</td>
<td>2</td>
<td>-</td>
<td>3.3</td>
<td>4.3</td>
<td>627</td>
</tr>
<tr>
<td>FGS$_{13}$</td>
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<td>13.9</td>
<td>26.1</td>
<td>62</td>
</tr>
<tr>
<td>erFGS</td>
<td>24</td>
<td>-</td>
<td>8.5</td>
<td>15.6</td>
<td>102</td>
</tr>
<tr>
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<td>6.6</td>
<td>8.8</td>
<td>73</td>
</tr>
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<td>4.0</td>
<td>5.6</td>
<td>133</td>
</tr>
</tbody>
</table>

2.3.4 Additional Observations: 2 D Aggregation Behavior of FGSs

A BAM was used to analyze the aggregation behavior of FGSs floating at the air-water interface of the LB trough as shown in Figure 2.13. A dark film is observed to form at each end of the trough which grows towards the center as additional drops of the FGS/DCE suspension are spread onto the water surface. The spreading of DCE at the air-water interface is rapid and appears to convectively[149] carry the FGSs to the edges where they remain aggregated in densely packed islands. Figure 2.13c shows a BAM
image of one of these islands before being compressed by the barriers. The dark contrast is the surface of the water and lighter contrast are the FGSs which are too small to be resolved by our microscope. Some pinhole defects in the film are observed but the islands appear to be at nearly full density. After ~1 h of floating in the trough, the islands begin to break into smaller ones – likely due to air currents in the laboratory generated as people move around or open/shut doors. The interface between two such islands is shown in Figure 2.13(d). After ~1 week of being agitated by air currents, the FGSs formed branched, chain-like aggregates which expanded to fill the entire trough surface area. These observations suggest that the floating FGSs are weakly attractive upon initial contact but become dispersed with time and may become repulsive at larger separation distance.
There are several possible explanations for the attraction at small separation distance. Floatation forces are active when the air-liquid interface is perturbed by the weight of a particle on the surface. Since the mass of our FGSs are small compared to surface forces, no significant deformation is expected. However, the water must make a finite contact angle with the FGSs or be pinned at the edge of a sheet. These wetting phenomena can lead to attraction between particles as small as proteins. Another possibility is that the inter-sheet van der Waals (vdWs) forces hold the sheets together upon contact. However, since the sheets typically only make point-like contacts...
and are only \(~1 – 2\) nm thick it is unlikely that this contact area is large enough to exert a large enough attractive force. As shown in Figure 2.14, monolayers were transferred to atomically smooth mica substrates and imaged by AFM. The deflection images are shown to improve contrast so that the contact between FGSs could be observed. In most cases, the sheets appear to contact edge to edge but some small regions of overlap do exist. However, in order to facilitate transfer of the films to mica, the monolayers were first compressed by the moving barriers of the trough and any overlaps may be due to this compression process not by the aggregation phenomenon. Experiments were also carried out by depositing films in a bath of 6 M urea. Urea is known to break the structure of water and eliminate so-called hydrophobic forces which are known to attract hydrophobic particles in water. The 2D aggregates still formed indicating that the attraction is likely not due to the hydrophobic effect.

Figure 2.14: Imaging of the contacts made between FGSs after compression. (left) 10 mN/m. (right) 20 mN/m.

Figure 2.15 shows a typical surface pressure (tension) vs. trough area plot. Typically with small amphiphilic molecules like fatty acids which are typically used to study LB films,
the molecules spread like a 2D gas over the entire trough area. As the area is made smaller by the adjustable barriers, the pressure increases and 2D phase transitions can be observed moving from gas to liquid to solid and is typically reversible. However, due to the strong aggregation of FGSs, we do not observe any reversibility and the isotherm changes depending on the initial state of aggregation of the film as shown in Figure 2.15. Therefore to reproducibly achieve the most uniform coatings I attempted to deposit all coatings with the same initial conditions. As described in the experimental section, films were compressed immediately after deposition as they were nearly dense and defect free at this point. If the films were compressed at an initial state similar to what is shown in Figure 2.13c an inhomogeneous film with lots of holes resulted. The coating was typically compressed to the maximum pressure before the film buckled as indicated by the change in slope shown above 30 – 35 mN/m in Figure 2.15.

![Figure 2.15: Surface pressure as a function of trough area adjusted by the moving barriers.](image)

The FGS\textsubscript{2} monolayers could not be observed by the naked eye because they are not as absorbing as the reduced FGSs. However, they too were observed to aggregate near
the edges of the trough using the BAM as shown in Figure 2.16. In contrast to FGS$_{13}$ which did not disperse even after ~1 week, FGS$_2$ formed discrete floating sheets ~1 – 2 h after deposition. This observation indicates that FGS$_2$ may be more repulsive than FGS$_{13}$. This could be attributed to a larger number of partially dissociated functional groups present on FGS$_2$ compared to FGS$_{13}$ that could act to charge stabilize the 2 D dispersion. Due to this rapid dispersion after deposition, more uniform films were obtained by compressing the monolayer in the dispersed state after waiting for several hours.

![Figure 2.16: Aggregation behavior of FGS$_2$ at the air-water interface. (a,b) BAM images showing the state of aggregation of FGS$_{13}$s floating at the air-water interface after various relaxation times. (c) After compression of film by barriers.](image)

**2.4 Conclusions**

Using densely tiled monolayers of functionalized graphene sheets (FGS$_{13}$s) deposited on passivated gold and HOPG, we have developed an electrode system with which we can isolate the electrochemical properties of various types of FGS$_{13}$s. Our method allows for the systematic study of different production and processing conditions for graphene materials and is not affected by artifacts induced through uncertainties in electrode porosity and accessible surface area. We demonstrated the capabilities of our system to
perform measurements on FGS monolayers prepared either by the thermal expansion and reduction of graphite oxide (resulting in a carbon to oxygen ratio (C/O) of 13 and 385) or by reducing graphene oxide (C/O ~2) electrochemically directly on the substrate. Instead of contacting a single graphene sheet and measuring mostly the properties of only the basal-plane, we analyze the response of ensembles of single sheets including both the basal-plane and edge-plane contributions. Our method therefore allows for the prediction of the electrochemical properties of bulk graphene electrodes.

We found that graphene oxide, due to the fact that it is electrically insulating, exhibits a blocking effect on the redox activity and lowers the capacitance of the underlying electrode. FGSs with a C/O of 13 produced by the thermal exfoliation of graphite oxide, were found to have a large capacitance of up to 32 µF/cm² that depended on frequency and on the explored potential range, indicating a possible contribution from pseudocapacitance. A similar behavior was observed for electrochemically reduced FGSs (erFGS). However, the capacitance of erFGS was significantly smaller than the capacitance of FGS₁₃. When FGS₁₃ was annealed at 1500 °C, its capacitance was shown to approach that of HOPG and pristine graphene.

This study demonstrates that the electrochemical properties of FGSs depend strongly on the reduction and annealing conditions used. The use of FGS monolayer electrodes to study FGSs will be critical for understanding how the composition and structure of FGSs affect important electrochemical properties like the intrinsic double-layer capacitance.
3 Enhancement of Double Layer Capacitance through Defect-Derived Intrinsic Doping of Graphene

In the previous chapter I demonstrated the capabilities of a model system for comparing the capacitance and redox activity of various types of FGSs. Several types of FGSs were compared and the capacitance was found to differ significantly depending on the type or degree of reduction. Since this work was carried out in an aqueous electrolyte, we could not directly attribute these changes to $C_{dl}$ alone due to contributions from $C_0$. In this chapter we carry out measurements in a non-aqueous electrolyte using FGSs produced over a wider range of heat treatments and follow changes in $C_{dl}$ directly. Elemental analysis and Raman spectroscopy are used to follow the structural and chemical changes to determine how these factors affect the double-layer capacitance. We find that an optimum level of functional groups and lattice defects is required to achieve high double-layer capacitance which we attribute to a doping-like effect which increases the average electronic density of states in the FGSs and therefore increases the space-charge capacitance on the electrode side of the interface.
3.1 Introduction

Materials based on reduced graphene oxide are promising electrode materials for EDLCs due to their high specific surface area (SSA) of 2630 m$^2$/g.[99, 100, 153] Most efforts to improve their capacitance have focused on enhancing the ion-accessible SSA.[102, 103, 109, 114] However, the observed capacitance is the product of both the SSA and the surface specific double-layer capacitance, $C_{dl}$ of the electrode-electrolyte interface. The $C_{dl}$ of pristine graphene[40, 41] and the basal-plane of graphite[20, 21] are known to be low and governed by the electronic properties of the electrode side of the interface.[31] This is thought to limit the theoretical capacitance of electrodes based on graphene,[40, 41] carbon nanotubes,[35] and activated carbons whose pore walls are composed of graphene-like domains.[42] However, other carbonaceous materials such as glassy carbon (GC) or the edge-plane of graphite can achieve a much higher $C_{dl}$.[30, 38, 39] This is attributed to the doping-like effect of the functional groups, dangling bonds and lattice defects inherent to these materials which cause the electrodes to behave more like a metal.[30, 33, 38, 154] If carbon materials could be engineered with such metallic properties while maintaining the high SSA, conductivity and open porosity promised by electrodes composed of graphene, substantial improvements to the capacitance of EDLCs could be made.

Thermally[64, 65] and chemically[63, 66] reduced graphene oxide typically possess similar defects and functional groups as those found on GC and the edge-plane of graphite. For these reasons we refer to this family of materials as functionalized graphene
sheets (FGSs). Lattice defects arise when graphene oxide is thermally decomposed and carbon is removed from the lattice in the form of CO and CO$_2$.[64, 65, 83] The removal of carbon creates vacancies in the hexagonal lattice which can form, or reconstruct into, a variety of stable structural defects in the form of 5, 7 and 8 member rings (ex. 5-8-5 (Stone-Waals), 5-7-7-5, etc.).[64, 65, 83, 89] Many of these defects are stable and known to persist even at high temperatures.[155] Chemical reduction methods using hydrazine,[63, 66] sodium borohydride,[84] etc. are thought to produce FGSs with fewer structural defects[63] but these methods typically leave a significant number of functional groups on the FGS surface leading to carbon to oxygen (C/O) of ~10 – 14.[90] Despite considerable interest in EDLCs based on FGSs,[156, 157], it is currently unknown how these defects and functional groups might affect the $C_{dl}$ of FGSs compared to pristine graphene.

Several recent studies have compared the performance of electrodes produced by different graphene oxide reduction procedures.[158-161] However, their measurements were all carried out in aqueous electrolytes where $C_{dl}$ cannot easily be distinguished from the pseudocapacitance ($C_{\Phi}$) that arises from redox active functional groups located on the surface and edges of FGSs.[1] Although $C_{\Phi}$ can significantly enhance the intrinsic capacitance ($C_{int}$) of a material in aqueous electrolytes (i.e., $C_{int} = C_{dl} + C_{\Phi}$, as the two capacitance contributions add in parallel),[1] these effects cannot typically be used in organic and ionic liquid electrolytes which are capable of operating at high voltage. High operating voltage ($U$) enables devices to reach much higher energy densities, $E$, for a
given mass specific or gravimetric capacitance, $C_G$ (since $E = \frac{1}{2} C_G U^2$). Furthermore, studies are typically carried out on porous electrodes which make it difficult to estimate the ion-accessible SSA. This is usually estimated by gas adsorption in the dry state, and cannot account for the different pore accessibility and wetting properties of various electrode/electrolyte combinations. In addition, the measured capacitance is typically frequency dependent due to the distributed resistance inherent to porous electrodes.[1, 12, 13] Such factors have precluded a direct comparison between the $C_{dl}$ of porous FGS-based electrodes prepared using different reduction/annealing conditions.

To avoid these ambiguities, we recently developed an approach for preparing and measuring $C_{int}$ of densely tiled monolayers of FGSs that exhibit negligible porosity.[119] By measuring the capacitance of various monolayers deposited on both highly ordered pyrolytic graphite (HOPG) and gold electrodes we demonstrated the ability to isolate $C_{int}$ of various FGS monolayers from the response of the underlying substrate. We compared $C_{int}$ of several types of FGSs in aqueous electrolyte using this system: FGSs produced by rapid thermal expansion at 1100 °C, FGSs annealed at 1500 °C and graphene oxide monolayers that were electrochemically reduced. We observed an HOPG-like capacitance-voltage behavior for the annealed FGSs with little frequency dispersion. The capacitances of the more functionalized and defective FGS types were higher but their charging behavior exhibited signs of $C_{\Phi}$ due to the fact that measurements were carried out in aqueous electrolyte.
The primary goal of this study is to determine the fundamental limits of double-layer capacitance of FGSs which will define the maximum achievable capacitance of graphene-based EDLCs in organic or ionic liquid electrolytes. From previous work, we know that when the properties of FGSs approach those of pristine graphene that the capacitance will be low.\[40, 41, 119\] If the capacitance of some types of FGSs is higher (~20 μF/cm² - in the electrolyte or Helmholtz limit), as has been suggested by several recent EDLC studies on porous electrodes,\[162\] then we expect the capacitance to be a function of type and degree of reduction of the FGSs. In this study, we use a non-aqueous electrolyte to measure $C_{dl}$ of a series of FGSs produced by thermal reduction and annealing at various temperatures ranging from 300 to 2100 °C. This series allows us to systematically vary the density of functional groups and lattice defects and to determine their influence on the measured $C_{dl}$. We use our recently developed Langmuir-Blodgett monolayer technique\[119\] for measuring the capacitance of densely packed FGS monolayers transferred to gold and HOPG electrodes, but adapted for use with organic electrolytes. In this way, we can directly compare our measurements to those made on flat or polished carbon electrodes such as HOPG or GC. The minimum $C_{dl}$ of the various FGSs tested was found to vary continuously over the reduction/annealing temperatures tested ranging from 3-4 μF/cm² (HOPG limit) to 16-18 μF/cm². The upper limit approached the $C_{dl}$ measured for polished GC electrodes. This work highlights the importance of considering material properties other than just the SSA when developing graphene-based EDLCs for high energy and power density.


3.2 Experimental

3.2.1 Exfoliation and Reduction of Graphite Oxide

Graphite oxide (GO) was donated by Vorbeck Materials Corp. (Preparation method proprietary). Several long fused silica tubes were loaded with ~75 mg of this powder and dried overnight under a stream of flowing dry nitrogen. The tubes were then evacuated and back-filled with ultrahigh purity (99.9995 %) argon three times to replace any oxygen from the atmosphere which could potentially oxidize the FGSs at high temperatures after rapid thermal decomposition. The tubes were held under vacuum (~10 Torr) while passing the GO loaded tube into the hot zone of a Lindburg furnace set at various temperatures ranging from 300 °C to 1100 °C for ~60 s. The pressure in the tubes was monitored with a vacuum gauge and a sharp increase in pressure was observed to occur upon thermal exfoliation. The time for the tube to reach the decomposition temperature of GO (~200 °C) is influenced by the rate of heat transfer to the GO which is increased at increasing furnace temperature. For the 300 °C sample this took ~50-55s due to the slower rate of heat transfer at low temperatures which is dominated by natural convection and conduction through the quartz tube. At 1100 °C exfoliation was nearly instantaneous due to rapid radiative heat transfer at such high furnace temperatures. The tubes were removed from the furnace, allowed to cool and the powder was collected for subsequent analysis or thermal post-treatment.

The same GO was also used to prepare FGSs by hydrazine reduction according to the procedure outlined by Li et al.[163] A 10 mL suspension of 0.25 mg/mL of graphene
oxide in water was prepared by tip ultrasonicating (Vibracell, Sonics & Materials Inc., CT) GO at 40% amplitude for 15 min in ammoniated water with pH adjusted to 10. This procedure resulted in a translucent suspension of single graphene oxide sheets (verified by AFM). To this suspension, 10 µL of hydrazine hydrate was added and the resulting dispersion was heated placed in an oil bath set to 95 °C for 1 h. After the reaction, the initially translucent yellow/brown dispersion turned opaque and black. Unreacted hydrazine was dialyzed out of the suspension using 50 kDa dialysis tubing against 3 × 4 L of pH~10 ammoniated water in order to maintain a charge stabilized dispersion of FGSs as suggested by Li et al.

### 3.2.2 Thermal Post-Treatments

Annealing of FGSs prepared by thermal exfoliation at 1100 °C for 60 s (as detailed above) was carried out at temperatures ranging from 1100 °C to 2100 °C in a resistively heated graphite furnace (Astro-1000, Thermal Technologies). The atmosphere was exchanged using three vacuum/purge cycles with ultra high purity (99.9995%) Ar. Under flowing Ar, samples were ramped to temperature at a rate of 5 °C/min and held for 2 h and then allowed to furnace cool. The furnace temperature was estimated by calibrating the furnace power with an optical pyrometer prior to the experimental series.

### 3.2.3 FGS Characterization

The C/O of FGSs was estimated by combustion analysis (Atlantic Microlabs, GA) and by energy dispersive x-ray spectroscopy (EDS, INCA x-act, Oxford Instruments, UK
attached to a VEGA1 scanning electron microscope SEM, Tescan USA). For EDS, dense, smooth pellets of FGSs were prepared by compression of ~5 mg of material in a KBr pellet pressing die. Elemental compositions were determined by averaging at least 4 regions at 10 kV acceleration voltage and under 500 × magnification. For samples containing low oxygen concentrations, spectra were recorded until at least 2000 counts of oxygen were recorded. This procedure was found to give more consistent results than combustion analysis, especially for FGSs with high C/O. Raman spectroscopy (Kaiser Optics, λ = 532 nm) was carried out on dense pellets prepared using the same KBr pellet pressing procedure as for EDS. As shown in Figure 3.1, spectra were fit using the Breit-Wigner-Fano (BWF) line shape for the G-peak and a Lorentzian fit for the D-peak.[164] The BWF lineshape is described by Equation 26, the parameter q is used to quantify the asymmetry of the G-peak. A small |q| indicates the presence of additional Raman intensity at low frequencies (~1100 and 1400 cm⁻¹) which is associated with sp³ hybridized carbons.[165] As |q| becomes large, the distribution approaches the Lorentzian lineshape:

\[
I = I_p \left( \frac{1 + (x - x_p)/q\gamma}{1 + (x - x_p)^2/\gamma^2} \right) = I_p \left( \frac{\gamma^2}{\gamma^2 + (x - x_p)^2} \right) \quad \text{as} \quad q \rightarrow \infty, \quad (26)
\]

where x is the frequency, \(\gamma\) describes the peak width and \(I_p\) is the maximum peak intensity. This was found to best fit the spectra for all the FGSs tested when compared to a fitting both peaks with either Gaussian or two Lorentzian fit. Powder X-ray diffraction
(XRD) was also carried out on thermally exfoliated and annealed FGSs using a Miniflex II (Rigaku Americas, Cu Kα radiation).

Figure 3.1: Comparing the Raman spectra of FGSs exfoliated for 60 s or annealed for 2 h at the indicated temperatures. Dashed red lines indicate the Lorentzian fit to the D-peak and the BWF fit to the G-peak and the solid red line is the sum of the two fits.

3.2.4 Preparation of Monolayer Electrodes

Monolayers were prepared by the method reported in our previous study. Suspensions of 5 mg FGSs dispersed in 20 mL of residue-free, electronic grade 1,2-dichloroethane (DCE) by ultrasonication at 40% amplitude for 30 min in an ice water bath. Suspensions were then transferred to clean 15 mL glass tubes for centrifugation at ~1500 g (IEC Centra GP8R centrifuge, 218A rotor) for 60 min to remove any remaining FGS aggregates. Care was taken not to expose the suspension to any polymeric materials that dissolve in DCE (ex., pipette tips, tube caps, syringe needles, etc.). Residues from
these materials can build up at the air-water interface or adsorb on the FGSs and could be observed by AFM as determined in our preliminary work. The concentrated supernatant was transferred to a glass syringe and dripped onto the clean air-water interface of a Langmuir-Blodgett (LB) trough (Nima Technology, maximum area of 280 cm²) via Teflon tubing with interconnects made of solvent resistant poly(ether ether ketone) (PEEK). The LB trough was cleaned prior to deposition with electronic grade chloroform and filled three times with deionized water (18 M Ω resistance). On the third fill the barriers were compressed and the air-water interface was cleaned by suction until the surface tension was measured to be that of pure water (~72 mN/m) and did not change upon barrier compression or expansion, which is indicative of a clean air-water interface. A porous paper plate attached to a tensiometer was used to measure the surface pressure in the trough. The suspension was dripped onto the air-water interface at a rate of 0.1 mL/min. Typically 3 – 4 mL of this suspension was added to create a faint dark film of floating FGSs. Immediately after deposition, the barriers were compressed at a rate of 30 cm²/min until the surface pressure was 25 – 30 mN/m. The procedure yielded homogeneous films with a relative surface coverage of 85 – 90 % FGSs.

Hydrazine reduced FGSs were deposited in a similar way. However, these FGSs were suspended in ammoniated water, and not miscible with DCE. Therefore we diluted the aqueous dispersion with methanol, a good water miscible spreading solvent,[132] at a volume ratio of 1:5 ammoniated water to methanol. Thermally exfoliated FGSs could also be deposited from water/methanol and water/ethanol suspensions. Such films yielded
similar results to monolayers deposited from DCE. However, FGSs with a high C/O were not as stable in pH adjusted aqueous dispersions as they were in DCE and tended to aggregate prior to or during LB deposition. Hence, DCE was the solvent of choice for the thermally exfoliated and annealed FGS series.

Freshly cleaved HOPG blocks (SP-2 grade, Structure Probe Inc.) and flame-annealed gold-coated silicon wafers, prepared by e-beam evaporation (Angstrom Engineering) consisting of a 10 nm adhesion layer of Ti, followed by a 50 nm Pt diffusion barrier and a final 300 nm Au coating, were used as electrode substrates to be coated with the FGS monolayers. These were placed on clean glass slides in the trough subphase on the opposite side of one of the barriers to the film. The electrodes were slid under the trough barrier and positioned under the LB film. Water was withdrawn from the subphase with a syringe pump until the monolayer of floating FGSs was lowered onto the electrodes. Coated electrodes were then removed from the trough and placed in an Ar-filled glovebox on a hotplate set at 120 °C to dry overnight prior to electrochemical testing. Gold substrates coated with FGS monolayers were placed in 1 mM hexadecanethiol (HDT) solution for at least 4 h prior to electrochemical testing to block any exposed Au. In this study, FGS monolayers coated on Au were only used as a sanity check to verify that we were not just measuring the response of HOPG. In all cases, results on the FGS-Au-HDT electrodes were the same (within error) as the results obtained on FGS-HOPG electrodes.
3.2.5 Characterization of Monolayer Electrodes

Electrochemical characterization was carried out in the electrode holder described in Section 2.2.4.[119] Monolayer coated electrodes were spring loaded in the electrode holder against an O-ring in order to define the geometric surface area ($A_G$) of the electrode exposed to the electrolyte. However, the use of non-aqueous electrolytes required switching from Viton or silicone O-rings (as described previously) to a perfluoroelastomer (Kalrez, McMaster-Carr) O-ring to minimize swelling. The cell was filled with 5 mL of 0.1 M tetraethylammonium tetrafluoroborate (TEABF$_4$) in acetonitrile (AN). A Pt quasi-reference electrode and a Pt wire counter electrode were used. The potential of the reference electrode was determined after testing each monolayer by measuring the redox potential of ferrocene dissolved in the supporting electrolyte. Each monolayer electrode was analyzed by cyclic voltammetry at 100 mV/s followed by electrochemical impedance spectroscopy (EIS) using a perturbation amplitude of 10 mV over a frequency range for 1 Hz to 100 kHz. The DC potential was held for 2 min before starting each EIS measurement. The capacitance was estimated from EIS testing using Equation 27:

$$C_{DL} = \frac{1}{2\pi f (Z'')}$$

where $f$ is the measurement frequency and $Z''$ the imaginary component of the impedance. Samples were first tested in a voltage window of -0.5 to 0.5 V vs. open circuit potential and then in an expanded window of -0.7 to 1 V beyond which Faradaic
currents due to residual oxygen and water in the electrolyte were observed. All EIS measurements were carried out by starting at the most negative potentials and stepping the DC potential more positive. As shown in Figure 3.2, $C_{\text{min}}$ was found to increase by $\sim 5\%$ to $10\%$ after cycling in the larger voltage window but was again reduced if the potential window was made smaller, indicating that the $C_{\text{DL}}$ had a small but measurable dependence on the potential history. Such an increase could be due to specific adsorption of cations at high negative potentials that do not desorb within the time scale of our measurements. Thus, to minimize any contributions to the capacitance from effects such as this we report $C_{\text{min}}$ from measurements taken in the smaller window where the $C_{\text{DL}}$ was not significantly influenced by the potential window.

**Figure 3.2: Dependence of measured $C_{\text{DL}}$ on the voltage window.** $C_{\text{min}}$ increased by $\sim 10\%$ as the voltage window was expanded and reversed upon cycling back to smaller windows. Data plotted were first collected at the largest potential window with subsequent measurements at decreasingly smaller windows.

There was only a slight increase in $C_{\text{DL}}$ (10–20%) measured for each monolayer with decreasing frequency over the range of 1 – 100 Hz. This relative increase was consistently observed for all samples (including various FGS monolayers, HOPG and GC).
and over all applied potentials and was likely due to some electrolyte leakage under the O-ring used to define the electrochemically active surface area. The upper frequency limit for measuring $C_{DL}$ is defined by the RC time constant. Typically the solution resistance in our cells was $\sim 100 \, \Omega$ but varied depending on the exact position of the reference electrode. Assuming a value of $C_{DL}$, an area of 0.35 cm$^2$ and a resistance of 100 $\Omega$ leads to a calculated characteristic frequency of $1/RC \approx 1 - 5$ kHz for the range of $C_{DL}$ (5 - 20 $\mu$F/cm$^2$) measured. These frequencies correspond to what was observed in Figure 3.3. Rearrangement of the double-layer structure and adsorption effects are also known to cause some frequency dispersion, especially in organic electrolytes which contain large, more polarizable anion/cations with weaker solvation shells compared to aqueous ones.[1]

![Image](image_url)

**Figure 3.3:** Typical frequency dispersion observed for various FGS monolayer electrodes

After electrochemical testing in the supporting electrolyte (0.1 M TEABF$_4$/AN), 100 $\mu$L of 5 mM ferrocene in AN was added to the cell and cyclic voltammetry was carried out over a series of scan rates from 10 to 2000 mV/s. As already mentioned, this was used to define the reference potential but was also used to estimate the geometric surface area ($A_G$) of each monolayer electrode. This was determined using the known
relationship between $A_G$, the diffusivity of ferrocene ($D \sim 2.4 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$), scan rate ($v$), peak current ($i_p$) and the ferrocene concentration ($C^*$) for a reversible one electron transfer reaction: [22, 146]

$$i_p = 0.4463 \left( \frac{D^3}{RT} \right)^{1/2} A_G D^{1/2} C^* v^{1/2} \quad (28)$$

Typically this area was estimated to be between 0.35 and 0.4 cm$^2$, depending on the level of O-ring compression and its degree of swelling.

**Figure 3.4:** Estimating relative coverage and surface roughness of FGS monolayer electrodes. (a) Secondary electron contrast SEM image of FGSs on Au after electrochemical testing. Gold appears brighter. (b) Relative surface coverage determined by SEM and pixel counting in Matlab based on contrast differences between Au and FGS. (c) Contact mode AFM image of FGSs on HOPG showing wrinkles and folds which introduce roughness. (d) Roughness factor ($S_R$) estimated by AFM for various FGS monolayers. Error bars indicated ± one standard deviation from the mean.

Since the capacitance depends on the true surface area ($A_T$) exposed to the electrolyte and not $A_G$ we used a combination of SEM and atomic force microscopy (AFM) to estimate $A_T$ as illustrated in Figure 3.4. The relative coverage ($A_R$) or projected surface
area of FGSs on the surface was estimated by pixel counting (Matlab) based on the secondary electron contrast differences between the Au and FGS coating. As shown in Figure 3.4b, $A_R$ was found to vary from $\sim 80 - 90\%$ FGS coverage. The surface roughness ($S_R = A_T/A_G$) of each monolayer coating was estimated using contact-mode AFM (MultiMode/Digital Nanoscope IIIa system, Veeco Instruments) using NP-S tips (radius of curvature $< 10$ nm). AFM images of at least 4 different $5 \times 5$ µm locations were used to estimate the average $S_R$ given in Figure 3.4d. Values ranged between 1.03 and 1.13 and tended to increase when monolayers prepared from FGSs annealed for 2 h at high temperature were analyzed. Corrections for surface coverage and roughness only changed the geometric surface area by 5-10% for all monolayers analyzed. These changes in monolayer morphology cannot explain the significant difference between the $C_{DL}$ measured for the various FGSs (discussed in the following section) which suggests that the observed changes are due, instead, to the chemical structure of the FGSs.

The electrochemical behavior of the FGS monolayers was also compared to glassy carbon (GC) electrodes (SPI-Glas 25 grade, 10 x 10 x 2 mm blocks, Structure Probe Inc.). GC blocks were polished to a mirror finish using a suspension of 0.05 µm alumina and a felt polishing pad (Buehler). Electrodes were then rinsed with deionized water and blown dry. No electrochemical activation/pretreatment of the GC was carried out prior to electrochemical characterization.
3.3 Results and Discussion

3.3.1 Differential Capacitance of Various FGSs

Figure 3.5: Electrochemical behavior of FGS monolayers in 0.1 M TEABF₄ in acetonitrile. Films were deposited after thermal exfoliation for 60 s or annealing (*) for 1 h at the indicated temperature. (a) Capacitance measured by EIS at 100 Hz and 10 mV amplitude. The geometric surface area was estimated by analyzing the dependence of the peak current for ferrocene as a function of scan rate and the relative coverage of FGSs on each electrode was estimated by averaging over at least four different SEM images of monolayers on Au. (b) CVs carried out at 100 mV/s between -0.5 and 0.5 V vs. Pt wire. After each measurement the Pt potential was estimated by adding ferrocene to the cell and carrying out CVs.

Figure 3.5A shows the $C_{DL}$ values for monolayers prepared from several types of FGSs, determined by electrochemical impedance spectroscopy (EIS), as a function of frequency and potential. For comparison, the results for GC and HOPG are also shown and agree with previous studies.[21, 38, 39] In particular, the capacitance-potential ($C$-$E$) curves for HOPG demonstrate the well-known, U-shaped dependence of $C_{DL}$ on the electrode potential with a capacitance minimum ($C_{min}$) between 3 and 4 $\mu$F/cm². For GC, the shape of the $C$-$E$ curves is dictated by the charge, size and orientation of the ions in the Helmholtz layer, all of which vary with potential.[1, 25] As the exfoliation
temperature increases, the $C$-$E$ curves of FGS approach those of GC. Conversely, annealing significantly reduces $C_{\text{DL}}$, with the material approaching the performance of HOPG. An intermediate case arose for FGSs annealed for 2 h at 1100 °C. In this case the $C_{\text{min}}$ is drastically reduced compared to the $C_{\text{min}}$ of the material only exfoliated at 1100 °C but exhibits enhanced capacitance at high positive potentials suggesting an asymmetric doping in this FGS.

As shown in Figure 3.5B, the CVs are nearly rectangular in shape except for the case where FGSs were annealed at 1100 °C for 2 h. The relative magnitudes of the capacitive current in the CVs are commensurate with the measurements carried out by EIS. The shape of the CVs, the relatively constant capacitance with measurement frequency (independent of DC potential), and the fact that our measurements are carried out in an aprotic electrolyte all indicate that our electrodes can be considered ideally polarizable and capacitance due to Faradaic contributions is negligible.[21, 25] For the sample annealed at 1100 °C for 2 h, the CV is not rectangular and we cannot definitively conclude that the increase is due to changes in $C_{\text{DL}}$ alone. There are several possible explanations for this behavior. The effect may solely be due to $C_{\text{DL}}$ if there was an asymmetric doping of the electronic density of states of holes rather than electrons within the material.[31, 33] Alternatively this behavior could be described by potential-induced specific adsorption and desorption of anions.[1] This would contribute a Faradaic pseudocapacitance to the measured capacitance at high positive potentials. This
asymmetry was not observed in the smaller potential window indicating this material can also be considered ideally polarizable within the range of -0.5 to 0.5 V vs. Pt.

These results suggest that as the structure and chemistry of FGSs are tuned their capacitive charging behavior can be made to resemble a more metallic phase of carbon (ex., GC) compared to a semi-metal with a low DOS like the basal-plane of HOPG or pristine graphene. By tailoring the structure and chemistry of FGSs, it is possible to achieve capacitances 3 to 4 times higher than HOPG and what has been observed for pristine graphene[40, 41]. In the next section, we attempt to elucidate the chemical and structural changes leading to these observed changes in \( C_{dl} \).

### 3.3.2 Chemical and Structural Properties of FGSs

![Figure 3.6: Estimating the degree of functionalization and defectiveness of FGSs. (A) C/O and (B) \( I_D/I_G \) as a function of heat treatment. Error bars indicate standard deviation between 5 different areas within a sample. FGSs were prepared by holding GO in a tube furnace for 60 s (black squares) and 5 min (green triangle). 60s samples were further annealed for 2 h (red diamonds) at the temperatures indicated.](image-url)
Figure 3.4 summarizes the results from elemental analysis and Raman spectroscopy performed on a series of FGSs exfoliated and/or annealed at temperatures ranging from 300 to 2100 °C. Examples of the Raman spectra collected for the series of FGSs were given in Figure 3.1. The D-peak near 1580 cm⁻¹ is the result of the breathing mode of aromatic rings with sixfold symmetry.[165] However, this mode is only active in the presence of lattice disorder and thus the peak intensity also depends on the characteristic distance between defects ($L_A$) or, alternatively, can be thought of as the average lateral crystallite size of pristine graphene domains.[166] The G-peak located near 1350 cm⁻¹ corresponds to the in-plane oscillations of any sp² carbon pair in the form of chains or rings of any order.[165] The change in the relative intensities of these two peaks ($I_D/I_G$), the peak positions and the breadth of the peaks (as indicated by the full width at half maximum, FWHM) gives information about the changes in the structure of the sp² phase that evolve after different reduction and annealing treatments.[165]

Visible Raman spectroscopy does not give information about the sp³ carbon content or the relative number of functional groups bound to the FGSs because the sp² signals are thought to be resonantly enhanced and effectively drown out any sp³ contributions to the spectrum.[165] As shown in Figure 3.6B, we follow these changes by determining the C/O of the FGSs after the various reduction and annealing conditions. The C/O after thermal exfoliation increased from ~4 to 20 with increasing temperature. This corresponds to an approximate range of oxygen concentrations of 20 to 5 % (mol/mol) if only carbon and oxygen are considered (i.e., neglecting hydrogen). The C/O increased
further to 180 and then to ~400 as the material was heat treated at higher temperatures for 2 h. The removal of oxygen partially restores of the aromatic network, as indicated by the increase in sheet conductivity.[167] However, some fraction is removed as CO or CO₂ which introduces vacancy defects in the lattice.[63, 64, 94]

The observed changes in the Raman spectra can be explained by considering the interplay between the degree of reduction, the C/O and the generation of lattice defects. The Raman features for many carbonaceous materials are well-understood and a thorough interpretation of the changes in \(I_D/I_G\) for a spectrum of carbonaceous materials from single crystal graphite, to nanocrystalline graphite, amorphous carbon and sp³ hybridized diamond-like carbon has been provided by Ferrari and Robertson[165] which I apply to describe the changes in FGSs as the material is reduced and annealed. The Tuinstra Koenig (TK)[166] relation \(I_D/I_G \propto \frac{1}{L_A}\) is typically used to approximate \(L_A\) for graphitic materials and this relation is often applied to reduced graphene oxide. This relation arises because beyond a certain \(L_A\) (~2 nm) the in-plane breathing mode oscillations are dampened. In perfect graphite, the D-mode is forbidden.[166] When \(L_A\) is smaller than ~2 nm, there is little damping effect and the intensity is proportional to the number of aromatic 6-member rings and \(I_D/I_G \sim L_A^2\).[165]. Therefore, \(L_A\) is a non-monotonous function of \(L_A\) and to make conclusions we must determine which side of the function we are on. In addition, both of these relations are only valid in the regime where the sp² content is approximately constant (i.e., \(I_G\) is constant and all changes reflect changes in \(I_D\)).[165, 166] To gauge where the various FGSs fall with respect to this
analysis, we can estimate the sp³ content and $L_A$ from the C/O data. If we assume that the decomposition of functional groups occurs randomly we can calculate the effective distance between functional groups (i.e., defects which act to disrupt the sp³ phase) as a function of C/O using the fact that there are ~54 carbons/nm² of graphene surface. This leads to $L_A \sim (x/54)^{0.5}$ where $x$ is the C/O. We also assume that the sp³ content is approximately the oxygen content. Both are plotted in Figure 3.7. The estimate for $L_A$ also assumed that no lattice defects are formed which would break up the graphitic domains further. We contrast this to a case where 1 defect per 4 oxygens desorbed is produced. As shown in Figure 3.7, this simple analysis indicates that $L_A$ is likely small (< 2 nm) even without assuming any defect formation for all materials exfoliated for 60 s. The oxygen % (or ~ sp³ content) drops continuously with increasing temperature but remains fairly constant for the samples annealed for 2 h.

![Figure 3.7: Estimating the oxygen content and the approximate distance between defects within the sp² phase.](image)

The distance between defects (~ $L_A$) was estimated assuming oxygen-containing functional groups are distributed uniformly over the FGSs. It is likely that some clustering and diffusion of functional groups occurs and number of lattice defects that form likely depends on the temperature, density of functional groups and their distribution.[80][94]
Therefore, for all samples that were not annealed, we expect there to be a competition between sp³ to sp² conversion (~$I_G$) and the growth of aromatic 6-member rings ($I_D$). As shown in Figure 3.6, the $I_D/I_G$ remains fairly constant over the entire range of exfoliation temperatures, dipping to a minimum near 700 °C and increasing up to 1100 °C for the 60 s case. For this regime it seems that sp² conversion must nearly balance the number of aromatic 6-member rings formed to maintain a nearly constant $I_D/I_G$. This phenomenon was also observed by Yang et al. for thermally reduced thin films of graphene oxide exhibiting C/O between 2.8 and 14.1.[90] The view that sp² growth and clustering is occurring in the FGSs at these temperatures is supported by intrinsic sheet conductivity measurements recently carried out on a similar series of thermally exfoliated FGSs.[167]

The other fitted parameters for the Raman spectra are plotted in Figure 3.8 and give more clues as to the structural changes that occur. The most notable feature is the G-peak position which increased from ~1580 cm⁻¹ to 1594 cm⁻¹ for the material exfoliated at 1100 °C for 60 s, 5 min and 2 h. The peak position for various carbon materials is known to approach 1600 cm⁻¹ as the carbon forms nanocrystalline graphite domains with decreasing size (approaching ~2 nm).[165]
Figure 3.8: Summary of Raman spectroscopy fitting parameters obtained for the FGSs exfoliated and annealed at various temperatures. (A) The \( q \) parameter in the BWF lineshape. (B) Absolute peak intensities of D and G-peak which vary due to differences in sample density and Raman cross-section. The ratio of the peak intensities does not drop considerably until above 1500 °C; (C) G-peak FWHM, (D) D-peak position; (E) G-peak position. Dashed line indicates position for single crystal graphite which is commensurate with the position measured for HOPG of 1581 cm\(^{-1}\). (F) D-peak FWHM with heat treatment. FGSs were prepared by holding GO in a tube furnace for 60 s (black squares) and 5 min (green triangle). 60s samples were further annealed for 2 h (red diamonds) at the temperatures indicated.

As shown in Figure 3.6, for the three materials heat treated at 1100 °C for different times, the \( I_D/I_G \) decreases. As shown in Figure 3.8F, this is a result of the D-peak FWHM decreasing from \(~150 \text{ cm}^{-1}\) to \(80 \text{ cm}^{-1}\) while the G-peak FWHM remains approximately constant (Figure 3.8E). A distribution of sp\(^2\) clusters with different sizes as well as bond disorder due to the presence of non-6-member rings are factors thought to contribute to the D-peak width.[165] There was a significant drop in the number of functional groups (\(~5 \text{ to } 0.5 \% \text{ oxygen}\)) as the material was held for longer times significantly removing
defects associated with functional groups. A drop in the $I_D/I_G$ after the 1300 °C treatment was also observed which could either indicate that some lattice annealing took place or, alternatively, could result from the removal of more functional groups since the C/O increased from 180 to 300. Between heat treatment temperatures of 1300 to 2100 °C, the C/O of the resulting FGSs remained nearly constant but the $I_D/I_G$ continued to drop. This indicates that the size of aromatic domains increases between 1500 °C and 2100 °C which is attributed to lattice annealing which is known to occur at temperatures above 1500 °C for graphitic materials.[140] In this region of constant C/O, it may be more appropriate to use the TK relation to qualitatively describe the growth of $L_A$ with decreasing $I_D/I_G$. However, a large fraction of defects in the form of non-6-member rings may still exist at the lower temperature range which would act to enhance the G-band intensity and not the D-band intensity and could possibly lead to an overestimate of $L_A$.

The constant C/O with increasing $L_A$ suggests that oxygen is not uniformly distributed on the surface of FGSs but likely clusters between graphitic domains and around defect sites. The G-peak frequency also decreases from 1594 to 1580 cm$^{-1}$ as the annealing temperature is increased towards 2100 °C.(Figure 3.8C) The shift in the G-peak towards 1580 cm$^{-1}$, the frequency associated with single crystal graphite,[165] with increasing temperature is also indicative of the growth of $L_A$.

Since our measurements were carried out on compressed pellets of FGSs, we did not analyze the second order peaks as they give information as to the stacking order between sheets, which would be significantly affected by the state of aggregation. As shown in the
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Figure 3.9, we observe significant change in stacking order as measured by powder X-ray diffraction (XRD).

![Figure 3.9: Powder XRD profiles of FGS powders after exfoliation (A) or annealing (B) at various temperatures. A peak corresponding to graphite (2θ ~ 27°) becomes narrower and more intense upon high temperature annealing indicating the emergence of small graphite domains.](image)

3.3.3 Evolution of $C_{dl}$ with Changes in Electrode Properties

![Figure 3.10: $C_{min}$ as a function of (A) integrated $I_D/I_G$ and (B) C/O as measured by EIS at 10 Hz in 0.1 M tetraethylammonium tetrafluoroborate in acetonitrile. Semitransparent bars indicate the position of $C_{min} \pm$ one standard deviation for HOPG and GC. Points refer to FGSs which have been thermally reduced (blue diamonds) and hydrazine reduced (red circle).](image)

To more clearly compare the capacitance with the structural and chemical changes which occur after the various thermal treatments, in Figure 3.10 we plot $C_{min}$ against both the C/O and $I_D/I_G$. Double-layer theory is only valid near the electrodes potential of zero
charge which, for carbon electrodes in non-adsorbing electrolyte, typically corresponds to the potential at \( C_{\text{min}} \) or the open circuit potential, which closely coincided in this work. \( C_{\text{min}} \) increases with \( I_D/I_G \) indicating that the effectively nanocrystalline nature of the FGSs enhances the capacitance, an effect which can be attributed to the large concentration of edge-like sites. The \( C_{\text{min}} \) peaks at a C/O between \( \sim 10 \) and 68. The transition from high capacitance to low capacitance occurs when FGSs already thermally exfoliated at a furnace temperature of 1100 °C for 60 s were annealed for an additional 2 h at 1100 °C.

The extended heat treatment significantly reduced the number of functional groups as indicated by the increase in C/O; however, at this temperature significant annealing of lattice defects is not expected to occur suggesting that a critical number of functional groups may be necessary to observe enhanced capacitance.[140] To determine whether functional groups alone are responsible for high capacitance we also tested FGSs produced by hydrazine reduction of graphene oxide. This method increases the C/O while generating fewer lattice defects than thermal reduction does. [63] FGSs formed by hydrazine reduction were found to exhibit a low \( C_{\text{min}} \), similar to our annealed material, indicating that both a sufficiently high concentration of functional groups and lattice defects may be required to observe enhanced capacitance.

The structure of the hydrazine reduced material was also investigated by Raman spectroscopy. As shown in Figure 3.11, compared to the thermally exfoliated material at approximately the same C/O, the \( I_D/I_G \sim 1.9 \) was higher while the D-peak FWHM was \( \sim 60 \text{ cm}^{-1} \) and G-peak FWHM (\( \sim 65 \text{ cm}^{-1} \)) were significantly smaller while the \( I_D/I_G \). The
narrower peaks suggest that the hydrazine material’s subnanometer-sized graphitic domains are more uniform in size/shape and/or contain fewer non-6 member rings compared to the thermally reduced material.[165] The larger \( \frac{I_D}{I_G} \) also suggests that \( L_A \) is larger than the comparable C/O thermally exfoliated material but is still just approaching the limit for nanocrystalline graphite. All indications suggest that this material has fewer lattice defects, commensurate with our expectations.

![Raman spectra for hydrazine reduced FGS.](image)

Assuming \( C_H \sim 20 \ \mu F/cm^2 \), a typical value for small ions in acetonitrile,[1, 19] it is possible to estimate \( C_{SC} \) or alternatively, the average density of electronic states, \( N_0 \), if the relationship derived by Gerischer[31, 32] is used: \( C_{SC} \propto (N_0)^{0.5} \) for the various FGSs, as shown in Figure 3.12.(see Section 1.2.2.3) This result allows us to predict the theoretical limit of \( C_G \) (in F/g) for electrodes based on defective FGSs if all 2630 m²/g of surface area were available to the electrolyte. Since \( C_H \) depends on the electrolyte used, we plot the theoretical limit for supercapacitors for values of \( C_H \) within the typical 16-25 \( \mu F/cm^2 \) range. Thus FGSs have the potential to exhibit \( C_G \) exceeding 420 F/g (assuming 16 \( \mu F/cm^2 \) while electrodes with properties similar to pristine graphene, highly reduced or annealed FGSs and other carbonaceous electrodes, may reach a limit about a fourth of this value due to the low \( C_{SC} \). It was recently suggested that the low electronic limit is
exacerbated when a graphene sheet,[41] or a thin pore wall within an activated carbon,[42] has to support a double-layer on both sides. In this case, the electronic charge within a FGS would have to be shared between both sides resulting in $N_0/2$ available electronic states. For more defective FGSs with a high $C_{SC}$, this effect is small; resulting in less than a 5% drop in the predicted $C_G$ compared to a 25% reduction for materials which exhibit a $C_{DL}$ similar to pristine graphene.

![Figure 3.12: Theoretical prediction of $C_G$ at the open circuit potential for the various FGSs used in this study assuming various electrolytes with different $C_H$ could be used.](image)

For low, medium, and high curves $C_H = 15$, 20, and 25 $\mu$F/cm$^2$. Data points calculated using the data presented in Figure 3.10.

From our results it is clear that the FGS production method significantly affects the $C_{DL}$. Thus, in addition to changes in the SSA of electrodes used in supercapacitors, it is likely that different processing routes contribute to the wide range of $C_{DL}$ reported in the literature (eg. 7-35 $\mu$F/cm$^2$ as estimated by reported $C_G$ and SSA values).[99, 100, 111, 158, 162, 168] To compare our results (Fig. 3) to those reported for thick, porous electrodes, we must consider that $C_{min}$ was measured at a frequency of 10 Hz in an attempt to isolate $C_{DL}$ from any artifacts due to electrolyte leakage beneath the O-ring used to seal the electrochemical cell or due to Faradaic processes which could contribute
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To the measured $C_{DL}$. In contrast, the capacitance of thick, porous electrodes is typically measured at much lower frequencies ($\sim 10$ mHz) and $C_G$ is calculated by integrating over the entire voltage window. Thus, the estimated theoretical $C_G$ in Figure 3.12 likely underestimates what we might expect from a real device if all theoretically available SSA was utilized. The values of $C_G$ reported in the literature for FGS typically range from 100 - 200 F/g\cite{99, 100, 111, 158, 162, 168} with several exceptional reports claiming $\sim 270$ F/g\cite{114, 115}. These materials have not reached the theoretical limit because their ion-accessible SSA is low, implying that better techniques must be developed to enhance the ion-accessible SSA.

The changes in $C_{DL}$ with thermal processing may also apply to other high SSA carbonaceous materials. For example, Chmiola et al. demonstrated a similar increase in $C_{DL}$ with increasing $I_D/I_G$ (i.e., disorder) with carbide-derived carbon\cite{(Figure 3.13)} However, as is typically the case with porous electrodes, the surface area, porosity and chemical structure are not independent parameters and the increase in $C_{DL}$ was attributed to pore-size effects\cite{50, 51}. The low $C_{DL}$ of the material reported in their study suggests that their high temperature annealed material is limited $C_{SC}$ ($\sim 6 - 11 \mu F/cm^2$) calculated assuming $C_H = 20 \mu F/cm^2$\cite{50, 51}. The mechanism of $C_{DL}$ enhancement suggested by these authors is one that increases $C_H$, but as is apparent in Figure 3.12, such an increase in $C_H$ would be difficult to observe in a material limited by $C_{SC}$ and an alternate explanation can be given in terms of changes in the carbon structure with heat treatment.
With graphene-based materials, we have shown how to isolate changes in $C_{SC}$ from changes in porosity and surface area by studying charging in a quasi-2D system using a series of thermally exfoliated FGSs. Our results suggest that it may be possible to tailor the structure of FGSs and other carbonaceous materials so that they behave more like glassy carbon or the edge-plane of graphite rather than like pristine graphene. A mechanistic understanding of the changes we observed would help to rationally design high performance electrodes. In any case, processing techniques to achieve high accessible surface area electrodes with metal-like $C_{SC}$ will be needed to continue advancing the limits of supercapacitor performance, and increase the commercial relevance of the technology.

![Figure 3.13: Dependence of capacitance on $I_D/I_G$ ratio determined by our work and compared to the data presented by ref. [50].](image)

To compare our data to theirs the Raman spectra were analyzed with a two Gaussian fit. Although the explanation for enhanced capacitance given by Chmiola et al. was attributed to a pore-size effect, our results suggest that it could also be explained the change in structure of the carbon material which was required to change its pore-size.

### 3.4 Conclusions

This work demonstrates that the theoretically attainable capacitance of EDLCs based on graphene materials depends largely on the state of disorder. If electrodes are
composed of pristine graphene or FGSs that are annealed to the extent that they possess a high C/O and low defect density, the capacitance is low and governed by the electronic side of the interface (3-7 µF/cm²). These changes in the interfacial double-layer capacitance imply that the theoretical limits in terms of a graphene-based material’s specific capacitance is dictated by the synthesis and post-processing routes used to generate and form the electrode material. The graphene monolayer system used in this study provides a convenient means of probing these changes and selecting electrode materials with the greatest potential to be used as high capacitance electrodes for electrochemical double-layer capacitors. Unfortunately, we were only able to correlate indicators of average structure and functionalization with double-layer capacitance in this study for a small subset of the possible reduction and annealing conditions that can be used to generated electrodes based on functionalized graphene. Future work on understanding the local molecular-level changes influencing the space charge capacitance within functionalized graphene would be beneficial to improve our understanding of how to design graphene-based electrode materials with enhanced capacitive properties.

Our work also emphasizes the importance of changes in the structure and chemistry of the carbon materials used in EDLCs when attempting to vary other properties like the pore size. In many cases, the pore size is tuned by adjusting the annealing temperature which significantly changes the structure and chemistry of the carbonaceous material. Since the results of this study can likely be applied to other structurally disordered forms of carbon, changes in the observed capacitance could be due (at least in part) to changes
in the electronic properties of the carbon electrode and should be considered in future work.
4 Specific Surface Area of Graphene in Aggregate Form

Retaining the high specific surface area (SSA) of a functionalized graphene sheet (FGS) when many sheets are processed into dense, porous films currently limits many of its potential applications. Factors that control the SSA of these porous assemblies are not well understood. Here, we demonstrate how aggregation of FGSs using different processing conditions lead to a wide range of SSAs accessible to nitrogen or methylene blue ranging from less than 1 m$^2$/g to 1750 m$^2$/g. The effects of capillary forces, van der Waals interactions and aggregation kinetics on the SSA are explored and an aggregation model is proposed to account for these effects.

4.1 Introduction

Experimentally, the highest SSA reported for FGSs is 1850 m$^2$/g, as measured in suspension using methylene blue (MB) dye adsorption.[65] This high value was also supported by atomic force microscopy (AFM) directly by proving the presence of single sheets in abundance.[65] However, the same material, as a dry powder prior to solvent dispersion had a nitrogen accessible SSA of 500-900 m$^2$/g. A large range of nitrogen accessible SSAs ranging from 8 to 700 m$^2$/g have also been observed in other studies involving FGS aggregates produced by chemical reduction of graphene oxide.[100, 103]
These values span more than two orders of magnitude and clearly indicate the sensitivity of the SSA of graphene aggregates to processing.

The problem of retaining the accessible SSA of FGSs is widely recognized and many strategies are being developed in an attempt to more closely approach 2630 m$^2$/g. We have categorized these into two general ideas: (a) Keeping sheets apart using spacers such as metal nanoparticles,[103, 104] mesoporous metal oxides,[102, 105] carbon nanotubes,[106] activated carbons,[107] or polymers,[108, 109] and (b) by changing the structure or morphology of FGSs, without the use of additives, through approaches based on crumpling individual sheet,[112, 113] by growth of graphene onto porous templates,[110] or by the chemical activation of graphene networks.[111] Many of these methods have been successful in improving device performance compared to low surface area controls but performance improvements do not yet match what would be expected from such a high SSA material.

Despite a large number of works that focus on generating FGSs with high SSA, an in-depth analysis of this problem has not yet been presented. A systematic understanding of the mechanisms which control the accessible SSA of FGS aggregates is needed to understand and improve processing of FGSs in ways such that the high theoretical SSA can be fully utilized. We expect that the SSA will be intimately linked to the aggregation behavior of FGSs which act as two-dimensional (2D) molecular colloids. It is known that the structure and density of such aggregated colloids is influenced largely by aggregation kinetics[169-171] which are dictated by the balance of attractive and repulsive forces acting between particles in the aggregation process.[172, 173] We must also consider that
Unlike typical colloidal particles, which in most cases can be considered as rigid spheres or plates, FGSs are atomically thin and have a low bending rigidity which allow them to fold\cite{174} or crumple\cite{112, 175-178} under the influence of capillary and van der Waals (vdWs) forces.

In the present work we explore the relative effects of vdWs and capillary forces on the accessible SSA of FGSs upon aggregation and consolidation through the use of various dispersion and drying techniques. We also assess their order of magnitude by a simple scaling analysis. To demonstrate the sensitivity of the SSA to aggregation kinetics we vary the interactions between FGS and solvent by tuning the chemical nature of the FGSs. This is accomplished by producing FGSs with different carbon to oxygen ratios (C/O) which we expect to change the FGS-FGS interactions in solvents due to changes in hydrophobicity. The aim of this work is to provide a roadmap for understanding how to control and explain changes in the accessible SSA when FGSs are processed to create high performance devices.

4.2 Experimental
4.2.1 Production of FGSs

GO was obtained from Vorbeck Materials Corp. Rapid thermal exfoliation/reduction of GO to FGSs was carried out as described previously.\cite{64, 65} Briefly, GO was dried overnight at 60 °C prior to exfoliation. Approximately 3 g of GO was slowly dropped through a long fused quartz tubes placed vertically within a Lindberg furnace at 1050°C under continuous flow of argon. This process typically yielded 1 g of FGS with a nominal
C/O of 20. In addition to our typical process, the residence time in the furnace was adjusted to vary the C/O between 2 and 48 as determined by combustion analysis (Atlantic Microlabs, GA). When referring to FGSs with varying C/O we denote this value as a subscript. For example, fully oxidized graphene oxide typically has a C/O of 2 and we refer to this as FGS2.

### 4.2.2 Drying Techniques

Various dispersions and drying experiments were carried out in an attempt to determine their effect on the SSA. In the first set of experiments we attempted to keep the aggregation kinetics and FGS-FGS interactions constant by processing in the same solvent (ethanol) and the same FGSs with a nominal C/O of ~20. We first disperse the as-exfoliated powder in ethanol and measure the SSA using MB as a probe as described by McAllister et al.[65] A known quantity of FGSs was dispersed in ethanol by tip ultrasonication (Vibra-Cell, Sonics & Materials Inc.) of a 1 L suspension for 3 h at 20% power. MB was added before or after ultrasonication. For the case when MB was added after ultrasonication, the FGSs were given time to aggregate and then the MB was added to the dispersions which were then vigorously stirred with a stir plate with a Teflon coated stir bar for 48 h. In both cases, the ethanol was then left to evaporate and free MB (i.e., MB not adsorbed to the FGSs) was dissolved in deionized water. The absorbance at 660 nm was read using a UV/visible spectrophotometer (IBM Instruments Inc.) and compared to prepared standards. From the known amount of FGSs in suspension and the amount of adsorbed MB, the SSA could be estimated using the assumed coverage of
1.3 nm² per MB molecule lying flat on a surface.[179] As discussed by McAllister et al., for graphite-based samples, flat monolayer coverage is expected. The SSA was measured in this way for FGS concentrations between 0.1 and 2 mg/mL and the results were averaged.

The effect of evaporative drying on the SSA was then studied. A 200 mL suspension of FGSs in ethanol at a concentration of 0.2 mg/mL was ultrasonicated for 30 min while stirring in an ice bath. Evaporative drying was carried out first at 60 °C in 4 × 50 mL centrifuge tubes. The semi-dry pellets were then transferred to glass scintillation vials for heating overnight under continuous flow of nitrogen at 200 °C to remove residual solvent. Since ethanol has a relatively low critical point, we also investigated the SSA of FGSs after supercritical drying. Capillary forces do not act during supercritical drying as liquid-vapor interfaces do not exist. This allowed us to isolate the effect of capillary forces on SSA of aggregated FGSs in the dry state. Supercritical drying was carried out using a home-made apparatus described previously.[180] In a typical drying procedure 200 mL of the ultrasonicated FGS-ethanol suspension was placed in the pressure vessel. In order to dry more material at low suspension concentrations, the dispersion was allowed time to aggregate and the resulting mixtures were centrifuged at 1000 g using an IEC Centra GP8R centrifuge (218A rotor) to collect the aggregates. The resulting ethanol soaked FGS pellet was transferred to open, marked, glass scintillation vials which were placed within the pressure vessel such that multiple samples could be dried simultaneously. The vessel was sealed and placed in an ashing furnace (Barnstead-Thermolyne)) and the temperature was ramped to 220 °C at 0.2 °C/min. When the pressure in the vessel
reached equilibrium, the temperature was raised to 270 °C at 0.2 °C/min. The pressure increased rapidly during this period and the chamber vessel was periodically vented to ensure that the pressure did not exceed 10 MPa to avoid an explosion hazard. As a precaution, a burst diaphragm was installed on the pressure vessel. The chamber was allowed to equilibrate for several hours and was then slowly vented to atmospheric pressure while maintaining the temperature at 270 °C. A vacuum pump was connected to the vessel and vacuum was applied for 4 h at a furnace temperature of 270 °C to remove residual ethanol vapor. The chamber was then furnace cooled to room temperature and the dry FGSs removed.

To determine the effect of evaporative drying from other solvents, the same procedure described for evaporative drying in ethanol was carried out with dimethylformamide (DMF), N-methyl-pyrrolidinone (NMP), dichloromethane (DCM), dimethylsulfoxide (DMSO) and ammoniated water adjusted to a pH of 11. The same drying experiments were also carried out with FGSs with varying C/O dispersed in ammoniated water. The effect of consolidation on SSA, in the absence of a solvent, was also determined by compressing the as-exfoliated powder mechanically in a stainless steel dye with a hydraulic press (Carver) to pressures up to 34 MPa.

### 4.2.3 FGS Characterization

To determine the SSA of dried FGSs, nitrogen adsorption was carried out using a Gemini V unit (Micromeritics Instruments) and the SSA extracted from the isotherm using Brunauer-Emmett-Teller (BET) theory. XRD was carried out using a Miniflex
II unit (Rigaku Americas, Cu Ka radiation). FGS morphology was characterized by scanning electron microscopy (SEM, Tescan) at 20 kV acceleration voltage using the secondary electron detector. The various FGSs were also imaged using contact-mode AFM (MultiMode/Digital Nanoscope IIIa system, Veeco Instruments) using NP-S tips (radius of curvature < 10 nm). Samples of FGS$_2$ were prepared for imaging by dispersing GO in ammoniated water, adjusted to pH 10, and ultrasonicating 100 mL of a 0.2 mg/mL suspension for 30 min in an ice bath. This suspension was spun coat onto freshly cleaved mica at 3000 RPM for subsequent imaging. Thermally exfoliated samples were prepared for AFM by ultrasonicating 20 mL of a 0.5 mg/mL suspension in 1,2-dichloroethane within an ice bath. The resulting suspension was centrifuged at 1000 x g to remove any aggregated material and deposited at the air-water interface and transferred to freshly cleaved mica according to the procedure outline by Pope et al.[119]
4.3 Results and Discussion

4.3.1 Dispersion and Drying Effects

Figure 4.1: SSA as a function of various processing paths. (a) Schematic of ethanol phase diagram (adapted from ref. [181]) illustrating the various dispersion and drying routes. (b) The SSA measured during or after processing by MB (1, 3) and nitrogen (5, 1, 4) adsorption.

Figure 4.1a illustrates the processing paths and the points where the SSA was measured. The SSA of FGSs resulting from these various stages of processing are shown in Figure 4.1b. The values ranged from $1740 \pm 70$ to $390 \pm 40 \text{ m}^2/\text{g}$. When the FGS suspension in ethanol was ultrasonicated, the MB was capable of adsorbing to a significant fraction of the theoretically available FGS surface area. Similarly high values were also demonstrated by other works which used the same protocol.[64] [65, 158] Only approximately half the SSA measured during ultrasonication was available for adsorption once the FGSs had aggregated and settled prior to adding the MB. These observations suggest that the continuous input of ultrasonic energy into the dispersion is required to transiently expose the available FGS surface area. Upon aggregation, significant overlaps must have formed between FGSs which prevented MB from adsorbing on this surface.
area. These contacts were likely formed by attractive vdWs forces between the sheets. Drying the FGSs by evaporation had the largest impact on the measured SSA. During evaporative drying compressive capillary forces acted on the aggregates which lead to significant overlap between the sheets. When capillary forces were avoided, by supercritical drying, it was possible to achieve nearly double the SSA compared to the evaporatively dried case.

The morphology and relative bulk densities of FGSs after processing are shown in Figure 4.2. Prior to dispersion, the as-exfoliated FGSs have a low bulk density (~$10^{-3}\text{g/cm}^3$) and exhibit a vermiculite-like structure similar to expanded graphite where each loosely stacked domain corresponds to the same initial GO particle. Dispersion of the powder by ultrasonication in ethanol was verified by AFM as shown in Figure 4.2 where most sheets range in thickness from 1 – 3 nm. Single sheets are thought to have an apparent thickness of ~1 nm due to the presence of lattice defects, residual functional groups[65, 174] and adsorbed solvent layers[182] between the FGS and the mica which increases their apparent thickness compared to the d-spacing of graphite (0.34 nm). Therefore the FGSs produced by our approach likely yields a distribution of single, double, and possible triple sheets. This distribution is a likely reason for the deviation in the highest measured SSA from the theoretical value (i.e., 1740 m$^2$/g vs. 2630 m$^2$/g). After dispersion in ethanol, re-aggregation and then drying, the FGSs formed aggregates with no apparent ordering at the length scales probed. All powders were analyzed by XRD and exhibited nearly featureless profiles. The most significant difference in the dry
powders besides changes in SSA was the increase in bulk density from \( \sim 10^{-3} \) g/cm\(^3\) to \( \sim 0.5 \) g/cm\(^3\) after evaporative drying. (See insets of Figure 4.2)

Figure 4.2: Morphology of FGS after processing. (a) SEM images of aggregate morphology obtained after the rapid thermal expansion of graphite oxide with no further processing. (b) Contact-mode AFM image of FGSs after being dispersed by ultrasonication and coated by the LB technique onto mica. Histogram of minimum FGS thickness shown below. (c) SEM image of FGS after dispersion in ethanol and evaporative drying. (d) SEM image of FGS after dispersion in ethanol and supercritical drying. Insets in (a), (c) and (d) are of 20 mg of FGS in a 50 mL scintillation vial as a qualitative measure of changing bulk density.
We also dispersed FGSs in other commonly used solvents and dried these dispersions by evaporation. As shown in Figure 4.3a, all SSAs measured were similar to the ethanol case within the typical sample-to-sample variation (350 ± 40 m²/g). In all cases, the bulk density increased to a similar extent. The stability of the FGS dispersions was different in each of these solvents. Dispersions in NMP and DMF did not aggregate as quickly as dispersions in ethanol, DCM, water or DMSO. However, during the course of evaporative drying, all dispersions were observed to flocculate and settle during the constant rate period of drying,[183] prior to being consolidated by capillary forces. The magnitude of these compressive forces is dictated by the surface tension, contact angle and geometry at the location of the liquid/vapor interface. Water has a higher surface tension than the other solvents used (i.e., 72 mN/m vs. ~20 mN/m) which might imply that capillary forces would be stronger. However, we did not observe a significantly lower SSA compared to the other solvents and this is likely due to the possibility that water wets the FGSs with a larger contact angle than the other solvents used. The contact angle of water on graphite is known to be 80-90°,[184] but we expect the functional groups on FGSs to lower the contact angle to some extent.

Since the decrease in SSA was correlated with a decrease in bulk density, we performed several experiments where the bulk density was increased by compression of the dry powder instead of by dispersion followed by capillary consolidation. We compressed the as-exfoliated FGSs under various loads and determined their SSA by nitrogen adsorption.(Figure 4.3b) At 12 and 32 MPa applied pressure, the FGS aggregates reached a bulk density of approximately ~0.1 and 0.5 g/cm³, respectively,
corresponding to SSAs of 450 and 390 m²/g. This is approximately the same decrease in SSA as was observed for the case of capillary consolidation and suggests that the SSA is directly related to the bulk density.

![Figure 4.3 SSA of FGS after dispersion and densification.](image)

4.3.2 C/O Effects

As shown in Figure 4.4, the C/O of the FGSs had a significant effect on the SSA measured after evaporative drying. When FGSs are completely oxidized (C/O ∼ 2), the SSA was 1 m²/g. In addition to changes in SSA, a significant difference is observed in the XRD profiles. FGS₂ aggregates exhibited a sharp peak near 2θ ≈ 10°, which corresponds to the d₀₀₂ spacing of GO, while other samples appeared nearly X-ray amorphous. This indicates that FGS₂ aggregates can more easily rearrange to form larger crystalline domains compared to FGSs with higher C/O. There are two possible causes for this difference in drying behavior: Morphological differences between the materials and/or changes in the strength of the FGS-FGS interactions which dictate aggregation kinetics. FGS₂ is atomically flat when observed by AFM on various substrates,[119] whereas thermally exfoliated FGSs are often highly wrinkled likely due to defects introduced
during the rapid thermal expansion process. [64] [65] These wrinkles may reduce the contact area between FGSs and sterically prevent alignment and restacking. [185] Also, since the materials are chemically different, the binding energy or the strength of vdW interactions may change as a function of C/O. The Hamaker constant, which describes the strength of the vdW forces between the FGSs has been shown to be lower for FGS$_2$ compared to graphene due to the increased thickness and lower density of FGS$_2$ compared to graphene. [65] Therefore, it is possible that FGSs effectively become stickier as the C/O is increased and this hinders the rearrangement and restacking of FGSs within an aggregate.

![Figure 4.4: Influence of C/O on the aggregation behavior of FGSs. (a) XRD profiles of dried FGS aggregates. Inset shows SSA ratio as a function of C/O after evaporative drying in water (b) and the theoretical SSA of a single sheet. Inset shows details of C/O between 0 and 50.](image)

When considering the effect of C/O we must also consider how the addition of oxygen containing functional groups changes the theoretical SSA. The theoretical SSA of graphene is the inverse product of the d-spacing and density of graphite. (i.e., $\text{SSA}_{\text{theoretical}} \approx \frac{1000}{(0.34 \times 2.24)}$) Since these parameters are unknown for FGSs and likely vary with C/O, we approximate the SSA in a different way. Starting with the SSA of
graphene we consider only the extra mass of placing oxygen on the graphene as given by Equation 1.

\[ SSA_{\text{theoretical}} \approx \frac{2630}{\left(1 + \frac{16}{12C/O}\right)} \text{m}^2/\text{g} \]  

(29)

As a first approximation, this estimate neglects the mass of hydrogen that may exist on edges, hydroxyls and carboxylic acids which would act to decrease the SSA further and also does not consider any effects that vacancy defects in the lattice could have on the SSA. As shown in Figure 4.4b, with FGS2 the theoretical SSA is decreased from 2630 m\(^2\)/g to 1578 m\(^2\)/g. The SSA changes significantly between a C/O of 2 to 30 and quickly approaches 2630 m\(^2\)/g. Although this likely contributes to the decrease in SSA observed, scaling the SSA by this factor does not account for the decreases observed experimentally when FGSs with varying SSA are dispersed and consolidated by evaporative drying. As discussed above, this decrease is likely due to changes in FGS morphology (i.e., the degree of wrinkling) and/or inter-FGS attraction which affect the ability of aggregates to rearrange into lower surface area structures.
Figure 4.5: Schematic of possible aggregate structures. House of card like structure which yield the highest SSA (left); Graphite-like aggregates which would arise if the material could completely restack (right); Intermediate structure which we obtain experimentally (middle).

It is clear from the results discussed above that some FGS-FGS overlap must occur within the aggregated material resulting in lower nitrogen or MB accessible SSA. However, from our SEM and XRD analysis it seems that, in most cases, the FGSs do not assemble into well ordered, aligned graphite like particles. Instead, at least for the case of attractive FGSs with higher C/O, the FGSs tend to aggregate somewhat randomly. Despite this random aggregation, we do not achieve a stable house-of-cards like structure that is capable of maintaining the theoretical SSA. Clays are known to form such structures under certain conditions and maintain nitrogen accessible SSAs close to their theoretical SSA.[186] However, clay platelets are typically thicker and smaller in diameter compared to FGSs. This causes them to behave more like rigid plates[187, 188] compared to thinner, larger diameter FGSs. As schematically illustrated in Figure 4.5, we propose that, although it may be possible to initially assemble FGSs into such a high SSA house-of-cards like structure, the low bending rigidity of FGSs cannot resist the attractive
or compressive forces acting on or between the sheets during processing such as vdWs and/or capillary forces. We analyze this situation more closely in the next section using a simple scaling analysis of elastic, vdWs and capillary forces and use it to help explain the changes in SSA with increasing bulk density.

### 4.3.3 Capillary & van der Waals Forces

![Diagram of graphene sheets separated by a distance and pinned at one end](image)

*Figure 4.6: Model geometry for comparing capillary, vdWs and elastic forces.* Two graphene sheets (widths extended into the page) are separated by a distance (d) and pinned at one end allowing the free end to bend under the action of capillary or vdWs forces.

To simplify the complex and unknown structure of an FGS aggregate we perform a scaling analysis on the geometry shown in Figure 4.6. An analogous geometry and analysis was used by Bico *et al.* to study wet hair bending under the action of capillary forces.[189] We consider two parallel graphene sheets pinned at one end, and separated by a distance, $d$. In the first case we fill the space between the sheets with solvent and allow the system to dry. As the solvent evaporates, the sheets either bend to remain wet by solvent or the solvent recedes as the volume is reduced due to evaporation. If the sheets bend into contact during drying, depending on the magnitude of the vdWs forces, they could either remain in contact or move apart. A similar analysis was carried out by
Schniepp et al. who investigated the mechanical properties of FGSs by folding single FGSs back onto itself with an AFM tip.[174] The contact region was used to estimate the vDWs forces in equilibrium with the elastic force induced by sheet bending.

Assuming that FGSs behave as elastic plates, the energy required to bend the sheets into a region of contact of length, \( L_C = L - L_A \) is:

\[
E_E = \frac{3\kappa d^2}{L_A^3},
\]

(30)

where \( \kappa \) is the bending rigidity of a FGS. To compare this energy to that of capillarity we fill the space between the sheets with a volume of solvent. The total surface energy when a solvent contacting the FGSs in the geometry shown in Figure 4.6 is:

\[
E_C = -2\gamma L_C,
\]

(31)

As this is an approximation, we assume that the concept of surface tension holds at nanometer length scales. However, as the thickness of the solvent layer approaches the size of the molecule, this continuum notion likely breaks down.[190] In the absence of a liquid layer between the sheets, the vDWs energy gained if the sheets contact over a length, \( L_C \) sheets is given by Equation 3, using the parallel plate approximation.[191]

\[
E_{vdw} = -\frac{A_{121}}{12\pi\delta^2} L_C,
\]

(32)

Here \( A_{121} \) is the Hamaker constant for two FGSs (1) separated by a medium (2) such as vacuum, air or solvent if in suspension. When only capillary forces are considered, the total energy of the system is:
\[ E_{total} = E_C + E_E = 2\gamma L_C + \frac{3\kappa d^2}{L_a^3} \]  

(33)

At equilibrium, the total energy is minimized by differentiating the total energy, with respect to length and equating this to zero:

\[ \frac{dE_{total}}{dL_A} = 2\gamma - \frac{9\kappa d^2}{L_a^4} = 0, \]

which leads to the definition of the elasto-capillary length (LEC) is defined as:[192]

\[ L_A = \left( \frac{d \cdot L_{EC}}{2} \right)^2, \]  

(34)

\[ L_{EC} = \left( \frac{9\kappa}{2\gamma} \right)^{\frac{1}{2}}, \]  

(35)

LEC gives an estimate of the radius of curvature to which a graphene sheet can be bent by capillary forces.[192] When the system is dry and capillary forces are not active, only elastic energy and contributions from vdWs forces need be considered. Following the same analysis as above leads to a length scale associated with the ratio of elastic forces to vdWs forces which we call the elasto-vdWs length (LEV):

\[ L_{EV} = \left( \frac{54\pi}{A_{121}} \frac{\kappa}{\delta^2} \right)^{\frac{1}{2}}, \]  

(36)

LEV gives an estimate for the radius of curvature that a material can be deformed by vdWs forces.

To determine reasonable values for these length scales, estimates for the bending rigidity and \( A_{121} \) for FGSs are required. Using the bending rigidity for a flat plate, \( \kappa = \) [521]
\( \frac{E\delta^3}{12} \), with \( E = 0.9 \) TPa and \( \delta = 0.34 \) nm leads to \( \kappa = 18 \) eV. However, several theoretical works have determined the bending rigidity of graphene to be an order of magnitude smaller, between 0.85 and 1.22 eV.[193, 194] As shown in Table 1, the assumed bending rigidity has a large effect on \( L_{EC} \) but in both cases is on the order of 10 nm or less. In the following discussion we will use the larger value to give an upper bound on both \( L_{EC} \) and \( L_{EV} \).

**Table 4.1: Length scales associated with bending of graphene sheets due to capillary forces**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( L_{EC} ) (nm, ( \kappa = 1 ) eV)</th>
<th>( L_{EC} ) (nm, ( \kappa = 18 ) eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethanol</td>
<td>5.9</td>
<td>25</td>
</tr>
<tr>
<td>water</td>
<td>3.3</td>
<td>14</td>
</tr>
</tbody>
</table>

A range of estimates for \( A_{121} \) also exists and depends on the type of FGSs used. If FGSs are fully oxidized to a C/O \( \sim 2 \), McAllister et al. estimated \( A_{121} \) to be \( 2.37 \times 10^{-21} \) J (0.015 eV) for two FGS2 separated by air/vacuum.[65] This is much smaller than what is estimated for pristine graphene, \( A_{121} \sim 1.3 – 3.7 \) eV.[195] As shown in Table 2, using these estimates changes \( L_{EV} \) by an order of magnitude between graphene oxide and graphene. Since we use FGSs derived from the thermal exfoliation of GO which contains residual functional groups and lattice defects,[64, 65, 83] it is likely that \( A_{121} \) for this intermediate material is somewhere between these two extremes. This was observed by Schniepp et al., who demonstrated that the functional groups and surface roughness inherent to FGSs decrease the magnitude of vdWs forces compared to pristine graphene.[174] For the same bending rigidity, \( L_{EC} \) is less than or approximately equal to \( L_{E-vdWs} \) indicating that both forces are similar in magnitude but capillary forces can be
stronger depending on the assumed value of $A_{121}$ used to define the vdWs force acting between FGSs. Even if capillary forces are stronger, when the aggregates are completely dry and capillary forces are no longer active, the system is limited by vdWs forces and $L_{E-vdWs}$ will be the length scale defining the deformation and resulting SSA of FGSs in the dry state.

**Table 4.2: Length scales associated with bending of graphene sheets due to vdWs forces.** The Hamaker constant used for graphene was $A_{121} = 1.3$ eV and for graphene oxide was $A_{121} = 0.015$ eV.

<table>
<thead>
<tr>
<th>Material</th>
<th>$L_{E-vdWs}$ (nm, $\kappa = 1$ eV)</th>
<th>$L_{E-vdWs}$ (nm, $\kappa = 18$ eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>graphene</td>
<td>4</td>
<td>34</td>
</tr>
<tr>
<td>graphene oxide</td>
<td>36</td>
<td>318</td>
</tr>
</tbody>
</table>

As shown in Figure 4.7, $L_A$ decreases with both capillary and vdWs forces as the separation distance becomes smaller. Physically, this means that the FGSs have to bend less at smaller separations. If we extend this idea to 3D, it translates to a decrease in SSA with increasing bulk density. Assuming FGSs that are on average, parallel within a loosely aggregated stack, we can relate the average distance between the sheets, $d_{avg}$, to $\rho_b$ of the FGSs according to Equation 7:

$$d_{avg} = \delta \left( \frac{\rho_g}{\rho_b} - 1 \right),$$  \hspace{1cm} (37)

The ratio of $L_A$ to $L$ can then be used to estimate the reduction in SSA as a function of $\rho_b$ if we assume that vdWs forces balance elastic forces. As shown in Figure 4.7, assuming an average diameter of $L = 500$ nm,[65] even at low bulk densities ($< 10^{-3}$ g/cm$^3$), the SSA is significantly lowered from the theoretical value (1000 m$^2$/g and lower).
At more practical bulk densities for device applications, 0.1 to 0.5 g/cm³,[118] the SSA is estimated to be between 100 and 300 m²/g. Although the actual situation is complicated by jamming effects, varying aggregate morphologies and contact regions of various sizes, this model qualitatively matches what we observe experimentally and possibly explains the decrease in SSA with increasing bulk density. Our experimental observations for larger bulk densities span a much larger range of SSAs. As discussed above, this is likely due to the ability of FGSs with lower C/O to rearrange after aggregation into better aligned aggregates which more effectively restack compared to FGSs which stick upon contact and cannot rearrange as readily.

**Figure 4.7: Model predicting influence of vdWs forces on SSA.** (a) Equilibrium accessible length (Lₐ) as a function of the separation distance between the model sheets defined in Figure 4.6 for capillary forces in ethanol and water and vdWs forces for graphene and graphene oxide. (b) Predicting the SSA for change in bulk density

### 4.4 Conclusions

This work demonstrates the various processing parameters that affect the SSA of aggregated FGSs and provides some explanations for the observed changes. The SSA is
found to decrease when FGSs are consolidated to higher bulk densities. Unlike, rigid, spherical colloids, FGSs are soft materials which are able to deform upon the application of an external pressure. We provide a scaling analysis which illustrates the extent to which a FGS can be deformed by capillary and vdWs forces. These forces are able to elastically deform sheets within aggregates to radius of curvatures on the order of tens of nanometers or even smaller. The C/O of the FGSs is also found to significantly affect the surface area upon aggregation. We provide two possible explanations for this: (1) FGSs produced by thermal expansion often display a wrinkled morphology which reduces sheet-sheet contact. (2) The interaction forces between FGSs change as oxygen containing functional groups are removed. This changes the aggregation kinetics and results in higher C/O FGSs acting as stickier particles which do not rearrange as readily as aggregates composed of FGSs with low C/O. These observations and analysis provide insight as to how to better design nanocomposite materials and electrodes from graphene-based materials.
5 Supercapacitor Electrodes Produced Through Evaporative Consolidation of Graphene Oxide-Water-Ionic Liquid Gels

In the following chapter I explore a new approach used to fabricate graphene-based electrodes with increased ion-accessible surface area. We use colloidal gels of graphene oxide in a water-ethanol-ionic liquid solution to assemble graphene-ionic liquid laminated structures for use as electrodes in electrochemical double layer capacitors. Our process involves evaporating the solvents water and ethanol yielding a graphene oxide/ionic liquid composite, followed by thermal reduction of the graphene oxide to electrically conducting functionalized graphene. This yields an electrode in which the ionic liquid serves not only as the working electrolyte but also as a spacer to separate the graphene sheets and to increase their electrolyte-accessible surface area. Using this approach, we achieve an outstanding energy density of 17.5 Wh/kg at a gravimetric capacitance of 156 F/g and 3 V operating voltage, due to a high effective density of the active electrode material of 0.46 g/cm². By increasing the ionic liquid content and degree of thermal reduction, we obtain electrodes that retain >90% of their capacity at a scan rate of 500 mV/s, illustrating that we can tailor the electrodes towards higher power density if energy density is not the primary goal. The ease of manufacturing, achieved by combining the steps of electrode assembly and electrolyte infiltration, makes this bottom-up assembly approach scalable and well suited for combinations of potentially any graphene material with ionic liquid electrolytes.
5.1 Introduction

Electrochemical double layer capacitors (EDLCs), also known as ultracapacitors or supercapacitors, operate by accumulating charge within the electrochemical double layer at the electrode/electrolyte interface.\cite{1} A typical EDLC device consists of two electrodes which are imbibed with electrolyte, separated by a porous, ion-permeable membrane, sandwiched between two typically metallic current collectors, and packaged in a gas-tight pouch or container. The energy density $E$ of such a device – specific to the entire device mass – is the performance metric of practical interest\cite{1} (alternatively, volume-specific values\cite{8} can be reported). $E$ depends on the gravimetric capacitance $C_G$ of the dry (active) electrode material, the operating voltage $U$, and the mass fraction $f$ of the active electrode material (typically $\sim$30 wt\% for commercially viable devices)\cite{8, 111} accounting for the mass of electrolyte, separator, current collectors and packaging: \cite{1, 7}

$$E = f \cdot C_G U^2$$ \hspace{1cm} (38)

In order to increase $E$, research is targeted towards increasing both $C_G$ and $U$, but the impact of the mass fraction $f$ is often neglected. Typically, an energy density $E^* = 1/8 C_G U^2$ is reported instead, which excludes the weight contribution of device components other than the active electrode material. The relation between $C_G$, $U$ and $E^*$ is illustrated in Figure 5.1, where we plot $E^*$ vs. $C_G$ for material/electrolyte combinations that can operate at voltages $U$ between 1 and 4 V: High values of $C_G$ up to 1000 F/g can be achieved with materials such as RuO$_2$\cite{1, 29} MnO$_2$ \cite{29, 196} or carbonaceous materials\cite{7, 29} in water-based systems, since these materials are redox active in aqueous
electrolytes, i.e., exhibit faradaic reactions akin to processes within batteries (pseudocapacitance). In spite of these high $C_G$ values, however, $E^*$ remains low since aqueous systems are not stable at $U > \sim 2$ V. On the other hand, in order to achieve $E^* = 100$ Wh/kg, an electrode material with $C_G = 200$ F/g suffices if the device can be operated at 4 V. High operating voltages have been attained with organic electrolytes and, more recently, with ionic liquids (ILs) which therefore are the electrolyte of choice for high energy density applications. ILs have been used in conjunction with carbonaceous electrodes such as activated carbons, carbide derived carbons (CDCs), or carbon aerogels achieving stable operation and reaching up to $E^* = 50$ Wh/kg at values of $C_G$ between 100 and 200 F/g. Besides exploring electrolytes which are stable at voltages in excess of 4 V maximizing $C_G$ of the carbonaceous electrodes is thus the route towards EDLCs with larger $E^*$.

Figure 5.1: Estimated energy density (specific to dry electrode mass) of a two electrode cell as a function of operating voltage and single electrode capacitance. (a) $E^*$ does not consider device components other than the active material. (b) Comparison of uncorrected ($E^*$) and corrected ($E$) energy densities for examples in non-aqueous electrolytes where $f$ could be estimated (see Table 3). Recent literature data for graphene-based electrodes in non-aqueous and aqueous electrolytes are shown as black and orange squares, respectively. Data plotted for other materials were taken from several recent reviews. [

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[197] [198] [199] [200] [201] [202] [203] [84] [99] [100] [109] [111] [114] [123] [158] [162] [202] [203] [87] [99] [100] [114] [158] [204-210]
$C_G$ is proportional to the surface area-specific double layer capacitance ($C_{DL}$) of the electrode material, its mass-specific surface area (SSA), and the fraction to which the SSA is accessible to the electrolyte in the final electrode. Due to their exceptionally high theoretical SSA (2630 m$^2$/g), functionalized graphene sheets (FGSs), derived by the thermal reduction and exfoliation of graphite oxide (GO)[64, 65] or the chemical reduction of graphene oxide,[66] are promising candidates for high-performance electrode materials. In addition to high SSA, our recent work suggests that FGSs also exhibit a larger $C_{DL}$ (14 - 26 $\mu$F/cm$^2$)[119] in aqueous electrolytes (0.5 M NaF) compared to pristine graphene (3 - 4 $\mu$F/cm$^2$)[40, 41] due to the presence of a large number of lattice defects and functional groups[64, 65, 83] while providing similar electrical conductivity.[211, 212] Combining FGSs and ILs therefore has the potential to yield materials with $C_G$ reaching 400 F/g (assuming $C_{DL} \approx 20 \mu$F/cm$^2$ in IL electrolyte[38] and an ion-accessible SSA of 2000 m$^2$/g) which is a value that cannot be achieved with pristine graphene[40, 41] whose $C_{DL}$ is limited by its low electronic density of states[21, 31] or with carbon nanotubes (CNTs)[57] which might exhibit high $C_{DL}$ through activation but can achieve only half the SSA.
Table 3: Comparison of various electrode properties from recent studies demonstrating the highest values of $C_G$. Energy density was estimated using $E = f/8 \cdot C_G \cdot U^2$.

<table>
<thead>
<tr>
<th>Approach</th>
<th>$C_G$ (F/g)</th>
<th>$\rho_{eff}$ (g/cm³)</th>
<th>$f$ (wt%)</th>
<th>$E$ (Wh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser-scribed FGSs[115]</td>
<td>276</td>
<td>0.05</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>Hydrated FGSs[114]</td>
<td>273</td>
<td>0.09</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>Activation of FGSs[111]</td>
<td>166</td>
<td>0.36</td>
<td>25</td>
<td>13.8</td>
</tr>
<tr>
<td>FGSs separated by poly-ILs[109]</td>
<td>164</td>
<td>&lt; 0.12</td>
<td>&lt; 9</td>
<td>&lt; 6</td>
</tr>
<tr>
<td>Carboide-derived carbon[51]</td>
<td>160</td>
<td>0.53</td>
<td>35</td>
<td>13.5</td>
</tr>
</tbody>
</table>

*Equation 38 was used to estimate either $\rho_{eff}$ or $f$ based on details reported in the cited works: Thermal gravimetric analysis data presented in ref. [109] indicate $f < 9$ wt%; In ref. [114], the water concentration in their films prior to solvent exchange with IL was 92 wt%, which corresponds to $\sim 93$ wt% IL if we assume all water is replaced by the IL during solvent exchange and the electrode volume remained constant leading to $f \sim 7$ wt%; Ref. [115] reported the mass of active material and electrode dimensions which were used to estimate $\rho_{eff}$. The volumetric capacitance ($C_V$) and $C_G$ were reported in ref. [111] and [51] and $\rho_{eff}$ was determined using $\rho_{eff} = C_V/C_G$.

However, obtaining a high ion-accessible surface area with FGS electrodes has proven difficult in practice due to aggregation and restacking of sheets during processing.[121] A number of recent studies therefore focused on processing and assembling FGSs into EDLC electrodes in ways such that the ion-accessible surface area was maximized,[111, 115, 197] yielding $C_G$ and $E$ as high as 276 F/g and 150 Wh/kg, respectively (see Figure 1 and Table 1). These examples either involve the use of spacers that act as inactive mass (“dead-weight”)[109] or involve the imbibition of excessive amounts of electrolyte.[115, 197] As a result, the effective density of the active graphene material $\rho_{eff}$ in the electrodes is low (see Table 3); electrode mass is dominated by the mass of the imbibed electrolyte and, if present, the spacers. The value of $\rho_{eff}$ determines the upper limit for the mass fraction $f$ that can be achieved if the electrode material is used in a device: For a thick electrode, i.e., neglecting the mass of charge collectors, membrane and packaging, $f$ can be approximated (by performing a mass balance) as
where $\rho_a$ and $\rho_i$ denote the densities of the active electrode material and the combined effective density of the electrolyte and any inactive components, respectively. Values for $f$ derived from published data on FGS-based electrodes (Table 3) range from 4 to 25 wt%. Accordingly, values of $E$ for these FGS-based electrodes (also reported in Table 3) are in most cases smaller than those obtained, for example, with CDC electrodes which due to their denser packing achieve high values of $E$ despite comparably low $C_G$.[118] Therefore, while FGSs exhibit superior gravimetric capacitance, the inability to pack them densely while preserving high ion-accessible surface area has so far prevented FGS-based electrodes from exceeding the performance of conventional carbonaceous materials. CNTs and carbon fibers which aggregate to form tangled mats with low $\rho_{\text{eff}} < 0.5 \text{ g/cm}^3$ are known to suffer from the same problem.[8] To maximize energy density, we therefore must engineer FGS-based electrodes with high ion-accessible SSA (i.e., high $C_G$) which, at the same time, exhibit high $\rho_{\text{eff}}$ and therefore high $f$.

$\rho_{\text{eff}}$ is an inverse measure for the electrode pore volume, i.e., it is directly related to the size distribution and number of pores within an FGS electrode. While a wealth of information exists on the formation of multi-scale porosity during aggregation of spherical particles,[213] very little is known about the structure of aggregated graphene sheets. We envision that both inter-lamellar pores (the primary pores between the sheets) as well as inter-aggregate pores will exist, as depicted in Figure 2(a). These inter-aggregate pores are found in almost all consolidated particulate materials (unless they can
be grown as single crystals) and arise because of the statistical nature of the particle aggregation process.[213] As a result, the electrode structure is “locked” in a low density state. For FGS-based electrodes, $\rho_{\text{eff}}$ could be maximized if the volume of these inter-aggregate pores was minimized and the inter-lamellar pores were just large enough to accommodate the electrolyte ions (assuming ionic transport was not limiting the performance). Such an optimization of the pore size distribution, however, will have an impact on the ionic transport[12] within the device and thus affect power density which needs to be considered as additional performance criterion.[1] Further complications arise in the case of small pore space when dry porous electrodes are imbibed with the electrolyte during device fabrication. For example, gases held within the pores can become trapped and block the electrolyte from entering, thus reducing the effective electrode surface area.[1] This phenomenon can be amplified if the electrolyte does not wet the solid with a sufficiently small contact angle. Some primary pores may also be too small to physically accommodate the electrolyte. For activated carbons, it has been shown that pores smaller than ~1.5 nm cannot be accessed by many ILs. Thus, the pore structure of an EDLC electrode needs to meet a variety of partially conflicting requirements: Ideally, the entire pore space should be electrolyte-accessible, i.e., electrolyte-filled, interconnected, and sufficiently large to not only allow for the accommodation[117] but also the efficient transport of ions. At the same time, the total pore volume needs to be small such that dense packing of the active material is achieved.
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Figure 5.2: Comparison of conventional electrode fabrication approach with the strategy used in this work. (a) Conventional approach: Consolidation of graphene by evaporative drying or filtration leads to partial restacking of the sheets and a distribution of inter-lamellar and inter-aggregate pores. The IL cannot access all pores either because they are too small, blocked, or the wetting properties are not ideal. (b) Our approach: Dispersion of graphene oxide in water (i) followed by the addition of EMImBF$_4$ (ii). When the water component is removed by evaporation (iii), the EMImBF$_4$ remains between the sheets acting both as the working electrolyte and as a spacer, maintaining a high SSA. (c) In-situ thermal reduction: Schematics of the chemical structures of the involved materials (generated with Avogadro) are shown on the left. The graphene oxide structure is based on the Scholz-Boehm model\[83, 214\] for the sake of simplicity as the true structure of GO is currently debated. The FGS model illustrates the presence of lattice defects and oxygen-containing functional groups in the material.

To meet these requirements, we have developed a new strategy for fabricating FGS-based EDLC electrodes using ILs as an electrolyte. We summarize our approach in Figure 5.2: Instead of imbibing the electrolyte into a high SSA dry electrode with a predefined porous structure\[1\] or performing a solvent exchange as final processing step,\[114\] we introduce the IL at an early stage of the electrode fabrication process. Graphene oxide is first dispersed in water (Fig. 2(b), (i)) where it forms a charge-stabilized dispersion.\[79, 215\] Addition of a water-soluble IL screens the charge on the graphene oxide, destabilizes the dispersion, and results in the formation of a gel (Fig. 2(b), (ii)). After subsequent consolidation by evaporation of the water (Fig. 2(b), (iii)), the
graphene oxide is reduced thermally in order to obtain the final, electrically conducting electrode material (Fig. 2(c)), eliminating processing steps such as the drying of GO prior to thermal exfoliation[64, 65] or the washing steps required to remove reactants after chemical reduction.[66] We demonstrate that IL remains between the sheets during this process, yielding a compacted FGS/IL nanocomposite. The IL acts not only as the electrolyte but also as a “spacer” maintaining high ion-accessible surface area of the graphene oxide during consolidation. Our procedure eliminates the necessity of imbibing IL into the porous material, thus avoiding the associated problems with pore filling and makes the use of inactive spacers which would add “dead weight” obsolete. By tuning the initial water/IL ratio we can vary the amount of IL residing in the pores, allowing us to achieve high effective electrode densities ($f = 40$ wt%) and values of $E = 17.5$ Wh/kg at $U = 3.0$ V. Furthermore, by variation of $f$ through the IL content, we can tune our electrodes from high energy density to high power density behavior.

5.2 Experimental

5.2.1 Synthesis of Graphene Oxide

GO was produced according to a modified Hummers method.[71] 3 g of natural flake graphite (Asbury grade 3061) and 18 g of KMnO$_4$ were added under stirring to 360 mL of H$_2$SO$_4$ and 40 mL of H$_3$PO$_4$. The resulting oxidation reaction was allowed to proceed at 50 °C for approximately 16 h. Then the mixture was cooled to room temperature and subsequently added to approximately 400 g of ice. 6 mL of H$_2$O$_2$ was added to the suspension causing the slurry to turn from purple/brown to bright yellow. The suspension
was distributed into two 500 mL centrifuge tubes and centrifuged for 15 min at 1800 g using an IEC Centra GP8R centrifuge (218A rotor). The supernatant was discarded and the material was re-suspended in water. This washing procedure was then repeated with 250 mL of HCl and again with ethanol three to four times until elemental analysis by energy dispersive spectroscopy (EDS) showed no change in residual chloride.

5.2.2 Electrode Fabrication

Ethanol was used to re-suspend the concentrated GO/ethanol slurry (obtained from the washing procedure) at a concentration of approximately 10 mg/mL. The electrode precursor suspension was prepared by mixing this ethanol slurry with deionized water at a volume ratio of 3:8. Typically 11 mL of this mixture was horn ultrasonicated at 40% amplitude (Vibracell, Sonics & Materials Inc., CT) for 10 min to break apart loosely aggregated GO particles into single graphene oxide sheets. Under stirring, 1 mL of a prediluted mixture of EMImBF_{4} in water was then added to the suspension. The addition of the IL caused the suspension to flocculate and form a gel that had to be broken up by stirring to facilitate mixing of all components. 450 µL of the resulting suspension was drop-cast onto 1.5 cm diameter Pt discs (99.9% purity) and allowed to slowly dry overnight in a crystallization dish to eliminate the volatile components (i.e., water and ethanol) while the non-volatile IL was retained in the film. Fast drying resulted in cracked films and this was avoided. The composite films were then placed in an ashing furnace (Model 47900, Barnstead-Thermolyne, NH) under a flow of nitrogen and heated to various reduction temperatures between 200 and 350 °C at a rate of 20 °C/min. The
samples were not held at the maximum temperature but allowed to cool down immediately to prevent significant loss of EMImBF$_4$ due to decomposition and evaporation at elevated temperatures.[216] The mass of the films was determined by weighing the Pt discs both before coating and after the application of the coating and the reduction procedure. An extra electrode was coated and thermally reduced in each batch so that the resulting film could be scraped off and analyzed by TGA and differential scanning calorimetry (DSC) (449 C Jupiter, Erich Netzsch GmbH & Co., Germany) to determine the fraction of EMImBF$_4$ in each electrode batch. This was done by determining the difference in mass between 500 °C (after IL decomposition) and 200 °C (prior to decomposition). Additional mass loss due to the further reduction of FGSs during this measurement does not contribute significantly (see Results). The mass of FGSs on each electrode was determined by multiplying the total mass of the reduced film by the mass fraction of FGSs determined by TGA. Typically, films contained 0.5–1 mg of active material.

5.2.3 Characterization of Films

The C/O of the FGSs before and after reduction was estimated using EDS (INCA x-act, Oxford Instruments, UK attached to a VEGA1 scanning electron microscope, Tescan USA). Our EDS procedure was found capable of determining the correct stoichiometry of the pure IL and closely reproduced the C/O data obtained previously by combustion analysis for FGSs produced by the thermal reduction method.[64, 65]. Powder X-ray diffraction (XRD) was carried out using a Miniflex II (Rigaku Americas, PA, Cu K$_\alpha$
radiation). The lowest detectable angle of $2\theta = 5^\circ$ corresponds to an upper limit in the observable d-spacing of 17.6 Å. Electrochemical testing of the electrodes was carried out in a two-electrode configuration using a spring-loaded stainless steel test cell (MTI Corp. CA) and a Celgard 3501 membrane separator pre-soaked with EMImBF$_4$. Electrodes were assembled in an argon-filled glovebox (Innovative Technology, MA). A drop of EMImBF$_4$ (10 µL) was placed between each electrode and the membrane before sandwiching them inside the test cell. This drop was added to ensure good ionic contact between the separator and the electrodes and also to show that the $C_G$ of the composite electrodes containing smaller amounts of IL was not limited by an insufficiently small amount of electrolyte. Addition of IL was unnecessary for films with higher IL content. Tests carried out with no additional IL showed no significant difference in performance. Cyclic voltammetry, electrochemical impedance spectroscopy (EIS), and galvanostatic charge/discharge tests were carried out on assembled test cells using a computer-controlled potentiostat (VSP, Bio-Logic USA). $C_G$ was calculated using the following equation:

$$C_G = 2 \cdot \frac{i_{avg}}{\nu \cdot m}$$ (40)

When analysing cyclic voltammograms (CVs), $i_{avg}$ is taken as the average of the absolute values of the anodic and cathodic current at the midpoint of the CV, $\nu$ is the scan rate and $m$ is the mass of FGSs on one electrode. $C_G$ was also estimated from galvanostatic discharge curves using the same equation with $\nu = (U - U_{drop})/\Delta t$, where $U = 3$ V is the initial potential, $U_{drop}$ is the voltage drop at the reversal of the scan
direction due to Ohmic losses and $\Delta t$ is the time needed to discharge the cell from 3 to 0 V at the discharging current $i_{avg}$. The equivalent series resistance was calculated as $R_s = U_{drop}/i_{avg}$.

5.3 Results and Discussion

5.3.1 Electrode consolidation

![XRD profiles for graphene oxide/EMImBF$_4$ composite films.](image)

Dispersions of graphene oxide in the water/ethanol mixture are stable, i.e., they show no sign of aggregation or sedimentation over several weeks. This is expected due to the high number density of carboxylic acids, phenolic hydroxyls and other functional groups present on graphene oxide which dissociate in water and charge-stabilize the suspended sheets.[79, 215] Adding EMImBF$_4$, however, causes a significant increase in suspension viscosity, indicating the formation of a graphene oxide/water gel network. Since EMImBF$_4$ is fully miscible with water, and since a similar gelation phenomenon is observed when adding other salts such as NaCl to the system instead of IL, we ascribe this behavior to screening of the charge on the graphene oxide (“salting out”) as a result
of the ionic strength increase, leading to subsequent partial aggregation of the graphene oxide by attractive van der Waals forces.[217] Drying these gels results in graphene oxide/IL composite films of typically 5 - 10 µm in thickness which exhibit different degrees of restacking and aggregation depending on EMImBF4 concentration in the initial gel. In Figure 5.3, we show XRD data obtained on composite films assembled with varying amounts of EMImBF4. The XRD profiles indicated that the characteristic spacing between the graphene oxide sheets varied with the amount of IL. In the absence of EMImBF4, we measured an XRD peak at 2θ ≈ 9.1° which indicated that restacking had occurred and domains with a d0002 spacing of 9.7 Å had formed. This spacing is similar to what has been reported for GO prepared using the same oxidation method employed here (9.5 Å).[71] The restacking of single sheets of graphene oxide into GO is in accordance with previous studies where suspensions of graphene oxide were dried or filtered.[218] We found that this restacking resulted in SSAs measured by N2 adsorption of less than 10 m2/g. With increasing EMImBF4 concentration, the XRD peak broadened, decreased in amplitude, and shifted to larger d-spacing indicating that EMImBF4 had disrupted the formation of GO domains and had increased the average distance between the sheets. Eventually, above 60 wt% EMImBF4, the films became X-ray amorphous. Hence, above 60 wt% the IL-filled inter-lamellar pores separating the graphene oxide sheets became too large to cause a significant signal in XRD. Additionally the arrangement of sheets may have become too disordered to be probed by XRD. As discussed in the introduction, in addition to IL in the inter-lamellar space, IL is also likely contained within larger inter-aggregate voids. Those can be generated at locations where the compressive strength of
the graphene oxide network exceeds the compressive forces generated by capillary
effects as the water component is removed by evaporation.[183, 219] These larger IL-
filled voids cannot be observed by XRD but are known to be present in all consolidated
powders and colloidal materials prior to annealing.[213, 219]

To obtain an order of magnitude estimate for the amount of EMImBF₄ required to
cover the theoretical surface area of graphene oxide (assuming no inter-aggregate voids
filled with IL are present), we used the molecular dimensions of the imidazolium cation
(7.8 Å × 5.8 Å × 3.3 Å)[220] to estimate the amount of IL necessary for monolayer
coverage. The exact orientation of the cation on the surface of graphene oxide is
unknown. Assuming that the IL molecule lies flat on graphene oxide (which is the least
favorable orientation for achieving high charge density) we approximated that about
70 wt% EMImBF₄ is required for a dense packing of IL on both sides of a sheet. This
results in two monolayers separating each graphene oxide sheet from the other, i.e., a
shared bilayer with an approximate thickness of 21–24 Å. A shared monolayer is
expected to form at half of this concentration (33-35 wt%). The fact that within this range
of IL concentrations we only observed a broad peak shifting to larger d-spacings and no
peak corresponding to shared monolayer coverage (shared bilayer spacing lies outside the
limits of our XRD unit) suggests that we did not achieve a uniform coverage and an
alignment of graphene oxide sheets in contrast to graphite and GO intercalation
compounds which form well-ordered crystalline structures.[72] Instead, we apparently
obtained a more random distribution of EMImBF₄ in between the sheets, giving rise to an
X-ray amorphous structure. Obtaining a uniform coating would require that the
EMImBF$_4$ completely wet the graphene oxide (vanishing contact angle).[221] The contact angle of EMImBF$_4$ on graphene oxide is unknown, but the fact that we observed neither a distinct peak in XRD nor a phase separation of IL and graphene oxide suggests that EMImBF$_4$ may only be partially wetting. As a consequence, the SSA of FGS$_2$ in direct contact with EMImBF$_4$ may have been reduced, and voids filled with either IL or air/argon may have formed within the films lowering their bulk density and CV. Enhancing wettability thus could lead to more uniform coverage and better packing efficiency and is a topic for future research.

Figure 5.4 The electronic charge accumulated by an EDLC electrode. $N_{\text{electronic}} = C_{\text{dl}} \cdot U/2$ assuming a symmetric electrode where each electrode traverses half the potential window.

The estimate for IL packing on graphene oxide is used in the following to illustrate how much IL is approximately required to charge the electrochemical double layer at high $U$. We calculated the electric charge stored for a given value of $C_{\text{dl}}$ and $U$ and estimated the number of accumulated elementary charges per nm$^2$ of electrode material ($N_{\text{electronic}}$) to be compared with the number of (monovalent) ions in a monolayer ($N_{\text{ionic}}$) in contact with one side of a graphene oxide sheet. In Figure 5.4 we compare several values of $N_{\text{electronic}}$ for realistic combinations of $C_{\text{dl}}$ and different potential windows to be compared to $N_{\text{ionic}} \approx 2.2 \text{ nm}^2$ which corresponds to a shared bilayer of cations lying flat.
between the sheets. The amount of energy stored is limited by the smaller of the two values, and the calculations indicate that with high values of $C_{dl}$ and large voltage windows, $N_{\text{electronic}}$ is similar to or even greater than $N_{\text{ionic}}$. Therefore, based on our estimations, an IL content resulting in coverage in the range from a monolayer to a shared bilayer is required to balance the electronic charge density in an EDLC operating at high voltage. While allowing for only a single shared layer of IL between each pair of graphene oxide sheets would decrease the device mass, it would also limit the maximum amount of charge that can be stored at the interface and furthermore limit the rate of charge transport in and out of the pore space between the sheets.
5.3.2 Thermal Reduction of Graphene Oxide/IL Composites

**Figure 5.5: Thermal analysis of neat materials and composite films.** (a) TGA/DSC of neat GO and EMImBF₄. (b) TGA/DSC of an electrode composite (FGS₂/EMImBF₄) prior to thermal reduction (c) C/O of thermally reduced FGSs estimated by EDS as a function of composite heat treatment temperature.

TGA/DSC was used to analyze the thermal stability of GO and neat EMImBF₄ (Figure 5.5a). Near 200 °C, an exothermic mass loss indicative of thermal decomposition and reduction of GO[64, 65] was observed while all of the EMImBF₄ mass was lost around 500 °C in an endothermic decomposition process. We also used TGA/DSC to characterize the FGS₂/IL composites as shown in Figure 5.5(b). Near 100 °C, an endothermic mass loss associated with the removal of residual water from the films was observed. The exothermic reduction of graphene oxide to FGSs was observed between
200 and 300 °C,[64, 65] and an endothermic mass loss at higher temperatures, between 350 °C and 500 °C, was associated with the decomposition of EMImBF₄. A fraction of the mass loss (approximately 5 wt%) in this temperature range is expected to be associated with further reduction of the FGSs as suggested by the TGA results for GO reduction shown in Figure 5.5(a). Compared to the TGA data of the neat materials, the graphene oxide reduction peak is broadened and shifted to higher temperatures. Mass loss and an endothermic peak corresponding to EMImBF₄ decomposition were observed at lower temperatures, shifting from approximately 500 to 350 °C as the amount of graphene oxide in the film was increased from 0 to about 70 wt%. Although many studies claim that ILs such as EMImBF₄ are stable at temperatures above 400 °C, it is now recognized that this apparent stability may be due to heat transfer limitations during fast heating ramps of 10 to 20 °C/min.[222] The high thermal conductivity of FGSs[223] as well as their high optical absorbance[93] compared to the neat IL likely increase the rate of diffusive and radiative heat transfer to the EMImBF₄, thus lowering the apparent decomposition temperature. Also, we cannot rule out the possibility that FGSs may catalyze the decomposition of the IL. The difference in temperature between thermal reduction of graphene oxide and EMImBF₄ decomposition results in the existence a temperature window within which graphene oxide can be thermally reduced without significantly decomposing the EMImBF₄.

The heat treatment of composite films resulted in a drastic colour change from an amber-yellow to black at reduction temperatures above 250 °C. This increase in optical absorbance of the films is the consequence of increased electrical conductivity of the
initially insulating material and the increasing number of conjugated and aromatic carbon structures forming within the material during thermal reduction.\textsuperscript{[93]} The C/O of FGS as determined by EDS ranged from 2 for the untreated material containing graphene oxide to just above 5 for heat treatments up to 340 °C as shown in Figure 5.5(c). The analysis also indicated that the N/F ratio deviated from the stoichiometric value of 4:1 when temperatures above 270 °C were reached. This deviation suggests that decomposition begins above 270 °C, changing the chemical nature of the IL. The slight degree of decomposition was also reflected in the mass loss of the samples during heat treatment and was consistent with the EMImBF\textsubscript{4} content measured by TGA.
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5.3.3 Electrochemical Characterization

Figure 5.6: Electrochemical characterization of films heat treated at 270 °C. (a) CVs carried out at various scan rates for composite electrodes containing 78 wt% EMImBF$_4$. (b) Capacitance of composite films assembled with varying amounts of EMImBF$_4$ estimated by cyclic voltammetry (scan rate 5 mV/s) and galvanostatic discharge (at 0.2 A/g) in a 3 V potential window. (c) Scan rate dependence of the capacitance for varying EMImBF$_4$ content.

CVs for an electrode with 78 wt% EMImBF$_4$ are shown in Figure 5.6(a) for a series of scan rates between 10 and 100 mV/s. The CVs are all approximately rectangular in shape and display a similar $C_G$ suggesting that capacitive charging is strictly non-Faradaic, as expected for electrodes operated in an aprotic electrolyte. In Figure 5.6(b),
the $C_G$ values estimated at 5 mV/s by cyclic voltammetry and at 0.2 A/g by galvanostatic discharge are shown for different IL contents. Values < 10 F/g were obtained when films were cast in the absence of EMImBF$_4$. $C_G$ increased with increasing EMImBF$_4$ content until above 60 wt% where $C_G$ reached saturation at an average value of 136 ± 10 F/g. The relatively constant value of $C_G$ above 60 wt% indicates that the ion-accessible SSA did not increase further as more EMImBF$_4$ was added. This suggests that additional IL (above 60 wt%) instead increases the average thickness of the IL-filled regions (i.e., inter-lamellar pores and inter-aggregate pores) between the sheets. This increase in effective pore size with increased IL loading was also observed in XRD as an increase of the d-spacing, as discussed earlier.

When we compared electrodes containing varying levels of EMImBF$_4$ above 60 wt% which were all thermally reduced at 270 °C, we found a significant difference in the scan rate-dependence of $C_G$. Figure 5.6(c) demonstrates that nanocomposite electrodes which contained more EMImBF$_4$ better retained their capacitance at high scan rates. At the highest IL content investigated (80 wt%), $C_G$ decreased by only 15% when increasing the scan rate from 5 to 100 mV/s. The same trend as that shown in Figure 5.6(c) was also observed in galvanostatic discharge testing at various current densities. As shown in Figure 5.7(a), the corresponding values of $R_s$ decreased from 100 to 30 Ω when the IL content was varied between 45 and 80 wt% which was expected based on the trends observed for the rate performance. These results suggest that we changed the ionic conductivity of the FGS/IL composite network which corresponds well to the hypothesised increase in the size of inter-lamellar pores filled with EMImBF$_4$ as the IL
content was increased. It is also likely that the amount of IL in the inter-aggregate voids increased which is also expected to improve the ionic conductivity. The fact that we did not observe a decrease in rate performance or increase in $R_S$ with increasing IL content indicates that, at least for the IL contents studied, electrical contact between the graphene sheets was not significantly affected by the increased IL loading and any loss in electrical conductivity was over-compensated by the improvement in ionic transport. This view is also supported by the fact that we did not observe a significant change in $C_G$ at higher loadings as would be expected if FGS-FGS contact area was lost and more ion-accessible surface area was created. As discussed above, the graphene oxide aggregated and gelled upon addition of EMImBF$_4$ to the suspension, which suggests that the FGSs formed regions for electrical contact prior to densification and the IL did not effectively separate the sheets at these points during solvent evaporation and further processing.

To determine how the degree of reduction affected the performance of our electrodes, we reduced several nanocomposite electrodes containing 75 wt% EMImBF$_4$ (prior to heat treatment) at various temperatures. We found that electrodes were not sufficiently conductive when reduced below 250 °C, and as a consequence $C_G$ was low ($< 10$ F/g). When test cells containing these poorly reduced FGSs were disassembled, the cathode was found to be darker than the anode, indicating that it had been electrochemically reduced during testing. The anode could be brought to a similar state by reversing the polarity of the device and employing it as the cathode in a subsequent measurement. However, $C_G$ was only increased to less than 60 F/g using this procedure. Thus, the electrochemical reduction in EMImBF$_4$ is not sufficient to achieve the necessary level of
electric conductivity. At a low scan rate (5 mV/s), $C_G$ of electrodes reduced at temperatures above 250 °C did not significantly vary with reduction temperature. With increased scan rate, however, differences between electrodes treated at different temperatures became apparent, indicating that, besides ionic transport, electrode conductivity is a performance-limiting factor in our system.

**Figure 5.7: Effect of temperature and IL content on the electrode resistance.** (a) $R_S$ estimated from the voltage drop in galvanostatic discharge after charging to 3 V for films treated at various reduction temperatures. The initial IL content in all films was 75 wt% and the final IL content is indicated under the data points. (b) $R_S$ estimated from the voltage drop in galvanostatic discharge carried out at 3 V for films assembled with varying amounts of EMImBF$_4$. (c) EIS measurements at a DC bias of 0 V for electrodes heat treated at two different temperatures. (d) Magnified view of the high frequency region of the Nyquist plot shown in (c). (e) Scan rate dependence of the capacitance of an electrode with 86 wt% EMImBF$_4$ heat treated at 300 °C.

We therefore examined the effect of heat treatment on $R_S$ of electrodes with the same initial content of 75 wt% EMImBF$_4$ (Figure 5.7(a)). $R_S$ dropped from 33 to 10 Ω as the
reduction temperature was increased from 270 to 340 °C. As indicated in Figure 5.7(a), the decrease in $R_s$ with increasing reduction temperature was accompanied by a loss of IL from the films. The fact that a loss of IL did not increase the resistance suggests that, in this case, our system was mainly limited by electronic transport. The change in electrode resistance was also apparent in the Nyquist plots of impedance spectra shown in Figure 5.7(c,d). Films reduced at 270 °C exhibited a Warburg-like 45° constant phase impedance in the mid-frequency range, typically associated with diffusive transport limitations in porous electrodes,[12] while the diffusion limitations were lessened in electrodes reduced at 340 °C. However, as mentioned above, the high-temperature heat treatment was accompanied by a significant loss of IL, and we therefore had expected the constant phase behavior to extend to lower frequencies (increased diffusive limitation) compared to the result obtained with lower reduction temperature. Since the opposite was observed, in our case the Warburg-like behavior may be predominantly due to electronic transport effects within the FGS network which, at this low degree of thermal reduction, may dominate over ionic diffusion effects. A similar phenomenon is observed in the impedance spectra measured for semiconductors such as TiO$_2$ used in dye-sensitized solar cells[224] and at the lowest C/O tested, our reduced graphene oxide may exhibit semiconducting behavior.[225, 226]

When high reduction temperatures are applied to the electrodes with the largest IL content, it is possible to achieve nearly constant $C_G$ over a wide range of scan rates. As shown in Figure 5.7(e), films thermally treated at 300 °C and containing 86 wt% EMImBF$_4$ retained more than 90 % of their capacitance (143 F/g) at scan rates up to
500 mV/s. This value of $C_G$ is one of the highest reported at such a high rate for electrodes using an IL as the electrolyte. For example, in a recent study[161] carried out with electrodes of similar thickness (7 - 30 µm) it has been demonstrated that activated graphene retains only 72 % of the electrode’s capacitance (120 F/g) at 400 mV/s despite the use of a higher-conductivity organic electrolyte. Adjusting the scan rate dependence and $R_S$ by tuning the IL content could thus provide a convenient means for preparing electrodes for special high power applications.

To properly compare our results to other FGS/IL data reported in the literature, we must consider the mass of both the FGSs and the IL as explained above. Our approach provides direct control over the fraction of each component in our electrodes, and in the thick electrode limit we only need to subtract the IL content from 100% to obtain the weight fraction $f$. Already at relatively low IL content of 60 wt% ($f = 40$ wt%) we achieve values of $C_G$ up to 140 F/g, and according to Eq. (38) therefore reach energy densities up to $E = 17.5$ Wh/kg at only 3 V operating voltage. Compared to values of $E$ from the literature (Table 3) which range from 5 to 13.8 Wh/kg for FGS-based electrodes and which have been obtained with $U > 3$ V, our approach thus yields significantly increased energy density. Preliminary tests have shown that we can operate our electrodes at $U = 3.5$ V, which for our best electrodes increases $E$ up to about 24 Wh/kg. We have achieved these values with thin film electrodes, similar to the other studies discussed in Table 3.[109, 114, 115] We therefore need to investigate whether the improved performance obtained with our consolidation approach can be maintained as we develop our process further and increase electrode thickness.
From our data we can also estimate the volumetric capacitance $C_V$ (in F/cm³) and $\rho_{\text{eff}}$, for the 60 wt% IL case using their pure component densities (IL: $\rho_i = 1.3$ g/cm³, FGSs: $\rho_a = 2.2$ g/cm³). If we assume the absence of gas-filled voids in the material we obtain $C_V \approx 93$ F/cm³ and $\rho_{\text{eff}} \approx 0.66$ g/cm³. However, since this estimate represents an upper limit for $C_V$, we also determined the volume of our electrodes by measuring their approximate thickness and diameter. These measurements indicate that we achieve only approximately 70% of the theoretically estimated bulk density (~0.46 g/cm³), leading to an estimated $C_V$ of 65 F/cm³ which is still the highest reported for an FGS-based electrode in an IL.

### 5.4 Conclusions

We have demonstrated a new strategy for the preparation of high-performance graphene-based electrodes for EDLCs with IL electrolytes. Instead of engineering a porous electrode structure and imbibing electrolyte or applying solvent exchange techniques, we employ an approach which results in the IL acting both as electrolyte and spacer preventing re-aggregation of the electrode material. Composites assembled with increasing amounts of IL increase the ion-accessible surface area of the electrodes and improve the performance of the EDLC electrodes at high scan rates by effecting changes in the pore structure of the electrode composite. The mass-specific capacitance of the electrodes reaches values as high as 140 F/g at an effective electrode density of $\rho_{\text{eff}} \approx 0.46$ g/cm³ (60 wt% IL) resulting in high energy density (17.5 Wh/kg at 3 V) and volumetric capacitance (65 F/cm³). At a higher IL content of 80 wt%, i.e., at lower
electrode density, our electrodes retain over 90% of their maximum capacitance at scan rates up to 500 mV/s. This constitutes the best capacitance retention at high rates reported for thin film carbonaceous electrodes operated in an IL.

Several steps in this approach need to be further improved before our results can be extended to predict the performance of a packaged device. Our current drop-casting approach yields thin film electrodes, and it is known that in many cases electrode performance decreases with increasing thickness.[8] Furthermore, the rate capabilities improve significantly with increasing IL content but this increase negatively affects $C_v$. Although our approach is promising, we believe there is room for improvement which will be facilitated by a deeper understanding of the interactions between various types of FGSs and ILs and their aggregation behavior to both improve the ion-accessible SSA while maximizing ionic transport within the composite matrix. Electronic transport could be improved by developing better reduction strategies which increase the C/O ratio without decomposing the IL, or, alternatively, by extending our electrode assembly approach to FGSs that have been thermally or chemically reduced to a higher C/O ratio prior to dispersion and assembly.
6 Conclusions and Future Work

6.1 Summary of Main Conclusions

The work presented in this thesis has contributed to the development and understanding of electrochemical double-layer capacitors based on functionalized graphene sheets. The two main factors, the intrinsic double-layer capacitance and ion-accessible surface area, which dictate device capacitance, were studied to determine the various processing/structure/function relationships.

Using a system of densely tiled monolayer electrodes of functionalized graphene I demonstrated that their intrinsic double-layer capacitance is not constant but can change significantly depending on the thermal treatment used to reduce graphene oxide to an electrically conducting state. Materials with properties approaching those of a pristine graphene were found to have a low capacitance, while sufficiently defective and functionalized graphene was found to exhibit a double-layer capacitance 3 to 4 × higher, approaching the electrolyte or Helmholtz limit. This work suggests that graphene-based materials or carbonaceous electrode materials in general should be chosen carefully such that they can achieve both high double-layer capacitance and high specific surface areas. The model system developed provides a means of experimentally assessing the intrinsic capacitance of nearly any type of graphene material and will be a key tool in optimizing the structure of functionalized graphene to achieve the maximum specific capacitance.
The specific surface area of graphene-based electrodes was found to vary significantly depending on the processing path. The main factors found to affect the surface area of functionalized graphene aggregates were the final bulk density of the aggregated material, aggregation kinetics and the morphology (wrinkled or flat) of single sheets. These sensitivities stem from the low bending rigidity of a single graphene sheet which causes functionalized graphene within an aggregate to be significantly deformed by forces exerted on the sheets during processing such as capillary forces and van der Waals forces. Because of this, functionalized graphene can bend into contact upon densification which reduces the ion-accessible surface area to a small fraction of the theoretically available surface area.

In order to prevent functionalized graphene from restacking during electrode consolidation, a new electrode fabrication strategy was developed. Instead of preparing an electrode with a pre-defined pore structure and surface area and imbibing the electrolyte into this material, I developed a method to co-assemble the electrode and electrolyte in the same process. In this way, the electrolyte (a non-volatile ionic liquid) can act as a physical spacer which prevents the sheets from restacking. This approach leads to electrochemical double-layer capacitors with vastly improved performance over controls where the electrolyte is imbibed into an aggregated electrode. In addition, such an approach eliminates the process of imbibing the electrolyte during electrode fabrication which will lead to improved manufacturing and the potential to reduce device costs.
6.2 Future Directions

6.2.1 Improving the Electrode Assembly Strategy

The strategy of using an IL as a spacer to prevent aggregation and restacking of functionalized graphene is a promising route to improving the specific capacitance of graphene-based electrodes. With the approach presented in Chapter 5 we were only able to achieve capacitances of 140-160 F/g. Although this is relatively high, our intrinsic capacitance measurements indicate that we should be able to reach capacitances exceeding 400 F/g, suggesting that we are still only accessing a small fraction of the theoretically available surface area. To improve this further I would like to develop a better understanding of the interactions between FGSs and ILs in various solvent systems. The system presented in Chapter 5 which used FGS2/water/EMImBF4 resulted in an FGS2 gel, which likely reduced the IL accessible surface area and evaporative drying likely resulted in an inhomogeneous distribution of IL within the composite. Ideally, we would like to controllably coat the FGSs in suspension with approximately a monolayer of IL which we would then consolidate into the final nanocomposite electrode. There are several strategies that I would like to pursue to more closely approach this ideal case. This will further improve the ion-accessible surface area and distribution of ionic-liquid in the final nanocomposite:

1) Probing adsorption of ILs onto FGSs in suspension – Some ILs specifically adsorb on carbon nanotubes (CNT) through interactions known as cation-Π interactions.[227, 228] It is possible that ILs may adsorb onto FGSs (which resemble defective, unraveled CNTs) in suspension. For cases where adsorption
is observed, we will take advantage of this phenomenon to both disperse the FGSs and control the amount of amount of IL which accumulates on the FGS surface prior to aggregation and densification into an electrode.

2) *Precipitation/emulsification routes* - ILs are classified as being hydrophilic or hydrophobic. Hydrophilic ILs can be completely miscible with water or partially miscible depending on the size of the hydrocarbon chains tethered to their respective ions while hydrophobic ones are immiscible with water but typically miscible with alcohols and other polar organic solvents. I propose to explore the formation of a new type of Pickering emulsion where the IL is stabilized in solvent by adsorbing to FGSs.

3) *Improved drying methods* – Even in the absence of any specific interactions between the FGSs and the IL, mixing of the FGS and IL may be improved by employing controlled drying techniques. Spray drying can be used to confine the assembly strategy to micron-sized drops containing FGSs and IL. The rate of drying can be controlled by the temperature of the inlet feed and the spray dryer outlet temperature which may allow us to tune aggregation kinetics and more evenly disperse the FGSs within the IL phase.

### 6.2.2 Tuning the Structure of Functionalized Graphene

In this thesis work I was only able to study a small subset of the possible functionalized graphene structures to determine the effect on the double-layer capacitance. There is an infinite parameter space of thermal reduction temperatures, times and starting material structures which likely dictate the final structure and function of FGSs as EDLC...
electrodes, as well as in other applications. One future direction would be to provide a course map of the structural and chemical evolution of FGSs over a large range of this parameter space. Experimentally, this would involve the production of various types of graphite oxide which exhibit a range of C/O. Since the initial ratio of epoxides/hydroxides are thought to be important in the structural evolution of FGSs during thermal reduction,[94] it would be informative to determine various oxidation techniques and times to generate materials with a range of epoxides/hydroxides and global C/O. These materials would then be thermally exfoliated at various temperatures and times and characterized to determine the type and number of functional groups remaining. Techniques such as Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, coupled with elemental analysis would be used for this. The defect structure of the final materials could be observed directly using high resolution, aberration corrected, transmission electron microscopy and coupled with techniques like Raman spectroscopy (UV and visible) and electron energy loss spectroscopy (EELS) which are capable of determining changes in the sp² carbon phase. This information would provide the criteria necessary for the rational design of FGS-based materials.
References


