THE FUNCTIONALIZED GRAPHENE-IONIC LIQUID INTERFACE
FOR ELECTROCHEMICAL DOUBLE-LAYER CAPACITORS

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To Mom, Dad, Chris and Matt with love.
Abstract

Functionalized graphene sheets (FGSs) are promising electrode materials for energy-dense electrochemical double-layer capacitors (EDLCs) as they can exhibit high electrical conductivity, specific surface area and intrinsic capacitance. However, engineering electrodes that capitalize on these attributes is challenging as FGSs tend to re-stack during processing, reducing the surface area available for capacitive energy storage. Furthermore, though room temperature ionic liquids (RTILs) have been introduced as next-generation electrolytes for EDLCs, a fundamental understanding of the capacitance of the FGS-electrolyte interface for concentrated electrolytes is lacking. This dissertation aims to develop approaches to produce energy-dense, FGS-based EDLC electrodes and elucidate the fundamental behavior of the electrochemical double-layer of the FGS-electrolyte interface.

A simple “bottom-up” approach was developed to evaporatively consolidate mixtures of graphene oxide, alcohols, and RTILs, producing thin-film electrodes having an energy density as high as 6.3 Wh/kg at 3.0 V, based on the total mass of the electrode. To improve the energy density, dehydrated sucrose nanoparticles (0.5-2.5 nm) were added to serve as inter-sheet spacers. Liquid-cell atomic force microscopy revealed that these nanoparticles adsorb onto graphene oxide in an aqueous environment, providing a physical barrier to inter-sheet collapse due to van der Waals and capillary forces during solvent evaporation. Thin film electrodes were prepared having a gravimetric capacitance as high as 330 F/g_{FGS} and, by tuning the nanoparticle and RTIL contents, an energy density of 13.3 Wh/kg was achieved. This energy density is the highest reported to date for an FGS-based electrode with a solid spacer.
Lastly, electrochemical impedance spectroscopy was used to measure the effect of diluting an RTIL with miscible organic solvents on the intrinsic capacitance of the glassy carbon-electrolyte interface. Diluting 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide with organic solvents revealed a maximum in the minimum differential capacitance near 5-10 mol% RTIL that was not predicted by classical electrochemical double-layer theory. Additionally, diluting with a low-dielectric constant solvent, 1,2-dichloroethane, resulted in the largest increases in capacitance near the open circuit potential, compared to acetonitrile and propylene carbonate. These results provide insight into the electrochemical double-layer for concentrated electrolytes and reveal the potential for the enhancement of double-layer capacitance through dilution.
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<th>Description</th>
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<tr>
<td>ATR</td>
<td>Attenuated total reflectance</td>
</tr>
<tr>
<td>DS</td>
<td>Dehydrated sucrose</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>EDL</td>
<td>Electrochemical double-layer</td>
</tr>
<tr>
<td>EDLC</td>
<td>Electrochemical double-layer capacitor</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>EMImBF$_4$</td>
<td>1-ethyl-3-methylimidazolium tetrafluoroborate</td>
</tr>
<tr>
<td>EMImTFSI</td>
<td>1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonylimide)</td>
</tr>
<tr>
<td>ESR</td>
<td>Equivalent series resistance</td>
</tr>
<tr>
<td>FGS</td>
<td>Functionalized graphene sheet</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>GO</td>
<td>Graphite oxide</td>
</tr>
<tr>
<td>LC-AFM</td>
<td>Liquid cell atomic force microscopy</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>RTIL</td>
<td>Room temperature ionic liquid</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Tunneling electron microscopy</td>
</tr>
<tr>
<td>TEOS</td>
<td>Tetraethylorthosilicate</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermal gravimetric analysis</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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1 Introduction

This chapter provides an overview of EDLCs including functionalized graphene materials and ionic liquids.

1.1 Electrochemical Double-Layer Capacitors

EDLCs, also known as supercapacitors or ultracapacitors, are devices that store energy through the accumulation of ionic and electronic charges at the interface between an electrolyte and a high surface area electronic conductor.\textsuperscript{1} The device is aptly named after this layering of ionic and electronic charges, well known in colloidal science as the electrochemical double-layer. The energy storage mechanism in EDLCs is distinctly different from that of batteries as EDLCs utilize physical interactions, namely electrostatic attraction, rather than chemical reactions to store energy.\textsuperscript{1-3} This key difference has garnered several advantages for EDLCs over battery technologies.\textsuperscript{4} As the energy storage mechanism relies on the restructuring of the double-layer, EDLCs can be charged and discharged very quickly, unlike batteries, which are often limited by the slow charge-transfer and mass-transfer kinetics involved in redox chemistry. Additionally, the absence of chemical reactions limits the mechanical stresses experienced within the device and, in turn, EDLCs have cycle lives much greater than batteries as they can be charged and discharged hundreds of thousands of times.\textsuperscript{5} Despite these advantages, the widespread
adoption of EDLC technology has been limited as they store much less energy than batteries—currently two orders of magnitude less, as shown in Figure 1.1.\textsuperscript{5-7} Therefore, much opportunity exists in improving the performance of EDLCs such that they can contribute more significantly to the electrochemical energy storage landscape.\textsuperscript{8}

The fast energy storage capability and reliability of EDLCs have enabled uses in high power applications such as low-temperature motor vehicle start-up, crane and lifting operations, regenerative braking, start-and-stop applications and wind turbine pitch control.\textsuperscript{8-9} China has recently unveiled wireless tram cars in the city of Guangzhou which are exclusively powered by EDLCs, which quickly charge while the tram car is stopped.\textsuperscript{10} Currently, there is particular interest in combining the attributes of EDLCs and batteries to develop a hybrid device that capitalizes on the unique features of both technologies. Such a hybrid device, holds much promise in the burgeoning market of electric vehicles as EDLCs could be used to quickly capture otherwise lost energy through regenerative braking and slowly discharge it to the battery at a rate which the battery can accommodate,
thereby increasing energy efficiency. The EDLC would also be used heavily in accelerating the vehicle to cut down on the high rate demands of the battery as these performance requirements often shorten the life of the battery. In this configuration, EDLCs would effectively function to increase the lifespan of batteries.

Efforts to increase the energy density of EDLCs without sacrificing their high rate performance will enable EDLCs to have a larger role in the electrochemical energy storage market. The aim of this thesis is to explore processing strategies for advanced EDLC materials to better understand the basic charge storage mechanisms of EDLCs and work toward designing electrodes with high energy density. The following sections provide background information regarding the device’s architecture and operation with a particular focus on state-of-the-art materials and electrolytes for next-generation EDLCs.

1.2 Architecture and Operating Principles

1.2.1 Device Architecture

In 1957, while researching materials for battery electrodes, H. I. Becker of General Electric observed that when a potential was applied between two porous carbonaceous electrodes submerged in a bath of electrolytes, the electrodes displayed a relatively large capacitance. The patent which he later filed on the invention detailed the basic components of an EDLC, which still serve as essential components for commercial devices today. Figure 1.2 shows a schematic for a typical EDLC. The device consists of two
metallic current collectors onto which a layer of conductive, porous carbon material is applied. These two electrodes are positioned to face one another and are separated by an electrically insulating membrane, aptly named the separator. The porous carbon material is infiltrated with an electrolyte solution, typically consisting of a solvent and a dissolved salt. When a potential is applied between the electrodes, the electrons move through the electrical circuit from one electrode to the other. The negative electrode is that toward which the electrons move, while the positive electrode is that where holes reside. As the separator provides an electrical barrier between the electrodes, the electronic charges are unable to complete the circuit and charges accumulate on each electrode. To balance the charge which develops on each electrode, the ions in the electrolyte partition and gather at the surface of each: cations accumulate at the surface of the negative electrode, while anions gather at the positive electrode.
As a result, an electrochemical double-layer develops at each electrode. Since an EDLC consists of two double-layers (one at the anode and the other at the cathode), the device is typically modeled as two capacitors connected in series, as shown by the electrical circuit in Figure 1.2. This fact is often overlooked in the literature as EDLCs are frequently treated as a single capacitor instead of a serial connection of two. This has important device-level implications as the capacitance of a device for a symmetric EDLC (i.e., a device in which the positive and negative electrodes are identical) is one-half the capacitance of a single electrode. This is a direct result of the fact that the equivalent capacitance $C_{eq}$ of two capacitors with capacitances $C_1$ and $C_2$ in series obeys reciprocal addition, shown as:

$$\frac{1}{C_{eq}} = \frac{1}{C_1} + \frac{1}{C_2}$$

(1.1)

Therefore, it is critical to explicitly state which capacitance is being reported. It has become common practice to report the capacitance of a single electrode normalized by the mass of the active solids in the electrode; the active solids typically refer to the conductive, porous carbon, which serves as the electronic conductor. This capacitance is referred to as the gravimetric capacitance ($C_G$) and is reported in units of F/g.

### 1.2.2 Performance Metrics

An electrochemical energy storage device, such as an EDLC or a battery, is evaluated based on two predominant performance metrics: energy density and power density. Energy density refers to the quantity of energy that is stored in a device per unit mass of the device. Power density describes how quickly the energy can be moved into and out of the device, also per unit mass. (I note that the word “density” typically refers to a quantity on per
volume basis, and, correspondingly some works do use “energy density” and “power density” on a per volume basis and prefer to use “specific energy” and “specific power” for values on a per mass basis.\textsuperscript{4} Here, density represents a per mass basis and any references to quantities on a per volume basis will be preceded with the descriptor, “volumetric.”) Though these metrics are often reported separately, they are intimately linked. As discussed in the following sections, electrode design often comes with unavoidable trade-offs between the maximum energy and power density of a device.

\subsection*{1.2.2.1 Energy Density}

As mentioned, the energy stored in an EDLC is modeled as two capacitors in series. The energy of a single parallel-plate capacitor is calculated from the work $W$ needed to move a total charge $Q$ against the voltage $U$ established by the electric field between the plates. This is mathematically represented as:

$$dW = U \, dq = \frac{q}{C} \, dq$$ \hspace{1cm} (1.2)

$$W = \int_{0}^{Q} \frac{q}{C} \, dq = \frac{Q^2}{2C} = \frac{1}{2}CU^2$$ \hspace{1cm} (1.3)

where $q$ is the charge and $C$ is the capacitance. Using the basic relationship in Equation 1.3, once can derive an expression for the energy density of two capacitors in series (provided in the Appendix). The result of the derivation is reproduced here as

$$E = \frac{f}{8}C_{g}U^2$$ \hspace{1cm} (1.4)

where $C_{g}$ is the gravimetric capacitance, $U$ is the operating voltage of the device and $f$ is the mass fraction of active electrode material in the device.\textsuperscript{13} I note that Equation 1.4 is
valid in the limit of infinitely thin electrodes, and that the thickness of the electrode will introduce additional factors which affect the electrode’s energy density. As a result, this equation can be viewed as a means to measure the electrode’s maximum energy density. As can be seen, the energy density of an EDLC is most affected by the operating voltage, as Equation 1.4 features a quadratic dependence with respect to that variable. The operating voltage is determined by the electrochemical breakdown and decomposition of the device’s components and is typically limited by the stability of the electrolyte. Early EDLCs employed aqueous electrolytes, and, thus, the operating voltage window was limited to ~1.2 V due to the electrolysis of water to hydrogen and oxygen gas. Most commercial devices today employ an organic electrolyte, which consists of an ammonium-based salt dissolved in a suitable organic solvent. The elimination of water allows the device to be operated at higher voltages, between 2.5 and 3 V, and significantly increases the energy density of the device. As will be discussed in subsequent sections, new electrolytes are being introduced with electrochemical stability greater than 4 V.14

As previously mentioned $C_G$ is the gravimetric capacitance of a single electrode normalized by the mass of the active solids contained in that electrode. The $C_G$ of the device can be further broken down into three parameters shown below:

$$C_G = C_{DL} \cdot SSA \cdot x_{IA}$$  \hspace{1cm} (1.5)

where $C_{DL}$ is the areal capacitance of the active material, often referred to as the intrinsic capacitance,15 SSA is the specific surface area of the active material and $x_{IA}$ is the fraction of the specific surface area which is ion-accessible. Essentially, Equation 1.5 shows that, the $C_G$ of the electrode depends upon how much surface area is available for charge storage
(SSA), how efficient that surface is at storing charge \((C_{DL})\) and, practically, how much of that surface area can physically accommodate the ions \((\chi_L)\). Though this decomposition of \(C_G\) into constituent parameters can be useful in analyzing EDLCs, we note that deviations from this prediction are expected as the pore size of the electrode material approaches the sizes of the ions in the electrolyte.\(^{16}\)

Lastly, \(f\) is included in Equation 1.4 as an engineering approximation to keep the reporting of energy density honest by accounting for the “dead-weight” present in the electrode.\(^{13,17}\) Though \(C_G\) is determined based on the weight of the active material in the electrode, the weight of the active material only accounts for a fraction of the device’s total mass. Other components such as binders, conductive additives and the electrolyte itself contribute to the total mass of the electrode and for practical purposes these components should be included when reporting the energy density of the electrode. I note that Equation 1.4 is meant to gauge the energy density of the electrode. One should keep in mind that the energy density of the total device will be still lower than the value calculated in Equation 1.4 as one must account for the mass of the device’s packaging, current collectors and separator in addition to the losses captured in \(f.\)\(^{18}\)

### 1.2.2.2 Power Density

Commercial applications of EDLCs have exploited the technology’s superior power density as compared to that of batteries. The power output of the device is governed by the resistance in the cell, known as the equivalent series resistance \((ESR)\). The \(ESR\) is dependent upon intrinsic material properties, such as ionic and electronic conductivity, as well as the architecture of the electrode itself \((i.e.,\) how the electrode is specifically
structured).\textsuperscript{1} The specific mathematical treatment of power density is complicated as it is dependent upon the time scale of the charging or discharging event due to the distributed nature of the \textit{ESR}. However, assuming that the EDLC can be modeled as a simple RC circuit, the maximum power density ($P_{\text{max}}$) of the device can be estimated from the voltage at maximum power ($U_{\text{max}}$) and the \textit{ESR} as

$$P_{\text{max}} = \frac{U_{\text{max}}^2}{4 \cdot \text{ESR}} \quad (1.6)$$

Typically, $P_{\text{max}}$ is normalized by mass and plotted versus the energy density of the device, a representation used to compare performance characteristics of different devices, known as a Ragone Plot (an example is shown in Figure 1.1). Though Ragone Plots are useful in obtaining a general sense of the layout of the electrochemical energy storage landscape, they often do not provide complete information about the performance of devices. For example, Simon \textit{et al.} showed that the thickness of the layer of active material, a metric which is often not reported in the literature, can significantly affect the shape and position of the Ragone curve.\textsuperscript{18} However, despite its shortcomings, the Ragone plot does capture the important trade-off inherent to EDLC electrode design: the inevitable competition between high energy and power density.

\subsection*{1.2.2.3 Energy and Power Trade-off in Electrode Design}

The ultimate goal of EDLC research is to create a device with maximum energy and power density; however, the design criteria which govern each of these performance metrics are diametrically opposed. Thus, given a set of materials (active material and an electrolyte) there exist configurations which maximize energy density, and others which
maximize power density. For example, imagine a hypothetical high specific surface area active material with an adjustable pore space. To achieve maximum energy density one could envision a structure in which the pore size is on the order of the size of the electrolyte ions. In a given volume, the amount of surface area of the active material will be maximized and the amount of electrolyte needed (i.e., electrolyte essentially serves as “dead-weight” in Equation 1.4) will be minimized and, therefore, we might expect the highest energy density. However, this electrode would suffer from a low power density as ionic transport will be greatly impeded by the extremely small pores. By engineering larger pores into the electrode, one might improve the power density, but it would come at the cost of decreasing
the energy density as the amount, and therefore, weight of the electrode will increase, primarily as a result of the extra electrolyte. Thus, engineering the pore space of an EDLC is critical in managing both the energy and power density of the device. This fundamental trade-off is highlighted in Figure 1.3 along with additional practical design considerations which can have a significant impact on device performance, such as low specific surface area materials, ion-inaccessible pores, void spaces which prevent electrolyte percolation, and high electronic contact resistance.

1.3 The Electrochemical Double-Layer

An overview of the history and current understanding of the theory of the electrochemical double-layer is provided in this section.

1.3.1 The Gouy-Chapman-Stern Treatment

As mentioned in Section 1.1, the electrochemical double-layer in essence consists of two layers of charges with opposing polarity separated by a small distance. This simple model was used by Helmholtz in the mid-1800s to describe the interface of colloidal particles in aqueous suspension. Colloidal particles presented a surface charge due to the ionization of acidic or basic groups attached to their surface, while the aqueous environment provided counter-ions to balance the net charge on the particle. These two layers of charge, one on the surface of the particle and the other a shell of ions in solution, comprised Helmholtz’s double-layer, shown in Figure 1.4(a). This concept of a double-layer was extended from colloidal science to other charged surfaces, namely a metallic electrode which is polarized by the application of a potential. This configuration is more
relevant in translating the concept of the electrochemical double-layer to the measurement of capacitance for energy storage devices.

Though a seminal contribution at the time, Helmholtz’s model did not account for entropic considerations as thermal fluctuations would prevent this perfect bi-layering of charges from occurring. Gouy introduced the concept of thermal fluctuations to the model of the double-layer, which he portrayed as a three-dimensional diffuse distribution of anions and cations, shown in Figure 1.4(b).\textsuperscript{20} This diffuse ionic cloud possessed a net charge equal and opposite to the charge at the surface of the electrode. However, the model did not accurately describe experimental results at the time as it contained an intrinsic flaw. Gouy’s model assumed that the ionic charges, which were realistically confined in physical ions, could be treated as point-charges. By neglecting the finite size of the ion, the capacitance of the electrode-electrolyte interface was grossly overestimated at high potentials as there were no physical limitations governing the extent to which ionic charge could accumulate at the interface. Though Chapman further addressed Gouy’s model by providing a more rigorous mathematical interpretation, the problem of overestimating the capacitance was not solved until the early 1920s when Stern reintroduced Helmholtz’s

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.4.png}
\caption{Models of the electrochemical double-layer. (a) Helmholtz layer, (b) Gouy’s diffuse double-layer, (c) Stern’s combination of Helmholtz and diffuse layers. Figure from Conway, B. E. \textit{Electrochemical Supercapacitors}, 1999.}
\end{figure}
model to Gouy’s “diffuse” model of the double-layer.\textsuperscript{21-22} Stern postulated that the inner region of the electrolyte, the ionic layer closest to the electrode surface, could be treated in terms of an adsorption process that coexisted with the diffuse ionic cloud, shown in Figure 1.4(c). He also noted the ions’ finite sizes, and thus proposed a geometric limit to the amount of ions that could be within the innermost plane near the electrode surface. Thus, a richer, more accurate, concept for the solution side of the electrochemical double-layer had been developed. The double-layer capacitance ($C_{DL}$) of the electrode-electrolyte interface came to be modeled as two capacitors in series, the first representing the Helmholtz layer ($C_H$) and the second representing the diffuse ionic cloud. Mathematically, this relationship is given as

$$\frac{1}{C_{DL}} = \frac{1}{C_H} + \frac{1}{C_{diff}}$$

(1.7)

while the individual capacitance terms are expressed as

$$C_H = \frac{\varepsilon^*}{\delta}$$

(1.8)

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

(1.9)

where $\varepsilon^*$ is the effective dielectric constant between the electronic and ionic charges, $\delta$ is the distance of the Helmholtz plane to the electrode surface, $z$ is the ionic valence, $e$ is the fundamental electric charge, $c_o$ is the bulk concentration of electrolyte, $\varepsilon$ is the dielectric constant of the solvent, $\psi_H$ is the potential at the Helmholtz plane, and $\psi_s$ is the potential in the bulk of the electrolyte.\textsuperscript{1}
As previously mentioned, the capacitance of capacitors in series obeys reciprocal addition, as seen in Equation 1.1, and therefore the double-layer capacitance is limited by the smaller of the two capacitances. However, the expression in Equation 1.7 only accounts for the liquid solution side of the double-layer. At the time of Stern’s contribution, it was assumed that the electrode side of the double-layer was not limiting. This assumption was valid for early experimental investigations as metals were often employed as electrodes. Metals possess a high density of charge carriers and, as a result, electronic charge can be concentrated to a sufficiently high extent at their surfaces. However, unlike metals, semiconductors feature a much lower charge carrier density and, as a result, a distribution of charges appears in the bulk material when an external potential is applied.\(^1\) The image of a distribution of charges within the semiconductor is conceptually analogous to the diffuse ionic cloud proposed by Gouy for the electrolyte side of the double-layer. As a result a “space charge” layer develops within semiconductors which can limit the overall double-layer capacitance despite sufficiently high values of \(C_H\) and \(C_{\text{diff}}\). Therefore, for completeness, Equation 1.7 is modified to include the serial contribution of this space charge layer (\(C_{\text{SC}}\)) which will become limiting in cases where the electrode is not a perfect or nearly perfect conductor:

\[
\frac{1}{C_{\text{DL}}} = \frac{1}{C_{\text{SC}}} + \frac{1}{C_H} + \frac{1}{C_{\text{diff}}} \tag{1.10}
\]

The Gouy-Chapman-Stern (GCS) treatment for the electrolyte-side of the double-layer, described above, is still regarded as the preeminent theory which explains the behavior of the electrochemical double-layer. After Stern’s contributions in 1947, Grahame modified
the structure of the compact layer by dividing the single Helmholtz plane into an inner and outer Helmholtz plane.\textsuperscript{23} He did this to account for both specifically adsorbed ions (inner) and solvated ions (outer). Grahame’s contribution was significant in that it accounted for the discrete presence of the solvent within the double-layer, instead of viewing the solvent as a backdrop for the ions, in a continuum sense. The distance of the ions away from the electrode surface was now being accounted for, and in 1954, Parsons introduced the concept of the distance of closest approach, which set a limit on how close ions could be at the interface while accounting for solvation shells, which would increase that distance.\textsuperscript{24} These considerations of ion and solvent interactions within the first few ionic layers of the electrochemical double-layer set the stage for discussions about the structure of the double-layer in concentrated electrolytes, a topic which is later explored in this dissertation.

As a brief aside, I would like to note, though it is quite evident, that the term “double-layer” in not a literally accurate description of the accumulation of electronic and ionic charges at an interface, in that it often does not consist of only two layers. However, for reasons both historical and conventional, “double-layer” prevails as the descriptor for this phenomenon. The reader should therefore keep an open mind when encountering the phrase “double-layer” in the Sections and Chapters to follow, as the complexity of the electrochemical double-layer is not only a matter of personal interest, but an extremely relevant consideration in the understanding the double-layer capacitance of the electrode-electrolyte interface.
1.3.2 Toward Concentrated Electrolytes

The GCS treatment of the electrochemical double-layer was developed with dilute electrolytes in mind, those in which the ionic concentration was much less than the concentration of the bulk solvent (typically \(<< 0.1 \text{ M}\)). As the diffuse double layer capacitance increases with the square root of the bulk ionic concentration (Equation 1.9), at sufficiently high concentration, the diffuse layer capacitance becomes larger than that of the Helmholtz capacitance (\(C_H\) is typically 20-30 \(\mu F/cm^2\)) and, due to reciprocal addition, the Helmholtz capacitance becomes the term that dictates the double-layer capacitance.\(^1\) However, the traditional view of the Helmholtz layer, as envisioned by Stern, Grahame and Helmholtz, himself, is poorly defined in concentrated electrolytes as ionic correlations between the densely packed cations and anions in the bulk begin to dominate. Mathematical descriptions regarding the theory of the double-layer for concentrated electrolytes have been proposed, but they are either exceptionally complex or simplistic, due to the complexity of the system, and are not generalizable over a range of electrolytes.\(^{25-26}\) I mention here that considerations regarding the structure of the double-layer for concentrated electrolytes is of particular interest as room temperature ionic liquids,\(^27\) a relatively new class of maximally concentrated electrolytes, are investigated as next-generation electrolytes for EDLCs.\(^{14}\) The theory pertaining to room temperature ionic liquids has roots in theories proposed for high-temperature molten salts (Section 1.5); however, recent publications have noted that such theories may be inadequate.\(^{28}\) Fedorov and Kornyshev published a review in 2014 that summarizes well the current understanding of the double-layer involving room temperature ionic liquids, which will be revisited in
Chapter 4. For now, suffice it to say that the GCS treatment of the double-layer does not adequately hold for systems with highly concentrated electrolytes (typically > 1 M) and that theories regarding the capacitance of such systems are currently being developed and refined.

1.4 Carbonaceous Active Materials

1.4.1 Activated Carbon

The initial use of porous carbonaceous materials as EDLC electrodes was one of fortunate happenstance as the discovery was made as an offshoot of current fuel-cell and rechargeable battery research being conducted at the time. Porous carbonaceous materials are exceptional candidates for the active material in EDLCs as they are typically more electrochemically stable, corrosion resistant and have a much higher mass specific surface area than most non-noble metals. Additionally, porous carbonaceous materials can be relatively inexpensive, depending upon the material, as they can be easily manufactured on a large scale.

Today, activated carbon is the material most commonly used in commercial EDLCs. Activated carbon is produced by charring a carbon-containing precursor, typically a type of biomass, in an oxygen-free environment and then subjecting the charred material to high temperature steam, hot caustic acids or potassium hydroxide to create nanometer-sized pores; the latter process is referred to as “activation.” This activated carbon is further purified to reduce redox-active halogen and heavy metal impurities in the material and ground into micron sized particles to create a product suitable for use in EDLCs. The
high nitrogen-accessible surface area of the material combined with its low-cost due to inexpensive feedstock materials and ease of scale-up has secured activated carbon as the dominant porous carbonaceous material for EDLCs.\textsuperscript{32} Despite its widespread use, activated carbons display two major disadvantages, which will reduce their appeal for next-generation supercapacitors.\textsuperscript{33} To obtain higher operating voltages, more stable electrolytes with larger molecules are likely to be used in future. The nanometer or sub-nanometer pore space of activated carbons may be inaccessible to these larger ions and thus, result in electrodes with low mass specific capacitance.\textsuperscript{34} Additionally, the array of densely-packed nanometer-sized pores creates a tortuous electrical path, which accounts for the material’s low electrical conductivity.

\textbf{1.4.2 Templated Materials}

Many additional carbonaceous materials have been studied in the EDLC literature and can be divided into monolithic and non-monolithic carbonaceous materials. Monolithic carbonaceous materials are those which are designed as bulk-structures (\textit{i.e.}, like activated carbon) and can be used as-processed or ground into smaller particles. Templated carbons are a type of monolithic carbonaceous material which allow one to tightly control the pore size of the monolith.\textsuperscript{16, 32, 35-37} Processing such materials typically involves the use of a molecular template, such as a surfactant, which directs the formation of a three-dimensional framework of silica.\textsuperscript{16, 38-39} A carbon precursor (\textit{e.g.}, sucrose; furfuryl alcohol; resorcinol and formaldehyde; \textit{etc.}) is infiltrated into the template and is carbonized at high temperature. The template is subsequently removed with strong acid or base. Though these processes allow one to adjust the pore size of the material on the nanometer length scale
by adjusting the structure of the template, they are cumbersome and costly. Furthermore, they require the imbibition of electrolyte after they are processed, a step which will become more difficult as more electrochemically stable electrolytes with higher viscosity and larger ion-sizes are introduced into EDLCs.

1.4.3 Nanomaterials

Non-monolithic carbonaceous materials are “building blocks” often used to construct bulk porous materials. These materials are typically regarded as “nanomaterials” as one of their dimensions is on the nanometer length scale and include single-walled carbon nanotubes, multi-walled carbon nanotubes, fullerenes, graphene and graphene-like materials. Single-wall carbon nanotubes have a theoretical specific surface area of 1315 m²/g (neglecting the inner tube area). ⁴⁰ Networks of carbon nanotubes can display high electronic and ionic conductivity due to both the high intrinsic conductivity of the nanotube itself and the large, accessible pore space which is obtained when the nanotubes are stacked in a vertical cross-hatch pattern. ⁴¹ Forests of vertical carbon nanotubes have been grown and proposed as electrodes for EDLCs as they facilitate one-dimensional ion transport, and lack tortuosity which can decrease the ionic transport resistance. ⁴²-⁴³ Multi-walled carbon nanotubes are less attractive for EDLC applications as they have lower ion-accessible specific surface areas than their single-walled counterpart.

If one were to slice a carbon nanotube along its cylindrical axis and unwrap it, one would have a carbonaceous material known as graphene. Graphene has become an exceedingly popular material in materials research as its unique properties, such as its high charge-carrier mobility and optical transparency, position it to compete with silicon-based
electronic components and serve as a transparent conductor. Additionally, graphene has an exceptionally high specific surface area of 2,630 m$^2$/g, twice that of single-walled carbon nanotubes, which is appealing for EDLC applications. Due to the popularity of graphene, a number of graphene-like materials have emerged in the literature under the guise of “graphene.” Here, I note that graphene, technically, is a nearly perfect (for entropic reasons, I attach a realistic qualifier before “perfect”) arrangement of sp$^2$ hybridized carbon in a honeycomb lattice. To distinguish this material from the host of graphene-like materials found in the literature, it has become common practice to refer to this material as “pristine graphene.”

Recently, the space-charge capacitance of pristine graphene was reported to be low (i.e., less than 10 µF/cm$^2$). This is a direct result of graphene being a semi-metal, as it lacks a sufficient density of states near the Fermi level, which results in a spatial charge distribution within the material very difficult to produce in bulk quantities. Mechanical exfoliation (including the “Scotch-tape” method), ultrasonic exfoliation, chemical vapor deposition and epitaxial growth generate. This low space charge capacitance is disadvantageous as it limits the overall double-layer capacitance of the graphene-electrolyte interface. Practically speaking, pristine graphene is also low quantities of pristine graphene, which is disadvantageous for the formulation of bulk electrodes.

However, other forms of graphene (i.e., the graphene-like materials previously mentioned) hold promise for EDLC applications. Specifically, a type of defective graphene, which I refer to as functionalized graphene sheets (FGSs), not only features a non-limiting space charge capacitance, but also is currently processed in an industrially
This graphene-like material is produced via the thermal exfoliation and reduction of graphite oxide (GO) or the chemical reduction of graphene oxide. Though I refer to this material as FGSs, several other names exists in the literature, including thermally exfoliated graphite oxide (TEGO) and reduced graphite oxide (RGO), among others. As this material and its precursor, GO, are at the focus of my Ph.D. work, I will take the time to describe them in detail in the following sections.

1.4.3.1 Graphite Oxide and Graphene Oxide

GO is the term used to describe graphite that has been heavily oxidized, that is, to an extent in which the $d_{002}$ spacing of the graphite crystal increases from its characteristic spacing of 3.4 Å to more than 8 Å, due to the presence of surface-bound oxygen-containing functional groups such as hydroxyls, epoxides and carbonyls. Like graphite, GO is a bulk, layered crystalline material. Commensurate with familiar terminology, one sheet of the GO crystal is referred to as graphene oxide (analogous to that of graphene and graphite). The distinction between GO and graphene oxide is tenuous at times, and the terms are often used interchangeably.

The oxidation of graphite was first reported in 1859 by Brodie who used a mixture of potassium chlorate and fuming nitric acid as oxidants. This procedure was modified by Staudenmaier almost 40 years later with the addition of sulfuric acid, a known graphite intercalant, which was likely employed to promote the expansion of the graphite crystal and ease the transport of oxidant to the basal plane. However, both of these protocols were extremely hazardous as they generated gaseous $\text{ClO}_2$, which is highly explosive. In 1958, Hummers and Offeman developed a new procedure in which they exchanged the
potassium chlorate and nitric acid with potassium permanganate and sodium nitrate. This procedure, referred to as the “Hummers’ method,” remains the most widely used protocol for preparing GO. Recently, this method was updated by Marcano et al. who replaced the sodium nitrate for phosphoric acid and doubled the amount of potassium permanganate as they found that this “improved Hummers’ method” (as it is called) yielded a product with a larger fraction of hydrophilic carbon material than in previous protocols. For reference, the carbon to oxygen ratio (C/O) of this material was reported to be less than 2 (>33 at% O) while that of previous methods is typically between 2 and 3 (33 and 25 at% O).

GO is a non-stoichiometric material which is not described by a singular molecular formula (though some have been proposed), but rather by its relative carbon to oxygen content. It is for this reason that I refer to the process of creating GO as a “preparation,” rather than a “synthesis” as the oxidation consists of the highly non-selective and largely uncontrolled modification of the pre-existing structure of graphite (i.e., graphene) with oxygen-containing functional groups. Several models for graphene oxide have been proposed as shown in Figure 1.5, in an attempt to visualize both the structure and chemical composition of the material. However, a single model has not been agreed upon or definitively confirmed by experimental techniques, and even still, the suggestion that one model can describe graphene oxide may be naïve given the fact that it is likely highly dependent upon its processing parameters.

Some specific chemical groups have been experimentally verified. Using $^{13}$C and $^{1}$H NMR, Lerf et al. showed the presence of tertiary alcohols and epoxides. Szabó et al. reasoned the presence of trans-linked cyclohexane chairs, ribbons of flat hexagons with sp$^{2}$
bonds, tertiary hydroxyls, epoxides, ketones, quinones, phenols, and aromatic diols, which are acidic. Carboxylic acid groups are also speculated to decorate the edges of the sheets. The material is also strongly hygroscopic and readily adsorbs water from the environment. Recently, Dimiev et al. suggested that the chemical composition of GO is greatly affected by the washing procedure after processing. As a result, pinpointing the exact chemical structure of GO is extremely difficult. Furthermore, the high extent of oxidation reported for GO produced from these processes renders the material electrically insulating due to a severely disrupted sp² network. In order to be used as an active material for EDLCs, the material needs to be reduced.

Figure 1.5: Models of proposed structures for GO. Adapted from Szabó et al. Chem. Mater. 2006.
1.4.3.2 Functionalized Graphene Sheets

In 2003, a process was invented at Princeton University to produce bulk quantities of FGSs via the rapid thermal exfoliation and reduction of GO and subsequent ultrasonication in an appropriate solvent.\textsuperscript{54} This was accomplished by quickly subjecting GO powder to high temperature. The rapid liberation of gaseous species such as carbon monoxide, carbon dioxide and water from the material generated enormous inter-sheet pressure, which effectively exfoliated the material through the reduction process (\textit{i.e.}, loss of oxygen). The violent de-oxygenation of the material rendered it defective, as carbon atoms were ejected from the carbon lattice in the form of gaseous products, such as CO and CO\textsubscript{2}. Depending upon the heat treatment temperature, the material was left decorated with a significant amount of residual oxygen-containing functional groups, as shown in Figure 1.6. Furthermore, the as-exfoliated material featured nanometer-scale wrinkles and planar corrugations that partially impeded the stacking of individual sheets to re-form a graphitic material. In addition to the thermal reduction, GO and graphene oxide can be chemically

\textbf{Figure 1.6: Schematic of a functionalized graphene sheet.} 5-8-5, 5-7-7-5 (Stone-Wales) and point-vacancy defects highlighted. Carbon and oxygen atoms are shown in grey and red, respectively. Image adapted from Punckt \textit{et al.} 
reduced via an aqueous reaction with hydrazine to form FGSs. Though the exact mechanisms of this reduction process are unknown, researchers speculate that it proceeds via a prototypical Wolff-Kishner reduction process, though the exact mechanism of hydrazine reduction has not been confirmed. Additionally, chemical and structural differences are expected to be observed between the two reduction procedures and, as such, the structures of the resulting FGSs is hypothesized to be significantly different.

The electrochemical properties of FGSs are highly dependent upon the degree of reduction as well as the defect density. Using Kelvin probe force microscopy, Punckt et al. showed that the sheet resistance of FGSs decreased from ~500 to ~30 kΩ/sq, with increasing reduction temperature corresponding to a C/O increase from ~7 to ~65. Annealing the material at 1500 °C reduced the sheet resistance to below 10 kΩ/sq, while increasing the C/O to ~340. The heat treatment and annealing procedures not only affect the material’s resistance and C/O, but also the defect density. Pope showed that the defect density of FGSs (the area of the graphene lattice that does not form a perfect hexagonal lattice), inferred from Raman spectroscopy, increases with increasing reduction temperature to 1100 °C; however, prolonged annealing treatments reduced the defect density through lattice healing as a result of the high thermal motion of carbon atoms at high sustained temperature. Interestingly, Pope further correlated this trend in defect density to the intrinsic capacitance (i.e., areal capacitance) of the material and showed that maximal defect density correlated with maximal areal capacitance. Pope was able to achieve areal capacitance values near 20 μF/cm², approaching that of glassy carbon. The
defect sites of FGSs have also been shown to electrochemically catalyze redox reactions such as nitric oxide\textsuperscript{69} and triiodide reduction.\textsuperscript{70}

1.5 Ionic Liquids

Conventional electrolytes for EDLCs consist of an ionic solid which is dissolved in a solvent, typically water or an organic small molecule, such as acetonitrile.\textsuperscript{5,71} In the case of EDLCs, the components of the electrolyte establish the operating voltage limit as the applied potential must be sufficiently smaller than the potential at which decomposition or redox activity occurs. For water-based electrolytes, that limit is \(\sim 1.2\) V, corresponding to the anodic and cathodic limits of oxygen and hydrogen gas formation, respectively. Devices using organic electrolytes (e.g., an alkylammonium salt dissolved in acetonitrile) can operate at higher voltages, usually between 2.5 and 3.5 V. As the energy density of an EDLC is proportional to the square of the operating voltage, electrolytes with electrochemical stability surpassing 4 V are attractive as they can greatly improve the energy density of the device, as shown in Equation 1.4. In this respect, ionic liquids are promising electrolytes for EDLCs as their electrochemical stability typically exceeds 4 V, while some ionic liquids have extremely high electrochemical stability windows exceeding 6 V.\textsuperscript{14} The following sections provide a brief background on the development of ionic liquids as electrolytes and address the physicochemical properties which position ionic liquids to become choice electrolytes for next-generation EDLCs. Particular attention is given to how molecular structure influences electrochemical properties.
1.5.1 Historical Context

The modern definition of an ionic liquid is a salt that is liquid below 100 °C. This definition, arbitrarily based on the boiling point of water, was proposed to distinguish a relatively new class of low-melting point ionic compounds from familiar predecessors with high melting points, typically greater than 300 °C. The latter compounds, typically halide-based salts, had been generally referred to as “molten salts,” “ionic melts,” and (to complicate matters) “ionic liquids.” However, the modern use of the term ionic liquid refers to compounds that are chemically quite different from high temperature molten salts as they consist of a cation-anion pair which is significantly larger than that of traditional salts (e.g., NaCl). Due to their unique structure and corresponding properties, these ionic liquids find use in a variety of applications, including organic syntheses, catalysis, protein extraction, chromatographic separation, lubrication and, as mentioned, electrolytes for electrochemical devices.

The first compound to fall within today’s working definition of an ionic liquid was documented in the mid-1800s. The chemical was described as a “red oil” which was a byproduct of Friedel Crafts reactions involving mixtures of anhydrous aluminum chloride, alkyl chlorides and benzene. The oil, which was characterized a century later, after the development of NMR, consisted solely of an alkylated aromatic ring-based cation and a chloroaluminate anion, two ionic species that produced a liquid oil at moderately low temperature. The structure of this oil is reflective of that of modern ionic liquids as it contains a bulky organic cation paired with a weakly coordinating anion.
In the early 1900s, the first ionic liquid that was liquid at room temperature was prepared. Though ethylammonium nitrate (m.p. 12 °C) was scientifically intriguing, it had little practical value at the time.\textsuperscript{79} Later, dialkyl and 1-alkylpyridinium chloroaluminates were prepared and used in the electrodeposition of metals, namely aluminum.\textsuperscript{77} However, still, the ionic liquids of the pre-1990 era had limited uses, and those which had practical value were largely corrosive and reached with water and oxygen.\textsuperscript{80} A major breakthrough in ionic liquid development occurred in 1992, when Wilkes and Zaworotko prepared the first air-stable room temperature ionic liquid (RTIL) via ion metathesis of 1-ethyl-3-methylimidazolium iodide and silver tetrafluoroborate in methanol, forming 1-ethyl-3-methylimidazolium tetrafluoroborate (EMImBF\textsubscript{4}), shown in Figure 1.7.\textsuperscript{81} This particular RTIL remains an extremely popular RTIL in the EDLC literature due to its relatively low viscosity, high conductivity and large electrochemical stability window (~4.3 V).\textsuperscript{82}

In the past decade, RTILs have been extensively studied as electrolytes for rechargeable lithium-ion batteries as their low flammability, low vapor pressure at ambient temperature and high electrochemical stability are touted as promising attributes for the development of safer, non-flammable devices with improved performance.\textsuperscript{83} These attributes are also

![Figure 1.7: Examples of ionic compounds in order of decreasing melting points. From left to right: ionic solid (i.e., potential molten salt), ionic liquid, and two examples of RTILs.](image)
attractive for EDLC applications, and, as was the case for activated carbon, the earliest uses of RTILs in EDLCs resulted as an offshoot of other electrochemical research occurring at the time. Several patents were filed in the mid-1990s detailing the use of RTILs for both battery and EDLC technologies. In the scientific literature, McEwen et al. reported one of the premier uses in EDLCs by constructing EDLC electrodes with activated carbon cloth impregnated with a mixture of EMImBF$_4$ and propylene carbonate.$^{84}$ Today, many combinations of cations and anions have been investigated in an attempt to find the most appropriate ionic liquids for electrochemical applications. However, as will be discussed in the following Section, this task is non-trivial as inevitable trade-offs between bulk solution properties and electrochemical stability exist.

1.5.2 Physicochemical Properties

Figure 1.8 presents common cations and anions for ionic liquids organized qualitatively in terms of increasing electrochemical window. As can be seen, the majority of ionic liquid cations are bulky, either containing cyclic carbon structure or long alkyl chains which occlude the positive formal charge of an electron-deficient nitrogen, sulfur or phosphorus atom. The bulkiness of the cation is majorly responsible for the low melting points of the ionic compounds as it impedes the formation of a crystalline lattice. Additional structural features, such as cation asymmetry also contribute, and generally the melting point of an ionic liquid decreases with the increasing size of its constituent ions (Figure 1.7). As can be gathered from Figure 1.8, pyridinium- and imidazolium-based cations as well as bis(fluorosulfonyl)imide and bis(trifluoromethylsulfonyl)imide anions feature delocalized charges due to resonance effect within the ions (Note: The sulfonyl groups participate in
the resonance structures for the anions). The delocalized charges on these ions further lowers the melting points of the ionic liquids as the Coloumbic interactions are weakened as they are distributed over a larger area.

Though the low melting points of ionic liquids allow these compounds to serve as solventless, stand-alone electrolytes, the low melting points come with a trade-off in the bulk transport properties of the ionic liquids. Though bulkier ions typically feature greater electrochemical stability, their large size usually results in a higher bulk viscosity and lower ionic conductivity. The former is a direct result of Stoke’s Law as the drag force on an ion in a fluid increases with increasing molecular radius. Furthermore, the strong cohesive forces within the ionic liquid, which directly account for their low vapor pressures at

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Figure 1.8: Examples of cations and anions for ionic liquids. The cations and anions are qualitatively arranged in order of increasing electrochemical window. This is not an absolute relationship as the trends depend heavily on the identity of the R groups and the particular cation-anion combination.
ambient temperature, also reduces the diffusive transport of the ions. Generally, the viscosities of ionic liquids fall within the range of 20-200 mPa s, values much larger than that of water (~1 mPa s) or organic solvents, such as acetonitrile (0.34 mPa s at 25 °C).\textsuperscript{77} Correspondingly, their conductivity typically lies between 0.1-10 mS/cm, depending on the sizes of and ionic correlations between the cation-anion pair. The presence of impurities, such as free halides, water and organic solvents have also been shown to drastically affect these physical properties.\textsuperscript{85} These considerations are important for EDLCs as the conductivity of the bulk liquid will greatly affect the bulk ionic transport, and further, reduce the power density of EDLCs. In this respect, the EDLC community faces another unavoidable trade-off between high energy and high power density devices.

The anion of the ionic liquid is strongly correlated with the miscibility of the ionic liquid in solvents. Generally, a designation is made between the miscibility of ionic liquids in water, with “hydrophilic” and “hydrophobic” used to describe ionic liquids that are miscible and are not miscible in water, respectively.\textsuperscript{86} Typically, ionic liquids with the tetrafluoroborate and hexafluorophosphate anions are hydrophilic, while those with the bis(trifluoromethylsulfonyl)imide anion are hydrophobic.\textsuperscript{87}

Figure 1.9 shows the relationship between the molar volume and molar mass for selected ionic liquids, as well as for conventional electrolytes used in electrochemical devices. Both the molar volume and molar mass of the electrolyte are important for EDLC design as the electrolyte assumes a significant fraction of the electrode’s total volume and mass. Therefore, to develop compact EDLCs with high energy density, one should aim to use electrolytes which do not take up much space (low molar volume) and are lightweight
(low molar mass). As can be seen, of the selected electrolytes, concentrated acids and bases have the smallest molar volumes and masses. Though one may suppose that these electrolytes would be best suited for EDLC applications, they are not ideal, as previously discussed, as they suffer from low electrochemical stability (~1-1.5 V). Though ionic liquids have larger molar volumes and molar masses, their electrochemical stability windows are much larger. I note that the electrolyte with the largest molar volume and mass is 1 M tetraethylammonium tetrafluoroborate in acetonitrile as the values are reported on a molar basis of ions only in the mixture. This electrolyte has an extremely large mass and volume per ion due to the “dead-weight” of the added solvent. In particular, two RTILs, EMImBF₄ and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMImTFSI) have remained popular choices for EDLCs as the have moderate voltage windows (up to 4.5 V), as well as moderate molar volumes and masses.

![Figure 1.9: Relationship between electrolyte molar volume and molar mass.](image)

Both the molar masses and volumes of ionic liquids are smaller than that of organic electrolytes. The smallest values are achieved for concentrated acids, such as sulfuric acid. Most of the data fall near the 45-degree line, plotted as a dotted line suggesting that molar mass scales (approximately) with molar volume.
1.6 Functionalized Graphene and Ionic Liquid-based EDLCs

The first report of an EDLC featuring both FGSs and an ionic liquid was published in 2008, one year prior to the start of my Ph.D. In this report, Vivekchand et al. showed that electrodes prepared with FGSs generated from the thermal exfoliation of GO prepared via the Staudenmaier method yielded a gravimetric capacitance of 75 F/g and 117 F/g (at 3.5 V) for N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide and concentrated sulfuric acid, respectively.\(^8\) The experiments performed with the ionic liquid were carried out at elevated temperature (60 °C). Soon after, Liu et al. used chemically reduced GO produced via the modified Hummers' method and the popular RTIL, EMImBF\(_4\), to produce electrodes performing at 154.1 F/g (at 4.5 V) at room temperature.\(^9\) The electrodes were produced by vacuum filtering the FGS from suspension, drying the electrodes and imbibing with the RTIL. In 2010, Kim et al. thermally reduced GO in propylene carbonate in the presence of a polymerized form of EMImTFSI, which they referred to as poly(ionic liquid), and achieved a gravimetric capacitance of 187 F/g (at 3.5 V).\(^9\) One year later, Zhu et al. applied the familiar chemical activation process used to make activated carbon materials to microwave-exfoliated GO (MEGO).\(^9\) They employed a series of electrolytes and achieved capacitances of 166 and 200 F/g for mixtures of 1-butyl-3-methylimidazolium tetrafluoroborate in acetonitrile and neat EMImTFSI, respectively. However, up until this point, EDLC performance was gauged primarily on the gravimetric capacitance values achieved. In 2013, just a few months apart, Pope et al. and Yang et al. reported EDLC performance results paying particular attention to the fraction of active material which was actually present in the device.\(^13\), \(^17\) Pope et al. showed that through evaporative
consolidation of graphene oxide and EMImBF$_4$ followed by thermal reduction, that a gravimetric capacitance of 156 F/g (at 3.0 V) could be achieved with an active material loading as high as 40% ($f = 0.4$). This corresponded to an energy density of 17.5 Wh/kg, the highest reported at the time for thin films. Yang et al. used a bio-inspired approach in which they vacuum filtered suspensions of chemically reduced GO and kept the films wet. They then exchanged the intercalated water with EMImBF$_4$ and showed that their devices reached gravimetric capacitances of ~210 F/g at high FGS packing densities of 1.25 g/cm$^3$. Their measurements were also performed with a mixture of EMImBF$_4$ and acetonitrile.

Over the span of 5 years, the EDLC literature exploded with reports of graphene-based materials as electrodes with ionic liquid electrolytes. As these 5 years overlapped with my graduate work, my time as a Ph.D. student was both exciting, and turbulent as the field was rapidly evolving with new knowledge on a consistent basis. But important questions come with rapid progress. In the final Section of this Chapter, I lay out my research and describe my contributions in the context of this accelerating field.

### 1.7 Goals and Layout of the Dissertation

Though the ultimate goal of EDLC research is to maximize both the energy and power density of the devices, the significantly low energy density of EDLCs is currently the bottleneck for their widespread implementation and use. As discussed in this chapter, there exists an intrinsic trade-off between energy and power density in EDLC design. In this dissertation I aim to explore, in particular, routes by which highly energy dense electrodes can be created. My work attempts to understand how to engineer functionalized graphene
and room temperature ionic liquid electrolytes in a manner to achieve a high energy density while keeping in mind the idea that larger scale porosity may be introduced at a later time, primarily to tune the power density of the device.

As discussed, much of the work in the EDLC literature focuses on the morphology and properties of the electronic conductor (i.e., the active carbonaceous material). However, recent work performed both in our laboratory and elsewhere has noted the importance of considering the amount and distribution of all the electrode components, namely the electrolyte which comprises a significant mass fraction of the electrode (> 50 wt%). Therefore, the challenge of designing highly energy dense EDLC electrodes consists not only of elucidating ways to organize the electrode materials as densely as possible, but also of properly accounting for the mass of all its components. In addition to this engineering challenge, my work explores the fundamental physics of the electrode-electrolyte interface when highly concentrated RTILs are used as electrolytes. As RTILs are regarded as next-generation electrolytes for EDLCs, it is critical to improve our understanding of such technologically relevant electrolytes to aid in the design of highly energy dense EDLC electrodes.

The remainder of this dissertation addresses both of these goals and is organized as follows. Chapter 2 begins by investigating electrode fabrication techniques using FGSs and graphene oxide in an attempt to control electrode morphology at two length scales, the sub-micron-scale and the nanometer-scale. More importantly, Chapter 2 introduces a facile processing technique to create FGS-RTIL electrodes and explores how electrolytes and solvents affect the stacking of graphene oxide, the precursor to conductive FGSs. The
experimental methods presented in Chapter 2 are pertinent to the remaining chapters as similar materials were used throughout all my Ph.D. work. Next, Chapter 3 introduces a third component into the electrode design, carbonaceous nanoparticles, which serve as inter-sheet spacers to prevent the FGSs from restacking. Nanoparticles derived from sucrose effectively adsorb onto graphene oxide and effectively disrupt the graphene oxide from restacking into GO when processed from suspension. Using this approach, non-optimized EDLC electrodes having an energy density of 13.1 Wh/kg were fabricated, suggested that carbonaceous nanoparticles can be used to increase the energy density of the electrodes. Chapter 4 departs from electrode engineering and presents model electrochemical experiments used to understand how the addition of common solvents to RTIL electrolytes can increase the differential capacitance of the electrode-electrolyte interface. RTIL/solvent mixtures are technologically relevant electrolytes, often employed in the EDLC literature, and this work provides insight into the possible benefits afforded by using mixtures over neat RTILs. Finally, Chapter 5 provides a summary of the main conclusions of the work and describes future research directions.
Appendix: Derivation of the Energy Density of a Double-Layer Capacitor

The circuit diagram for a supercapacitor consists of two capacitors in series. The energy stored in a parallel-plate capacitor has been shown to be

\[ E^* = \frac{1}{2} C_{eq} U^2 \]  \hspace{1cm} (A1)

where \( E \) is the energy stored in the device, \( C_{eq} \) is the capacitance and \( U \) is the potential difference between the two plates. A supercapacitor effectively consists of two capacitors in series as two double-layers are formed, one at the positive electrode and the second at the negative electrode. As a result, the equivalent capacitance of two capacitors (\( C_1 \) and \( C_2 \)) in series is given as:

\[ \frac{1}{C_{eq}} = \frac{1}{C_1} + \frac{1}{C_2} \]  \hspace{1cm} (A2)

Assuming that the capacitances of the positive and negative electrode are equal yields

\[ \frac{1}{C_{eq}} = \frac{2}{C} \] \hspace{1cm} (A3)

Where \( C \) now represents the capacitance of each electrode. Substituting A3 into the energy equation A1 yields:

\[ E^* = \frac{1}{4} C U^2 \] \hspace{1cm} (A4)
To obtain energy density (energy per mass) of the electrode, I divide both sides of the equation by the total mass of the electrode, \( m_T \), which includes the masses of both solids and electrolyte:

\[
\frac{E^*}{m_T} = \frac{1}{4} \frac{CV^2}{m_T}
\]  

(A5)

The total mass of the electrode \( (m_T) \) can be expressed as:

\[
m_T = \frac{m_1 + m_2}{f}
\]  

(A6)

Where \( m_1 \) and \( m_2 \) are the masses of the active solids contained in the positive and negative electrode, respectively, and \( f \) is the mass fraction of the active solids in the device. Assuming that the masses of the positive and negative electrode are equivalent, A6 can be substituted into A5 to yield:

\[
\frac{E^*}{m_T} = \frac{1}{4} \frac{fCU^2}{2m}
\]  

(A7)

where \( m \) is the mass of the active solids in one electrode. The expression A7 can be further simplified to the final expression:

\[
E = \frac{f}{8} C_G U^2
\]  

(A8)

where \( E \) is the energy density of the supercapacitor and \( C_G \) is the “gravimetric capacitance” of the device, or \( C/m \).
References


Ordered Metal Oxide–Graphene Nanocomposites for Electrochemical Energy Storage. 


Chapter 2

2 Engineering Functionalized Graphene-based Films at the Sub-Micron- and Nanometer-Length Scales

This chapter presents work inspired by discussions with Benjamin Hatton from the laboratory of Prof. Johanna Aizenberg at Harvard University and Michael Pope at Princeton University.

2.1 Introduction

The microstructure and nanostructure of an FGS-based EDLC electrode will ultimately govern its performance. In this respect, understanding how nanomaterials can be assembled is critical to designing EDLCs with tailored energy and power densities. This chapter explores two approaches to design FGS-based electrodes at two different length scales: the sub-micron (0.01-1 µm) and nanometer (1-10 nm) scales, shown in Figure 2.1. Though engineering the porosity at the sub-micron scale is not the bottleneck impeding the design of high energy density EDLCs, as will be discussed, porosity at this length scale holds promise in developing hierarchically porous structures with improved rate performance.1-4 More importantly, my initial work in developing porous FGS-based structures on the sub-micron length scale revealed the scientific and technological problem upon which the foundation of this thesis was constructed. As such, the work in this chapter is presented in the order in which it was performed to not only give broader context to the complexity of “porosity” in graphene-based devices, but to reflect the general progression of my work.
and the scientific research conducted in the field of graphene-based electrodes during my graduate studies.

The first processing strategy relies on a technique used to develop inverse opals, a type of photonic crystal typically constructed from the templation of a metal oxide onto an organic-based colloidal crystal. An example of a titania-based inverse opal is shown in Figure 2.1(c). Hatton and his colleagues at Harvard University developed a facile route to co-assemble colloidal particles and a solution of a small-molecule silica precursor into ordered, crack-free opal structures.5 Michael Pope and I proposed to substitute FGS for the silica precursor, in an attempt to create three-dimensional macrostructures of FGSs with interconnected porosity, structures which held promise not only for EDLCs, but also for lithium-ion batteries, dye-sensitized solar cells, sensors and adaptive materials.

These efforts sparked questions and subsequent ideas about not only controlling the sub-micron scale porosity, but also the “porosity” between individual FGSs at the nanometer length scale as the dense packing of active material and electrolyte is currently hypothesized to produce the EDLC electrode with the highest energy density. The second

**Figure 2.1: Porosity of FGS-based films.** (a) Cartoon highlighting inter-aggregate porosity formed between densely packed FGSs and (b) the intra-particle porosity between the individual FGSs. High energy density EDLCs will require the clever engineering of the intra-particle porosity, while high power density devices will require larger, inter-particle porosity featured in (a). (c) Example of an inverse opal film composed of titania after the opal template has been removed, reproduced by Hatton et al. *PNAS*, 2010.
processing strategy, inspired by the co-assembly concept of prior inverse opals work, consisted of consolidating functionalized graphene directly with high-voltage room temperature ionic liquid (RTIL) electrolytes. By controlling the RTIL content, we investigated whether a simple processing procedure, such as the mechanical mixing of the two components, could produce electrodes with high gravimetric capacitance. In effect, these efforts were beginning to use the electrolyte as a structural component in the construction of the EDLC electrode.

2.2 Experimental Methods

The following sections contain experimental information pertinent to the work discussed in this Chapter.

2.2.1 Materials

2.2.1.1 Preparation of GO and graphene oxide

GO was prepared using the “improved Hummers method” detailed by Marcano et al. and reproduced here with slight modifications. Briefly, 360 mL of concentrated sulfuric acid (98%) and 40 mL of concentrated phosphoric acid (85%) were added to a 1 L beaker placed in an oil bath. The acids were mixed with a PTFE stir bar. Next, 3.0 g graphite (Asbury Grade 3061) was added to the mixture followed by 18.0 g of potassium permanganate. Initially, the reaction mixture is a deep green color. The temperature of the reaction mixture was maintained between 40 and 45°C, which is 5-10°C lower than that suggested by Marcano et al. and was stirred for 16 h, (a time 33% longer than that recommended by Marcano et al.) The reaction was cooled by pouring the reaction mixture
into a 2 L beaker filled with 400 g of ice. At this stage the reaction mixture was a deep purple color. Aliquots of 3 mL hydrogen peroxide (35 wt%) were added to the reaction mixture until it turned a bright yellow color (about 3-4 aliquots). A “perfect” processing occurs when all of the flecks in the reaction mixture are completely white, i.e., when no grey/black flecks, which are indicative of un-oxidized graphite are observed. At the end of the reaction, the solid product is referred to as GO.

The reaction mixture was partitioned between two 500 mL centrifuge tubes and centrifuged at 3000 RPM (2000 g-force, IEC Centrifuge with 269 swinging bucket rotor) for 45 min. The supernatant was decanted and the GO pellet was re-suspended in 300 mL of water, mechanically stirred and centrifuged again; ultrasonication was not used. This washing procedure was repeated with 35 wt% hydrochloric acid (3x) and finally with anhydrous ethanol (3x). After the final ethanol wash, the GO was stored in ethanol in an Erlenmeyer flask until use or powder processing (detailed in the next Section). Mechanical stirring of the graphene oxide-ethanol mixture resulted in exfoliation of individual graphene oxide sheets. Therefore, the suspension likely contains a majority of graphene

![Graphene oxide, GO and thermally reduced GO](image)

**Figure 2.2: Graphene oxide, GO and thermally reduced GO.** From left to right: graphene oxide-ethanol suspension, GO powder and thermally reduced GO powder produced via thermal exfoliation and reduction of GO powder (1100°C for 60 s).
oxide single sheets and aggregates and a trace amount of GO. The concentration of the graphene oxide suspension at this stage is typically between 10-20 mg/mL. A sample of the suspension is shown in Figure 2.2.

The ethanol in the graphene oxide-ethanol can be easily exchanged with other alcohols, if desired. This is achieved through successive centrifugations, in which the pellet of the graphene oxide-ethanol suspension is washed and re-suspended via mechanical agitation in the desired alcohol. The ethanol can also be exchanged with water, though at comparable concentrations (10-20 mg/mL) we find that the graphene oxide suspension forms a gel.

### 2.2.1.2 GO Powder

The graphene oxide-ethanol suspension can be used as-is or the material can be further processed into a “dry” powder by spray drying. To process the material into a powder, the graphene oxide-ethanol suspension was again centrifuged, and the GO pellet was re-suspended in water to achieve a suspension which is approximately 2 mg/mL. At this concentration and in an aqueous environment, the suspension was highly viscous and gel-like. To prevent clumping of the material, the water was added slowly to the GO under constant stirring and was left stirring for 24-48 hours prior to spray-drying. The suspension was spray dried (Niro portable spray dryer, Niro, Inc.) with an inlet air temperature near 300°C and outlet air temperature below 110°C. The powder was collected and stored in a scintillation vial. A sample of the spray-dried material is shown in Figure 2.2.

### 2.2.1.3 Preparation of Thermally Reduced GO and FGSs

Thermal exfoliation and reduction of GO was performed in a tube furnace according to a procedure developed in our group. Typically, 100 mg of the as-prepared GO powder
was placed in the bottom of a fused quartz tube. The powder was dried overnight under nitrogen flow in an attempt to remove adsorbed water which may have remained on the material. The tube was evacuated and filled with ultra-pure argon gas (99.9995%) three times to ensure that the atmosphere in the tube was oxygen-free. The tube was then held under vacuum and passed into the hot zone of a Lindburg furnace which was pre-heated to a desired temperature (typically between 300°C and 1100°C) for 30 to 60 s. The tubes were removed from the furnace and allowed to cool on graphite-coated bricks as the tube can be red-hot especially at the higher temperatures. The powder was vacuumed out of the tube, collected and stored in aluminum foil to shield the low-density material from static charge. Figure 2.2 shows a sample of this low-density material. The carbon to oxygen ratio (C/O) of the material was measured via energy dispersive X-Ray spectroscopy (Section 2.2.2.3) is typically used as a measure of the degree of reduction (with GO having C/O ~2). The C/O of thermally reduced GO prepared at 1100°C for 60 s is approximately 20.

The thermally reduced GO features a vermiculite structure composed of expanded, yet stacked domains of the original GO particle. FGSs are produced by suspending thermally reduced GO in an appropriate solvent and ultrasonicating to exfoliate the vermiculite structure into individual sheets; these sheets are referred to as FGSs.

2.2.1.4 Synthesis of Polystyrene Spheres

Polystyrene spheres were prepared via an aqueous surfactant-free emulsion polymerization detailed in the literature. After synthesis, the polystyrene spheres were extensively washed by dialyzing against Picopure® water (18 MΩ from tap) for two weeks. Approximately 20 volume exchanges were made with the ratio of the volume of the
reservoir to the volume of the dialysate being 100. The spheres were characterized via SEM and dynamic light scattering. The experimental protocol was tailored to produce spheres of two different sizes: 300 and 700 nm. The larger spheres had a polydispersity index of 0.3. The concentration of the stock suspension of polystyrene spheres was measured to be 80 mg/mL.

2.2.1.5 Evaporation-Induced Colloidal Assembly

The procedure used to make the inverse opal structures was adapted from Hatton et al. and encompasses an evaporation-induced co-assembly of colloidal spheres (which serve as the opal template) and an additional component to fill the void space between the spheres. Removal of the spheres via heat treatment results in a structure described as an “inverse opal,” which features an array of inter-connected pore spaces. Briefly, strips of silicon wafers (1 x 4 cm) were soaked in “piranha” base (1:1:5, ammonium hydroxide:hydrogen peroxide:distilled water by volume, heated to 85°C) for 10 min. to both remove organic contaminants from the surface and also hydroxylate the wafer as a hydrophilic surface is needed for the assembly. The cleaned silicon wafer strips were placed vertically along the perimeter of a 25 mL beaker. A suspension of polystyrene spheres (4 vol%) in water was prepared from the stock suspension and bath sonicated for 20 min. to ensure the spheres were dispersed.

Two types of graphene-based suspensions were prepared. The first was an aqueous suspension of FGS (Batch 3030 provided by Vorbeck Materials, C/O of 33 measured by EDS) with triblock copolymer surfactant (ethylene oxide<sub>100</sub>-propylene oxide<sub>65</sub>-ethylene oxide<sub>100</sub>, F-127, Pluronic), which is added to enable the dispersion of the hydrophobic
material (FGS) in water. Briefly, 10 mg of triblock-copolymer was dissolved in 10 mL water. 10 mg of FGS was slowly added while tip sonicating (40% amplitude, Vibra-Cell, Sonics) on ice for approximately 1 h. The prepared suspension was centrifuged at 900 g for 10 min to remove large agglomerates. Two concentrations, 0.1 and 0.45 mg/mL were prepared by further diluting this stock suspension with distilled water. Secondly, aqueous suspensions of graphene oxide were prepared by dispersing GO powder in water (1 mg/mL). These suspensions were briefly tip sonicated on ice for 10 min before use. Additionally, a hydrolyzed tetraethylorthosilicate (TEOS) precursor solution (1:1:1.5 weight ratio of TEOS:0.10 M hydrochloric acid:ethanol) was used to reproduce the silica inverse opal structures reported by Hatton et al. These structures serves as our control to ensure that the original procedure was being executed correctly.

Either the FGS-triblock copolymer or graphene oxide suspension (20 mL) was added to the beaker followed by 1 mL of the 4 vol% polystyrene suspension. The beaker was placed in a 65°C oven and was removed when the liquid had evaporated and a film had deposited on the silicon wafer strip, shown schematically in Figure 2.3. The composite
films on the silicon wafer strips were analyzed as-is or subjected to heat treatment to remove the polystyrene spheres (and/or triblock-copolymer) and reduce the graphene oxide to conductive FGS. The films were heated under nitrogen in a tube furnace at a 2°C/min ramp rate to 400°C with a 30 min. hold at this temperature to ensure complete polystyrene degradation.

2.2.2 Physical Characterization

2.2.2.1 Scanning Electron Microscopy

FGS-based films were visualized using scanning electron microscopy (SEM, Tescan 5130MM) under 10 or 20 kV accelerating voltage. For cross-sectional images, the samples were fixed to aluminum sample holders with a 45° incline using conductive carbon tape. Images of insulating samples were taken after sputter coating with a 2 nm thick layer of iridium.

2.2.2.2 Powder X-Ray Diffraction

To analyze the spacing between the graphene oxide sheets (referred to as the $d_{0002}$ spacing, based on the crystallographic structure of GO), XRD spectra were recorded using a desktop diffractometer (Rigaku MiniFlex II) with a Cu Kα radiation source ($\lambda = 1.54$ Å). Typical measurement conditions feature a sampling of 2°/min at 30 kV and 15 mA. The $d_{0002}$ spacing of GO is fairly variable (~0.8-1 nm), but the peak is typically located near a scattering angle ($2\theta$) of 9-11°. Larger spacing corresponds to peaks at lower scattering angles. The $d_{0002}$ spacing is calculated from Bragg’s Law as:

$$d_{0002} = \frac{\lambda n}{2 \sin \theta}$$  \hspace{1cm} (2.1)
where \( n = 1 \).

### 2.2.2.3 Energy Dispersive X-Ray Spectroscopy

The C/O of materials was determined via energy dispersive X-ray spectroscopy (EDS, INCA x-act, Oxford Instruments) performed within the Tescan SEM noted above. The samples were analyzed at 10 kV accelerating voltage. The samples were prepared by drop casting a slurry of graphene oxide or FGS suspension onto conductive SEM sample holders. Typically, 5-10 areas on each sample were measured (500x magnification, 15 mm working distance) and the results were averaged and reported. Therefore, the C/O reported for the materials represents an average value for the bulk material, not necessarily the elemental composition of each, individual sheet.

### 2.2.2.4 Optical Microscopy

Images of the FGS-based suspensions were taken using bright-field optical microscopy (Zeiss Axioplan 2, Carl Zeiss MicroImaging, Inc.) and recorded using a 12-bit digital CCD camera (Zeiss AxioCam HRc, Carl Zeiss MicroImaging).

### 2.2.3 Electrochemical Characterization

#### 2.2.3.1 Electrode Preparation

The EDLC electrodes were produced as follows A prescribed amount of FGS-based material, RTIL and solvent was deposited onto platinum pucks (1.5 cm diameter) and the electrodes were left at room temperature to allow the solvent to evaporate. The electrodes were heat treated in a nitrogen-blanketed ashing furnace to 300°C (ramp rate of 20°C/min). The electrodes were weighed again and the mass of the platinum puck was subtracted from each to obtain the mass loading after heat treatment. Thermal gravimetric analysis was...
performed (449 C Jupiter, Erich Netzsch GmbH & Co., Germany) to determine the fraction of RTIL in the sample. This was executed by determining the mass difference between 500°C and 200°C (prior to RTIL decomposition). The mass of active carbonaceous material was determined by multiplying the total mass loading by the fraction of active material, as determined via TGA.

### 2.2.3.2 Cyclic Voltammetry

Cyclic voltammetry was performed on assembled EDLC electrodes using a computer-controlled digital potentiostat (VSP Bio-Logic USA Inc.). Scan rates from 5 to 500 mV/s were investigated. Gravimetric capacitance was calculated using the following equation:

$$C_G = 2 \frac{i_{avg}}{v \cdot m}$$  \hspace{1cm} (2.2)

where $i_{avg}$ is taken as the average of the absolute anodic and cathodic currents at the midpoint of the cyclic voltammogram, $v$ is the scan rate, and $m$ is the average mass of FGS on both electrodes. The cyclic voltammetry studies were performed using 3.0 V windows scanning from the open circuit potential.

### 2.3 Results and Discussion

#### 2.3.1 Large-Pore FGS Films

Figure 2.4 shows SEM images of inverse opal films generated using polystyrene spheres as the sacrificial template employing either silica or FGS-triblock copolymer as filler for the inter-particle void spaces. A prototypical silica inverse opal is shown in Figure 2.4(a) after the polystyrene spheres have been removed via heat treatment. As can be seen from the top-down surface image, the inverse opal features a regular hexagonal
arrangement of sub-micron pores separated by walls of silica. The pores are approximately 700 nm in diameter, a size which reflects the diameter of the polystyrene spheres used for the templation. As seen in Figure 2.4(b), the silica inverse opal film is relatively thin, as the cross-section of the film shows a thickness of 1.5 μm. Hatton *et al.* reported that the silica inverse opals remained crack-free while the film thickness remained below 5 μm, an observation which our results corroborate.

We attempted to reproduce this ordered inverse opal structure by substituting FGS for the silica precursor in the evaporative co-assembly. Figure 2.4(c) shows the composite film of FGSs-triblock copolymer and polystyrene spheres prior to heat treatment. As can be seen, the polystyrene spheres are not arranged in an organized hexagonal array, but are disordered. Some of the spheres appear to be partially coated by the FGS-triblock copolymer suspension.
copolymer. After heat treatment (Figure 2.4(d)) the carbonaceous film remains disordered and little evidence of the polystyrene sphere template can be seen. This observation suggests that the triblock copolymer-coated FGSs disrupt the packing of the polystyrene spheres, thereby preventing access to the previous low-energy crystalline state in favor of a new low-energy state or that the particles undergo reaction limited aggregation. Further studies would be needed to confirm either hypothesis. Reducing the concentration of the FGS-triblock copolymer suspension succeeds in re-establishing the dense packing of the polystyrene spheres in the top-layer of the film, as shown in Figure 2.4(e), though the packing is largely polycrystalline. However, after heat treatment a similar disordered carbonaceous structure is produced, which bears no resemblance to the inverse structure of the original polystyrene sphere template. The use of FGS-triblock copolymer in the evaporative assembly process results in disordered structures and appears to interfere with the crystalline templation. Additionally, the structure of the template is not maintained after heat treatment suggesting that the FGS-triblock copolymer material does not form mechanically stable structures.

The co-assembly procedure was repeated using aqueous suspensions of graphene oxide (which had been prepared via sonication of graphite oxide powder in water, as described in the Experimental Methods). Figure 2.5(a) shows the macroscopic films of graphene oxide and polystyrene spheres formed after the evaporative co-assembly. After heat treatment, black regions, which represent reduced graphene oxide (now conductive FGSs), are observed on the centimeter length scale. Figure 2.5(b) shows a freeze-fractured cross-sectional SEM image of the film after heat treatment. As can be seen, the morphology of
this as-processed film is significantly different than that of the FGS-triblock copolymer films. There is clear evidence of templation as the shape of the polystyrene spheres remains in the film even after the spheres are decomposed via the heat treatment. Unlike the FGS-triblock copolymer system, the graphene oxide appear to wrap around the polystyrene spheres, coating them prior to deposition on the silicon wafer. Figure 2.5(c) shows a top-down image of the film after heat treatment and provides further evidence that the void spaces are hollow as one can see dimpling of the FGSs on the surface of the film, likely due to local collapse of the sheets. However, like the FGS-triblock copolymer films, the packing of the polystyrene spheres is disordered suggesting that, like FGS, the graphene oxide too disrupts the crystalline packing of the spheres during evaporative assembly.

Though the polystyrene spheres can be used to introduce large, sub-micron scale pore sizes into FGS-based films, one can question the practicality of the resulting stand-alone films as electrodes for EDLC application. First, the pore space in an EDLC electrode should be continuous and readily accessible. However, the accessibility of the large pore

![Figure 2.5: Graphene oxide-based inverse opal films.](image)

(a) Silicon wafer strips after the co-assembly shown for graphene oxide suspensions in order of decreasing concentration (0.5, 0.3, 0.05, and 0.03 mg/mL) before (top) and after (bottom) heat treatment to remove the polystyrene spheres. (b) Freeze-fractured cross-sectional SEM image of the film produced using 0.3 mg/mL graphene oxide suspension after heat treatment. (c) SEM image of the top of the same film.
spaces in Figure 2.5 is questionable; though the pores are large, entrance into the pores appears to be restricted. More importantly, the size of the pores that we introduce is extremely large for an EDLC and the amount of electrolyte which will be needed to fill these pores is excessive. Back of the envelope calculations show that the electrolyte would account for more than 99% of the total electrode’s weight, which will drastically lower the device’s energy density ($f \sim 0.01$). Lastly, the ion-accessible specific surface area of the structure is expected to be low, as the majority of the FGSs are likely re-stacked in the FGS shell seen in Figure 2.5(c). At the time this work was performed (ca. 2010) there were no reports in the literature showing a stable FGS-based structure via the evaporative assembly templation procedure, though composites of graphene-based materials and colloidal spheres had been produced.\textsuperscript{11-14} Reports of low-density graphene-based structures had been published and touted as promising electrodes for EDLCs.\textsuperscript{15-17} However, the authors of these works do not properly account for the total weight of the device (electrolyte, binders etc.), a consideration which was not appreciated by the EDLC community until the middle of my Ph.D. work.

However, the design of large-pore FGS structures turned my attention to the critical problem at hand for EDLCs. Instead of developing methods to engineer the sub-micron-scale pore size of FGS-based films, I realized that I needed to focus on developing methods to control the structure of the “wall” in Figure 2.5(b), or, more specifically, understand how to control the spacing of the FGSs on the nanometer length scale. This length scale is critical to the development of high energy density EDLCs as nanometer-sized pores will ensure the highest packing density of FGS and the lowest electrolyte content, two factors
which will increase the energy density of the device. I acknowledge that for appropriate rate performance, porosity at multiple length scales will be needed, and therefore a device which consists only of nanometer-sized pores is not expected to be the optimal configuration for the device. As I have shown, methods can be implemented to introduce porosity at larger length scales, but understanding the nanometer-scale spacing of FGSs is a scientific and technical challenge which currently limits the energy density of the device. The remainder of the work detailed in this chapter aims to address this engineering problem.

2.3.2 Graphene Oxide-Alcohol-Ionic Liquid Ternary Systems

Instead of employing complex processing routes, such as the inverse opal procedure, I aimed to study two-component FGS and RTIL system, in which the RTIL served as a spacer to keep the FGSs separated, thereby increasing the ion-accessible surface area. In an attempt to study this system, I investigated whether electrodes could be processed simply from the starting graphene oxide-ethanol suspension.

In order to perfectly coat graphene oxide with a monolayer of RTIL, one must find a RTIL that completely spreads on the graphene oxide (i.e., achieves a vanishing contact angle). Measuring the contact angle of liquids on nanomaterials such as graphene oxide is challenging, as macroscopic films of the nanomaterials feature porosity and roughness, which complicates the experiment. RTILs have been categorized as “hydrophilic” or “hydrophobic” based on the physicochemical properties of the anion in the compound, which largely dictates its miscibility in water. In this respect, one may expect a “hydrophilic” RTIL to wet graphene oxide significantly better than a “hydrophobic” RTIL
as graphene oxide is decorated with hydroxyl groups and disperses well in water. Therefore, by tuning the properties of the RTIL we would expect to tune the degree of RTIL wetting. Additionally, solvent considerations are also important for the coating procedure as the solvent can compete with the RTIL for space at the surface of the graphene oxide, depending on its affinity.

Figure 2.6 shows four mixtures of graphene oxide with two different alcohols (ethanol and 1-hexanol) and RTILs (EMImBF$_4$ and EMImTFSI). As can be seen in Figures 2.6(a) and (b) EMImBF$_4$ is not miscible in either ethanol or 1-hexanol, forming distinct phase boundaries, highlighted by the dotted lines in the images. When EMImBF$_4$ is added to graphene oxide-ethanol and GO-1-hexanol suspensions, a dense pellet forms and falls out of suspension. TGA of the pellet revealed that it featured a mass ratio of graphene oxide:EMImBF$_4$ identical to that of starting suspension (89:11), before the pellet formed.

![Figure 2.6: Ternary mixtures of graphene oxide with alcohol-RTIL combinations.](image)

Graphene oxide with (a) ethanol and EMImBF$_4$, (b) 1-hexanol and EMImBF$_4$, (c) ethanol and EMImTFSI, (d) 1-hexanol and EMImTFSI. Mixtures of the alcohol-RTIL combinations are shown to the left of each image. A pellet is observed in the ternary systems of (a) and (b).
This suggests that the graphene oxide completely entered the EMImBF$_4$ phase. However, when EMImTFSI was added to the same suspensions, a pellet did not form, but a concentrated slurry remained, which did not settle on the time scale of days. Figure 2.7 shows optical microscopy images of the graphene oxide-1-hexanol system in the presence of a small amount of GO powder. As can be seen, a Pickering emulsion forms with the GO trapped at the interface between an EMImTFSI droplet and the bulk 1-hexanol phase; this behavior has been observed for graphene oxide-oil-water systems.\textsuperscript{18} Figure 2.7(b) confirms that GO is not present within the droplet, and remains only at the interface. However, the optical microscopy image of the actual system (\textit{i.e.}, starting with a GO suspension rather than “dry” GO powder), shown in Figure 2.7(c), does not show obvious signs of a Pickering emulsion. This is likely due to the better dispersion of graphene oxide prepared in alcohol than GO powder added to alcohol-RTIL emulsions.

To study how the spacing of the graphene oxide sheets is affected during drop-casting into electrodes, XRD was performed on the as-prepared, drop-cast films. Figure 2.8 shows XRD spectra for the graphene oxide-ethanol-RTIL mixtures after the alcohol has evaporated. As can be seen, when no RTIL is added to the graphene oxide-ethanol

\textbf{Figure 2.7: Optical microscopy of EMImTFSI-1-hexanol emulsions.} (a) GO powder added to a mixture of 1-hexanol and EMImTFSI; (b) Cross-sectional image of the droplet showing the GO particles trapped at the interface between the two phases; (c) Actual GO-1-hexanol-EMImTFSI system, diluted 20x with 1-hexanol.
suspension, the characteristic GO peak at a scattering angle of 9.4° is observed. The dense pellet which resulted from the graphene oxide-ethanol-EMImBF$_4$ ternary system showed no measurable GO peak at EMImBF$_4$ content of 77 and 89 wt%, indicating that the presence of the RTIL has disrupted the regular packing of the sheets and prevented the formation of discrete GO domains, such that the sample appears X-ray amorphous. Additionally, the XRD spectrum for the sample containing 75 wt% of EMImTFSI did not show a discernable GO peak, indicating that this combination of graphene oxide and RTIL also successfully disrupted the stacking of graphene oxide into GO. This is surprising as one may have expected the “hydrophobic” RTIL to have phase separated from the graphene oxide; however, the results suggest that both RTILs can be used to eliminate the GO peak.

EDLC electrodes were prepared from the graphene oxide-RTIL composites in order to measure their gravimetric capacitance. Before testing, the electrodes were heat treated to reduce the graphene oxide to conductive FGSs. Though I intended to test both the graphene
oxide-EMImBF$_4$ and graphene oxide-EMImTFSI composites prepared from the ternary systems, the former could not be processed into electrodes for testing: the dense pellets which formed from the graphene oxide-alcohol-EMImBF$_4$ system could not be reproducibly pressed into thin films needed for testing. As a result, the thick films that I was able to prepare had poor rate performance; the resistance of such cells was found to be on the order of 1 kΩ. However, I was able to test electrodes produced from the graphene oxide-alcohol-EMImTFSI ternary system. Figure 2.9 presents the gravimetric capacitance of the electrodes fabricated from the graphene oxide-EMImTFSI composites. At low loadings of FGS (0.5 mg/cm$^2$) and high EMImTFSI content (85 wt%), an impressively high capacitance of 134 F/g for RTIL-based electrodes is achieved at 5 mV/s. Accounting for the RTIL content in the electrode, this gravimetric capacitance corresponds to an energy density of 6.3 Wh/kg, which is on-par with the energy density achieved in commercial devices. However, at a more practical loading (3.5 mg/cm$^2$) the capacitance decreases to 80 F/g and the energy density decreases by 40%. A similar decrease is observed when the total EMImTFSI content in the composite electrode is reduced (but the electrode is kept
In comparison, electrodes fabricated in a similar manner using FGS-ethanol suspensions yielded exceptionally low capacitance (~40 F/g) at similar mass loading (0.5 mg/cm$^2$). This is likely due to the poor FGS dispersion in ethanol resulting in a relatively low surface area.

### 2.3.3 $d_{002}$ Spacing of Stacked Graphene Oxide During Drying

In the preparation of GO, after the washing procedure the material is typically stored as a suspension in ethanol. It is well-known that GO exfoliates into graphene oxide with subtle mechanical agitation in water and henceforth can form stable, charge stabilized suspensions.\textsuperscript{19-22} However, the aggregation state of this material in alcohols is unclear and has not been thoroughly investigated.\textsuperscript{23-26} Figure 2.10 shows XRD spectra for samples of concentrated graphene oxide suspensions (~10 mg/mL) in either ethanol or mixtures of ethanol and water to study how the inter-sheet spacing of the material is affected by the solvent.

Figure 2.10(a) shows XRD spectra for graphene oxide suspensions in 100 vol% ethanol (with trace water from atmospheric exposure). As can be seen, initially the spectrum is featureless (black line) as no peaks are observed. At early drying times, a broad peak at a scattering angle of 5.9° is observed while the characteristic GO peak (typically observed near a scattering angle of 10°) is absent. As the ethanol evaporates, the peak at 5.9° initially increases and then begins to shift toward larger scattering angles and decreases in intensity. Around 30 min, two peaks are observed, one at 8° and the other at 10°, the characteristic scattering angle of GO. Toward the end of the drying process, only the peak near 10° is present, indicating that the sheets have restacked and achieved the spacing of GO.
Figure 2.10: XRD of graphene oxide suspensions during solvent evaporation. XRD of GO suspended in (a) 100 vol% ethanol, with trace water, (b) 14 vol% water, 86 vol% ethanol and (c) 83 vol% water, 17 vol% ethanol during solvent evaporation.

Figure 2.10(b) shows the drying behavior of a graphene oxide-ethanol suspension in which a small amount of water has been added. Again, initially peaks are not observed for the sample; however, at early drying times a large, broad peak is observed near 4.5°, a lower scattering angle than that observed for the 100 vol% ethanol suspension (Figure 2.10(a)). The breadth of the peak appears to extend to scattering angles lower than
4.0°, and then settles between 4 and 6° for the first 30 min of drying. A similar transition is observed with time in which the former peak decreases, while the GO peak begins to emerge. Interestingly, when the water content is increased to 83 vol%, as seen in Figure 2.10(c), a peak near 5.0° at early drying times is absent and only slightly emerges at intermediate drying times (~54 min).

In Figure 2.10(a), the peak at a scattering angle of 5.9° corresponds to a $d_{002}$ spacing of 1.51 nm, while the GO peak corresponds to a $d_{002}$ spacing of 0.92 nm. Interestingly, the difference in the $d_{002}$ spacing between these peaks is ~0.5 nm, or approximately the size of a single ethanol molecule. These results suggest that the graphene oxide sheets are not restacked as GO while in suspension, but that ethanol molecules are likely intercalated between the graphene oxide sheets, effectively keeping their spacing larger than that of neat GO. The lack of either peak at the onset of the experiment suggests that initially the graphene oxide sheets are substantially swollen with ethanol, and only after some evaporation occurs, do the sheets maintain a consistent $d_{002}$ spacing. This presence of ethanol between the sheets is plausible as one might expect significant hydrogen bonding to occur between the alcohol group of ethanol and the oxygen-containing functional groups on the graphene oxide.

The addition of water (Figure 2.10(b)) enhances the swelling between the sheets as the $d_{002}$ spacing of the peak at low scattering angle (referred to as the “ethanol peak”) increases to 1.9 nm ($2\theta = 4.5^\circ$). As ethanol and water form a 96:4 vol:vol minimum boiling azeotrope, we expect the intermolecular interactions between ethanol and water to be non-ideal. Additionally, the presence of water will change the degree of ionization of the sheets due
to proton transfer from the acidic groups on the graphene oxide to the water solvent. The subsequent electrostatic repulsion may serve to drastically separate the sheets. Interestingly, the ethanol peak in the presence of water (Figure 2.10(b)) does not gradually move toward the GO peak, but rather, two discrete peaks are observed. Though conclusions cannot be drawn about the final structure of the intercalants for the ethanol/water mixtures given these data alone, it is clear that the drying process in ethanol is significantly different than that in water.

2.4 Conclusions

Sub-micron sized pores introduced into FGS-based thin films (< 5 μm thickness) were assembled via an evaporation-induced co-assembly of graphene-based materials and polystyrene spheres. Films constructed from graphene oxide suspensions featured robust pores which did not collapse after heat treatment, while films fabricated from pre-reduced graphene oxide (FGSs) exhibited disordered structures which did not resemble the original opal template.

To gain insight into controlling the spacing of individual FGSs on the nanometer-length scale, the simple addition of RTILs to graphene oxide-alcohol suspensions was studied. The addition of EMImTFSI to a graphene oxide-ethanol suspension and subsequent thermal reduction of the GO to conductive FGSs resulted in electrodes with a gravimetric capacitance of 134 F/g and corresponding energy density of 6.3 Wh/kg. The drying of graphene oxide from alcohol suspensions was investigated and the results showed evidence that alcohols intercalate between the graphene oxide sheets in suspension, and effectively
increase the $d_{0002}$ spacing. This suggests that the sheets are not collapsed into a GO structure before the solvent completely evaporates. These processing strategies hold promise in developing bottom-up techniques to assemble EDLC electrodes from graphene oxide-alcohol suspensions.

References


3 Dehydrated Sucrose as a Spacer for Functionalized Graphene-Ionic Liquid EDLC Electrodes

This chapter is adapted from work to be submitted to ACS Applied Materials & Interfaces coauthored with Sibel Korkut, Michael Pope and Ilhan Aksay. S. Korkut provided input in every aspect of the experimental design: she helped with material preparation, assembled and ran the EDLCs, performed the XRD measurements and took optical microscope images of the FGS-DS suspensions. M. Pope processed the graphene oxide and provided input on the experimental design and electrochemical measurements.

Chapter 2 explored two processing strategies to control the architecture of FGS-based electrodes: (i) evaporative co-assembly with polymer templates and (ii) evaporative consolidation. The latter approach, which consisted of simply drop-casting mixtures of graphene oxide and RTILs and subsequently heating the resulting films showed promise; however, the procedure suffers from a fundamental problem. In order to coat each FGS with RTIL, the RTIL will have to perfectly wet the sheets. This is difficult to achieve in the proposed processing strategy as the hydrophilicity of the material changes during processing: a hydrophilic material (i.e., graphene oxide) is reduced to a more hydrophobic material. Tuning the wettability of the RTIL so that it is compatible with the FGSs at a particular reduction state is challenging. Alternatively, in this Chapter, we explore the
addition of solid-state nanoparticles into the FGS-RTIL composite electrodes to investigate whether they can serve as physical spacers for the FGSs. As mentioned in the previous chapters, to properly account for the energy density of the device, one must consider the mass of all components in the electrode. Thus, any additional component in the electrode must provide a benefit (e.g., increasing capacitance or surface area) which outweighs its mass contribution to enhance the energy density of the electrode. Here, we show that sucrose-derived nanoparticles can be used as spacers to prevent graphene oxide sheets from restacking during processing. We also show that the energy density of the electrodes can be increased through the use of these nanoparticles and provide evidence that further optimization of the system will afford improvements in the energy density of the devices.

3.1 Introduction

As discussed in Chapter 1, EDLCs are devices that store energy by accumulating charge within the double-layer between an electrolyte and a high surface area electrode.\(^1\) This rapid and efficient charge storage mechanism provides EDLCs with advantages such as high power density and long cycle life.\(^2\) However, the energy density (\(E\)) of EDLCs (5 Wh/kg) is markedly lower than commercial lead-acid (35 Wh/kg) and lithium-ion (200 Wh/kg) batteries, a disadvantage which currently limits their widespread use.\(^3-5\) Consequently, current research efforts are focused on increasing the energy density of EDLCs without sacrificing their high rate performance. These efforts involve not only selecting appropriate materials, but also carefully engineering the electrode’s architecture.

The \(E\) of an EDLC can be estimated in the limit of an infinitely thin film as
\[ E = \frac{f}{8} C_G U^2 \]  

where \( f \) is the mass fraction of the active electrode material, \( C_G \) is the gravimetric capacitance of the active material and \( U \) is the operating voltage.\(^6\) Historically, much attention has been given in the literature to maximizing \( C_G \). Efforts to increase \( C_G \) have relied on using electrically conductive materials with a high ion-accessible specific surface area as \( C_G \) is represented as the product of the mass specific surface area (SSA), the areal capacitance of the material (\( C_{DL} \)) and the fraction of the material which is ion-accessible. Currently, activated carbons are employed in commercial EDLCs as they are low-cost materials which are electrically conductive and feature a high SSA.\(^7-8\) However, the distribution of the smallest pore sizes within each particle of the material is extremely narrow with pore sizes often below one nanometer.\(^9-10\) With the use of larger, more electrochemically stable electrolyte molecules, such as RTILs, the fraction of ion-accessible surface area is expected to be low.\(^11-12\) In an attempt to improve upon the current EDLC active material, other carbonaceous materials such as carbon black,\(^13\) carbon nanotubes,\(^14\) carbide-derived carbons\(^15-16\) and graphene materials\(^6, 17-20\) have been studied as active materials for EDLC electrodes. In particular, functionalized graphene sheets (FGSs), a class of graphene-like materials produced via the thermal reduction and exfoliation of GO,\(^21-22\) or the chemical reduction of graphene oxide,\(^23\) are promising materials for EDLCs as they boast an exceptionally high SSA up to \( 2,630 \text{ m}^2/\text{g} \),\(^24\) and can exhibit a \( C_{DL} \) up to 5 times greater than pristine graphene due to their high density of residual functional groups and defects.\(^25\) Additionally, unlike activated carbon, the FGSs
do not contain an intrinsic, rigid network of nanopores as they are flexible, one-dimensional sheets. Consequently, the pore size and, hence, SSA of the bulk material is almost exclusively dependent upon how the individual FGSs are assembled. Typically, FGS-based electrodes are processed after from suspensions of dispersed FGSs in an appropriate solvent as the SSA of the sheets has been measured to be as high as 1850 m$^2$/g (measured via methylene blue adsorption) in such suspensions. However, upon solvent evaporation, capillary and van der Waals forces cause the sheets to collapse and re-stack, reducing the SSA of the resulting material dramatically. Thus, one of the greatest challenges in reaching the potential performance of FGS-based EDLCs is processing the FGSs in a manner which maintains a high, ion-accessible SSA.

Attempts to prevent the re-stacking of FGSs focus primarily on two approaches, either the physically alternation of the morphology of the FGSs, or the addition of a second component to serve as an inter-sheet spacer. For example, Luo et al. demonstrated the former approach by showing that crumpled FGSs produced via controlled capillary compression during spray drying resulted in a SSA nearly twice that of in-crumpled sheets. However, the pore sizes of the resulting material were difficult to control and were often large, on the order of 0.1-1 μm. Though these large pores may improve the ionic transport in the device, the excess electrolyte required to fill these pores will reduce $f$ by adding extra weight to the electrode and, hence, decrease the $E$ of the EDLC. Thus, maximizing the SSA of the electrode is necessary but not sufficient in achieving highly energy dense electrodes as one must consider how the mass of all components of the electrode (activate materials and electrolyte) will affect $f$. 
The addition of a secondary component to serve as an inter-sheet spacer for FGS is a more promising approach as one can theoretically tune the inter-sheet spacing of the FGSs in the electrode. Metal nanoparticles, inorganic nanoparticles, small molecules, polymers, carbon nanotubes and carbon blacks have been proposed as spacer materials for FGSs. Though these works report high \( C_G \) for their resulting electrodes, as shown in Table 3.1, they often fail to report critical details, such as the total weight of the added spacers or the total electrolyte content, two components which will significantly affect the performance of the electrodes.

<table>
<thead>
<tr>
<th>Spacer</th>
<th>( C_G ) (F/g)</th>
<th>Electrolyte</th>
<th>Spacer content</th>
<th>Additives</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>tin nanoparticles</td>
<td>320</td>
<td>2 M KNO(_3)</td>
<td>n.r.</td>
<td>n.r.</td>
<td>Wang et al.(^{39})</td>
</tr>
<tr>
<td>carbon nanotubes</td>
<td>318</td>
<td>30 wt% KOH</td>
<td>50 wt%</td>
<td>10% PTFE binder</td>
<td>Wang et al.(^{54})</td>
</tr>
<tr>
<td>carbon nanotubes</td>
<td>290.6</td>
<td>1 M KCl</td>
<td>50 wt%</td>
<td>n.r.</td>
<td>Cheng et al.(^{45})</td>
</tr>
<tr>
<td>p-phenyldiamine</td>
<td>282</td>
<td>1 M ( \text{H}_2\text{SO}_4 )</td>
<td>n.r.</td>
<td>Few drops of Nafion(^\circledR)</td>
<td>Sk et al.(^{41})</td>
</tr>
<tr>
<td>platinum nanoparticles</td>
<td>269</td>
<td>“acid”</td>
<td>n.r.</td>
<td>n.r.</td>
<td>Si et al.(^{27})</td>
</tr>
<tr>
<td>calcium carbonate nanoparticles</td>
<td>240</td>
<td>2 M KCl</td>
<td>n.r.</td>
<td>n.r.</td>
<td>Salgado et al.(^{40})</td>
</tr>
<tr>
<td>melamine resin</td>
<td>210</td>
<td>1 M LiPF(_6) in EC/DEC</td>
<td>n.r.</td>
<td>10 wt%% Super P(^\text{TM}) &amp; 10 wt% PVDF</td>
<td>Lee et al.(^{57})</td>
</tr>
<tr>
<td>carbon black</td>
<td>138</td>
<td>6 M KOH</td>
<td>n.r.</td>
<td>n.r.</td>
<td>Wang et al.(^{56})</td>
</tr>
</tbody>
</table>

n.r. = not reported

Minimum spacer content calculated from experimental parameters is indicated in parentheses when available.
affect $E$. Additionally, the resulting electrodes are typically processed into a dry film and hence require subsequent imbibition of the electrolyte, a difficult process which is often complicated by wettability issues or the presence of air in the dry electrode.\textsuperscript{1} Furthermore, the performance of such electrodes using high voltage RTIL electrolytes is not reported by most.

More recently, techniques have been developed to use RTILs as both an electrolyte and spacer for FGS-based electrodes.\textsuperscript{6,38,47} Non-dehydrating approaches succeed in preventing the sheets from re-stacking by keeping the processed films hydrated.\textsuperscript{47} However, these approaches require an unwieldy FGS consolidation step requiring vacuum filtration and a lengthy solvent exchange process (typically more than 12 hours) in which the water is exchanged with a hydrophilic RTIL. Hence, the process is cumbersome and difficult to scale commercially. Pope \textit{et al.} developed a bottom-up approach that is industrially scalable by showing that aqueous gels of graphene oxide and RTIL could be evaporatively consolidated and subsequently heat treated to produce EDLC electrodes.\textsuperscript{6} This facile processing route eliminated difficulties regarding electrolyte imbibition; however, the resulting $C_G$ of the electrodes was low (143 F/g) compared to reported theoretical values (> 280 F/g) suggesting that the RTIL alone may not have served as an adequate spacer for the FGSs. This may be due to imperfect wetting of the FGSs by the RTIL.

Herein, we combine the processing ease of the evaporative consolidation approach with the addition of nanometer-sized carbonaceous particles which we synthesize from sucrose and which we call “dehydrated sucrose” (DS) in an attempt to improve the $E$ of the electrodes. We show that this material can serve as a spacer to prevent graphene oxide
sheets from restacking into GO. In our analysis of electrodes fabricated from graphene oxide-DS composites, we pay particular attention to how the added weight of both the spacer and RTIL affect $E$ and investigate the trade-off that occurs between $C_G$ and $f$. By adjusting the RTIL content in the electrodes, we show that the $C_G$ of the resulting electrodes can be significantly increased with the addition of spacers. However, despite the gains in $C_G$, the gains in $E$ are largely affected by the amount of spacer and RTIL in the final electrode. In properly accounting for the $f$ of each electrode, we show that a maximum energy density of 13.3 Wh/kg is obtained for electrodes with a spacer mass fraction of 0.6 (based on total solids fraction) and a total RTIL content of 61 wt%. Interestingly, though electrodes with a larger RTIL content had larger $C_G$ values at high charge and discharge rates, the resulting $E$ of the electrodes was comparable to that of electrodes with lower RTIL content, as the added mass of the RTIL did not outweigh the gains in capacitance. Our analysis shows that considering the added inactive components is critical to gauging accurate insight into the practical $E$ of the prepared electrodes.

3.2 Carbonaceous Nanoparticles

3.2.1 Terminology

Before presenting results, information about carbonaceous nanoparticles is presented here as backdrop for understanding the chemical composition and structure of the DS, which we synthesize. An extensive literature exists regarding the production and use of carbonaceous nanoparticles. In referring to carbonaceous nanoparticles in this Section, materials such as carbon nanotubes and graphene are excluded, though they have
nanometer-scale dimensions, and am referring primarily to nanometer-sized spherical particles. The terminology which the community uses to refer to these particles is poorly defined and often misleading. Names such as “carbon nanoparticle,” “carbon nanodot,” “carbon nanodiamond,” and “carbogenic nanodot” are used in the literature and though they sound similar, they describe materials that are rather different from each other and, additionally, often different from what their literal names imply. For example, the “carbon nanoparticles” or “carbon nanodots” reported in the literature are misleading as they do not consist solely of elemental carbon, but contain a significant amount of oxygen. They are typically produced via carbonaceous precursors, such as candle soot, carbohydrates or resins using oxidation protocols or hydrothermal treatments. Though such materials typically feature sizes below 10 nm, their carbon contents vary widely, from ~50 to ~90 at%. Carbon nanodiamonds are truer to their name as they typically have carbon contents greater than 90 at%. These materials are formed from a variety of processing routes, including milling microdiamonds, chemical vapor deposition, and shockwave or detonation procedures. However, the carbon-carbon bonding of these nanoparticles have a high sp³ character, characteristic of diamond, and are hence considered to be electronically insulating. The term “carbogenic nanodot” was first popularized by Bourlinos et al., and currently stands as the most correct, literal term to describe this class of nanomaterials. They explicitly admit in their work that their particles are not solely composed of elemental carbon, but contain a significant amount of oxygen which exists as various oxygen-containing functional groups. Due to the hazy terminology which exists in the literature, we prefer to categorize our nanoparticles as
“carbonaceous” as the word is sufficiently general and inclusive of all of the aforementioned materials.

3.2.2 Hydrothermal Synthesis via Sucrose

Originally we had aimed to produce conductive carbonaceous nanoparticles having sizes less than 5 nm and a sufficiently high carbon content. Additionally, we wanted the particles to be able to be dispersed in aqueous suspension, as the processing route that we aimed to employ was water-based. We adapted a synthesis protocol from Zhang et al. to produce “hydrophilic carbon nanoparticles” based on the hydrothermal, acid-catalyzed decomposition of sucrose.49 This material, in particular, was appealing as Zhang et al. showed that it not only featured a particle size distribution between 2 and 5 nm, but also contained graphitic domains as evidenced by XRD, a piece of evidence which suggested that the particles were conductive. However, the synthesis was highly dependent on the details regarding the kinetics of the chemical reaction, which were not provided. Particle size, concentration and chemical composition were all dependent on the rates at which (i) concentrated sulfuric acid was added to the carbohydrate precursor and (ii) the reaction product was quenched by concentrated base. (Note: For full experimental details, see Section 3.3). Therefore, though we aimed to produce conductive carbon nanoparticles, the material which we were able to produce did not feature a graphitic peak, nor did it show other experimental signs indicating carbon–carbon conjugation. Additionally, the particles were not entirely carbon, but contained a significant amount of oxygen. The implications of the characterization details will be discussed fully in Section 3.4.
3.2.3 Thermal Decomposition of Sucrose

The thermal decomposition of carbohydrates has been well-studied, especially for applications in the food industry. In particular, Tomasik et al. provide an excellent review of the thermolysis of carbohydrates.⁵⁸ Here, I use historic context to better understand the DS material which we are synthesizing. According to the literature, our DS can be classified as a type of caramel containing a polymeric component, referred to as “texture,” and a small molecule component, regarded as “flavor.”⁵⁹ Caramels produced from aqueous sugar solutions are typically acidic, and the chemical composition of the caramel at low heat treatment (below the boiling point of water) is very similar to that of the starting sugar.⁶⁰ Based on information in the literature, our DS may be more of a condensed polymer than a dense particle.

The chemistry we use (adapted from Zhang et al.) is a type of browning reaction, aptly named as this class of reactions turns the carbohydrates a brownish color.⁴⁹ There are two classes of browning reactions: enzymatic and non-enzymatic.⁶¹ Enzymatic browning reactions are responsible for turning a freshly cut piece of apple brown and are typically naturally occurring. Non-enzymatic browning reactions are synthetically used in the food industry to impart color and add flavor to foods. There are two types of non-enzymatic browning reactions: Maillard reactions and caramelization. Maillard reactions involve sugars reacting with the amino acids of proteins; these reactions are used to make chewy candies by heating sugar and milk together.⁶² Caramelization is the thermally catalyzed decomposition of sugar and, to date, is a poorly understood process. Caramelization encompasses the removal of water from the carbohydrate, the restructuring of the
dehydrated products and polymerization of the products to form larger molecules. We expect the acid-catalyzed dehydration to mirror this latter reaction as amino acids are absent in our synthesis.

Rosalind Franklin, in her seminal 1951 work entitled “Crystallite growth in graphitizing and non-graphitizing carbons,” studied the carbonization of organic compounds, including sucrose (or “sugar” as she calls it) using XRD. She used four terms to categorize her carbonaceous materials:

- **Graphitic carbon**: carbon materials in which the three-dimensional graphite structure is partially developed.
- **Non-graphitic carbon**: carbon materials which may contain graphite-like (i.e., graphene) layers but are not oriented as in the crystalline structure of graphite.
- **Graphitizing carbon**: carbon materials which upon heating between 1700 and 3000 °C form graphitic carbons
- **Non-graphitizing carbon**: carbon material which upon heating to 3000 °C shows no homogeneous development of the graphitic structure.

Using these definitions, she defined pyrolyzed sucrose as a *non-graphitizing carbon* as even at extremely high temperatures, it resists rearranging into dense, three-dimensional graphite. Based on her XRD results, she attributes sucrose’s poor graphitization to a high degree of carbon-carbon crosslinking which occurs during heat treatment. Additionally, evolution of carbon dioxide, carbon monoxide and water during the heat treatment of carbohydrates may also contribute to the disordered structure of the carbonized product. Franklin claims that the crosslinking occurs in three dimensions (i.e., it is not confined to
two dimensions) impedes the reorganization of the carbon atoms and traps the material in an amorphous state. Franklin’s assertion has been supported by tunneling electron micrographs, reproduced in Figure 3.1, comparing sucrose and anthracene, a solid polycyclic aromatic hydrocarbon (C\textsubscript{14}H\textsubscript{10}) consisting of three fused benzene rings, after thermolysis at 1000 °C under nitrogen.\textsuperscript{64} As can be seen, the carbonaceous material resulting from thermolysis of sucrose (non-graphitizing carbon) has structural anisotropy characteristic of an amorphous material, while the carbonaceous material formed by thermolyzing anthracene (graphitizing carbon) is more ordered.

### 3.3 Experimental Methods

Experimental details specific to this chapter are provided, including the synthesis of DS and the preparation and electrochemical testing of EDLC electrodes. Characterization techniques such as contact-mode and liquid cell atomic force microscopy (LC-AFM), XRD, and Raman spectroscopy are also discussed. Details regarding the processing of graphene oxide can be found in Chapter 2.
3.3.1 Synthesis of Dehydrated Sucrose

DS was synthesized according to an acid-catalyzed dehydration of sucrose adapted from Zhang et al., as shown in Figure 3.2. Briefly, 3 g of a saturated aqueous suspension of sucrose (2.0 g sucrose per 1 mL water) was added to a scintillation vial containing a PTFE stir-bar. Concentrated sulfuric acid (98%) was added drop-wise from a glass syringe (inner diameter: 10.3 mm) at a rate of 0.25 mL/min under vigorous stirring. After adding 2 mL of the concentrated sulfuric acid, the reaction mixture was quickly diluted in 40 mL of DI water and stirred for an additional 30 s. At this point the reaction mixture appeared dark brown in color. Lastly, two aliquots of 3 mL of 0.5 g/mL NaOH were pipetted sequentially into the mixture and, visually, the mixture turned a light shade of orange. This batch procedure was carried out 15-20 times and each batch of reaction product was consolidated and distributed into 3.5 kDa dialysis membranes and dialyzed for 10 days against DI water which was exchanged daily. The pH was not tracked during the reaction; however, it was measured after dialysis to be between 4.0 and 5.6. We refer to the solid material which remained in aqueous suspension after dialysis as DS. The concentration of the aqueous suspensions of DS was determined to be 0.23 mg/mL by weighing the residual

![Figure 3.2: Synthesis of dehydrated sucrose.](image)

Overview of the experimental protocol used to synthesize aqueous suspensions of DS. Product shown in aqueous suspension of 0.23 mg/mL DS.
mass of a 20 mL sample after allowing the water to evaporate. To increase the concentration, the stock suspension was concentrated by placing a large volume in a crystallization dish on a hot plate set to 70 °C and evaporating a portion of the water. This concentrated suspension was used to prepare the EDLC electrodes.

### 3.3.2 Preparation of Electrodes

The procedure for electrode preparation is based on modifications to the evaporative consolidation approach proposed by Pope et al. Aqueous suspensions of graphene oxide and DS were prepared having different mass ratios of graphene oxide to DS, while maintaining the total solids content at 8 mg/mL. 1-ethyl-3-methylimidazolium tetrafluoroborate (EMImBF$_4$) was purchased from Sigma-Aldrich at its highest available purity (> 99%) and used as received. This RTIL was selected as it is miscible with water and is commonly used in the EDLCs as an electrolyte due to its high conductivity and large electrochemical stability window.$^{65}$ Two batches of electrodes were prepared, each differing in the way in which the total EMImBF$_4$ content was maintained. For the first batch of electrodes, the EMImBF$_4$ content was maintained at a mass ratio of 70:30 with respect to the total initial amount of graphene oxide in the electrode; we refer to these electrodes as “electrolyte-lean.” For the second batch of electrodes, the EMImBF$_4$ content was maintained at a mass ratio of 70:30 with respect to the total initial mass of solids, and these electrodes are referred to as “electrolyte-rich.” Volumes of the prepared suspensions were drop-cast onto platinum pucks (1.5 cm diameter, 99.9% purity) such that a total loading of 1.5 mg graphene oxide was achieved. The electrodes were left to dry overnight. The evaporatively consolidated electrodes were placed in an ashing furnace and heat
CHAPTER 3

treated in an inert nitrogen atmosphere to 300 °C (ramp rate of 20 °C/min.) after which the furnace was shut off and the electrodes were left to cool back to room temperature. This effectively reduced the graphene oxide to conductive FGSs.

3.3.3 Characterization

The mass of the thermally reduced FGS-DS-EMImBF$_4$ films was determined by weighing the electrode after heat treatment and subtracting the mass of the platinum puck. To experimentally measure the solids loading post-heat treatment, a sacrificial electrode was prepared and the film is scraped off and analyzed with thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC, 449 C Jupiter, Erich Netzsch GmbH & Co., Germany). This was performed by heating the films to 500 °C, beyond the decomposition temperature of EMImBF$_4$, and determining the residual mass of the film at this temperature. Previous work has shown that the additional mass loss due to the further reduction of FGSs does not contribute significantly to the total mass loss measured.$^6$ By means of independent TGA analysis of the DS material we also determine that the additional mass loss from the DS in the film is minor. The mass of FGSs on each electrode was determined by first multiplying the total mass of the reduced film by the mass fraction of total solid material in the film determined by TGA, and secondly by multiplying by the mass fraction of FGS based on the initial graphene oxide:DS solids ratio. Despite the thermal reduction of the materials, as the mass loss of both graphene oxide and DS is similar to 300 °C, we find that this ratio still accurately represents the ratio of FGS:DS in the heat treated film.
Additional characterization of the materials was performed. The carbon to oxygen ratios (C/O) of the materials before and after heat treatment were estimated using EDS. Contact mode and liquid cell AFM (MultiMode AFM with a NanoScope IIIa controller and an FC type contact-mode liquid cell, Veeco Instruments) were performed on samples of DS as well as graphene oxide which were deposited onto a freshly cleaved mica substrate, in the presence of aqueous suspensions of DS. Raman spectroscopy (Horiba Raman Spectrometer, \( \lambda = 523 \) nm) was performed on pressed pellets of GO, FGS as well as DS pucks which were produced by drop-casting concentrated suspensions onto PTFE and peeling the pucks from the substrate.

### 3.3.4 Electrochemical Measurements

Electrochemical testing of the electrodes was performed using a spring-loaded stainless steel test cell (MTI Corp. CA) in a two-electrode configuration using a Celgard 3501 membrane separator which was dipped in EMImBF\(_4\) prior to assembly. All devices were assembled in an argon-filled (99.9999%, AirGas) glove box (Innovative Technology) Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were carried out on assembled test cells using a computer controlled potentiostat (VSP, Bio-Logic, USA). \( C_G \) was calculated from the cyclic voltammetry data using the following equation:

\[
C_G = 2 \frac{i_{avg}}{v \cdot m} \tag{3.2}
\]

where \( i_{avg} \) is taken as the average of the absolute anodic and cathodic currents at the midpoint of the cyclic voltammogram, \( v \) is the scan rate, and \( m \) is the average mass of FGS on both electrodes. The cyclic voltammetry studies were performed using a voltage
window of 3.0 V centered at the open circuit potential. The impedance measurements were performed at open circuit potential over a frequency range of 200 kHz to 10 mHz with a sinusoidal voltage perturbation of 10 mV. Measurements were taken at 10% of one period of the oscillation.

### 3.4 Results and Discussion

#### 3.4.1 Electrode Performance

Figure 3.3 shows the $C_G$ for the two batches of electrodes (as detailed in Section 3.3.2) as a function of the initial mass fraction of DS in the electrode on a solids basis ($w_{DS}$) at both low (5 mV/s) and high (500 mV/s) scan rates. Figure 3.3(a) shows that the $C_G$ for the electrolyte-lean electrodes at 5 mV/s remains approximately constant at up to a $w_{DS}$ of 0.4. At $w_{DS}$ of 0.5, $C_G$ increases and upon further addition of DS reaches a maximum value of 271 F/g at $w_{DS}$ of 0.6, which is approximately double that achieved by the control electrodes without DS ($w_{DS} = 0$). This maximum is achieved despite having a lower EMImBF$_4$ content.

![Figure 3.3: Gravimetric capacitance as a function of dehydrated sucrose content. $C_G$ data at 5 and 500 mV/s for (a) electrolyte-lean and (b) electrolyte-rich electrodes. Capacitance data are reported per gram of FGS after heat treatment.](image-url)
(61 wt%) than the control electrode (75 wt%). Increasing $w_{DS}$ beyond 0.6 resulted in a decrease in $C_G$. A similar trend in $C_G$ is observed for the electrolyte-lean electrodes at a high scan rate of 500 mV/s; however, the values of $C_G$ are significantly lower at this high rate, especially at $w_{DS}$ of 0.6, where $C_G$ at 500 mV/s is less than one-third that of the $C_G$ at 5 mV/s. As seen in Figure 3.3(b), the $C_G$ of the electrolyte rich electrodes increases with increasing DS content, reaching a value of 330 F/g at a $w_{DS}$ of 0.7 at 5 mV/s. Correspondingly, the rate performance of the electrolyte-rich electrodes is significantly better: at $w_{DS}$ of 0.7 the $C_G$ at 500 mV/s is 211 F/g. The improved rate performance of the electrolyte-rich electrodes when compared against the decreasing trend of the total EMImBF$_4$ content of the electrolyte-lean electrodes suggests that decrease in $C_G$ for the electrolyte-lean electrodes beyond $w_{DS}$ of 0.6 may be attributed to an insufficient amount of EMImBF$_4$ in the electrode.

The $C_G$ data in Figure 3.3 are reported solely with respect to the mass of thermally reduced graphene oxide (FGS) as DS is not expected to serve as an active material in the electrode.

![Figure 3.4: Raman spectroscopy and C/O of graphene oxide and dehydrated sucrose before and after heat treatment. C/O shown in the inset.](image-url)
electrode. Figure 3.4 shows Raman spectra for both graphene oxide and DS before and after heat treatment to 300 °C. Prior to heat treatment graphene oxide exhibits two prominent peaks. The D-peak near 1350 cm\(^{-1}\) results from the breathing mode of six-membered aromatic rings, while the G-peak near 1580 cm\(^{-1}\) represents the in-plane oscillations of any sp\(^{2}\) carbon pair in the material. The Raman spectrum for DS before heat treatment is notably different as both the D- and G-peaks are absent. This result illustrates a key structural difference between both materials as the sheet-like honeycomb lattice characteristic of the basal plane of graphite remains largely intact for graphene oxide; however, this organized structure is not present in the DS, which is presumed to be amorphous and lacking C–C sp\(^{2}\) bonds. The D- and G-peaks are still present in the thermally reduced graphene oxide; however, the significant increase in C/O (see inset) likely contributes to the increase in the material’s conductivity, as previously reported. After heat treatment, the DS still lacks a D-peak, and only the early onset of the G-peak can be observed. The dearth of sp\(^{2}\) domains along with the material’s low C/O lead us to assume that DS is not significantly conductive and therefore would not serve as an active solid component in the electrode when heat treated to 300 °C.

3.4.2 Dehydrated Sucrose as Spacer for Graphene Oxide

AFM of the as-synthesized DS shown in Figure 3.5 reveals that the material is composed of discrete particles with heights ranging from 0.5 to 2.5 nm. We performed XRD on composites of graphene oxide and DS formed via drop casting from aqueous suspension to determine if DS was serving as a spacer. Figure 3.6 presents the signal
intensity of the graphene oxide-DS composite as a function of the scattering angle. The signal intensity was normalized based on the total graphene oxide content such that the degree of restacking could be compared across all samples. For $w_{DS}$ of 0, the characteristic GO peak is observed at 10.1°, which corresponds to a $d_{002}$ spacing of 0.8 nm for graphene oxide. Upon increasing $w_{DS}$ to 0.2, the peak shifts to a lower scattering angle signifying that the spacing between the sheets has increased. Also, the original peak at 10.1° is absent, which suggests that the addition of DS does serve as a spacer and that this DS content is sufficient to completely disrupt the regular stacking of graphene oxide. Furthermore, the signal intensity at $w_{DS}$ of 0.2 is less than one-tenth of that measured at $w_{DS}$ of 0. This observation indicates that the increase in $d_{002}$ spacing is not uniform and that the addition of DS may result in a heterogeneous spacing distribution which renders the majority of the sample X-ray amorphous. Additionally, if the DS specifically adsorb onto graphene oxide then we could expect the $d_{002}$ spacing to be greater than the measured primary particle sizes (Figure 3.5) as each pair of graphene oxide sheets will be separated by two layers of DS. Thus, it is possible that the graphene oxide-DS composite contains regions where the $d_{002}$ spacing is larger than 2 nm due to particle stacking or aggregation during drying as a

**Figure 3.5: Height of dehydrated sucrose nanoparticles.** Atomic force microscopy of a DS suspension drop-cast on mica and scanned in tapping mode.
$d_{0002}$ spacing larger than 2 nm lies outside the detection limit of our instrument. Given this qualification the $d_{0002}$ spacing in Figure 3.6(a) should be viewed as the minimum $d_{0002}$ spacing in the composite.

As the DS content increases the peak continues to shift toward lower scattering angles and reaches a minimum $d_{0002}$ spacing of 1.54 nm at $w_{DS}$ of 0.5, which is almost double the spacing of GO. For reference this spacing is large enough to accommodate the EMIm$^+$ ion, the larger of the two ions of EMImBF$_4$, based on published estimates of its van der Waals radius. The increase in the minimum $d_{0002}$ spacing is also below the lower end of the particle size distribution up to a $w_{DS}$ of 0.43. As graphene oxide is flexible, it likely can conform to the DS and bend, thereby achieving a $d_{0002}$ spacing which is smaller than that of the DS particle. Additionally, the slope of the $d_{0002}$ spacing, shown in the inset of Figure

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**Figure 3.6: XRD and LC-AFM of dehydrated sucrose and graphene oxide composites.** (a) XRD for graphene oxide-DS composite at the indicated DS content ($w_{DS}$). (b) Liquid cell AFM of DS on graphene oxide deposited on a mica surface in an aqueous environment. (c) Differences in high and low force contact mode scan on the DS-decorated graphene oxide.
3.6(a), increases from a $w_{DS}$ of 0.33 to 0.43. This observation is particularly interesting as we begin to see an increase in $C_G$ for the electrolyte-lean electrodes (Figure 3.3) for DS contents beyond $w_{DS}$ of 0.4.

Figure 3.6(b) shows a LC-AFM micrograph of graphene oxide deposited on a mica substrate in the presence of an aqueous suspension of DS. This micrograph confirms that DS adsorbs onto graphene oxide in aqueous suspension as we observe a roughness on the graphene oxide on the order of the average heights of the DS particles. Furthermore, Figure 3.6(c) shows that the DS can be removed from the graphene oxide by applying a high force to the cantilever tip. These observations suggest that DS is physisorbed rather than chemisorbed onto the graphene oxide. Graphene oxide has been shown to contain acidic functional groups which are expected to dissociate in an aqueous environment and leave the graphene oxide negatively charged. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy of the DS, shown in Figure 3.7, reveals that DS contains many of the same oxygen-containing functional groups as its parent molecule, sucrose, though the total oxygen contents of neat DS and sucrose are significantly different, 25 and 48 at%, respectively. Additionally, the FTIR spectrum for DS shows a peak near 1700-1725 cm$^{-1}$, which can be assigned to the C=O stretching mode in carboxylic acid groups. The presence of this peak coupled with the observation that the pH of the DS suspension is between 4.0 and 5.6 after dialysis provides strong evidence for the presence of acidic groups on DS particles. As both materials are expected to be negatively charged in water, we would expect them to repel one another. However, as the acidic functional groups on graphene oxide are thought to be located primarily at the edges of the graphene
oxide the electrostatic repulsion may be weak on the surface of the material. Hence, we attribute the adsorption to weak forces including van der Waals interactions and hydrogen-bonding between the oxygen-containing functional groups on both DS and graphene oxide. This hypothesis is further supported by the selectivity of DS adsorption onto graphene oxide over the mica substrate. Adsorption may also take place at lattice vacancy sites on the graphene oxide; however, though observed, there is little evidence to suggest that these sites form at high density on graphene oxide. Additionally, as the interactions between DS and graphene oxide are not electrostatic, we do not expect the DS to desorb once the EMImBF$_4$ is added to the aqueous suspension of DS-decorated graphene oxide as a result of electrostatic screening. We acknowledge that the EMImBF$_4$ could compete with the DS for space on the graphene oxide if the EMImBF$_4$ were to specifically adsorb onto graphene oxide. However, we have not been able to investigate this phenomenon at this time.

3.4.3 Post-Heat Treatment Characterization

In the previous section, we presented strong evidence that DS can not only adsorb onto graphene oxide, but also serves as an inter-sheet spacer. However, the electrode material that is responsible for the performance shown in Figure 3.3 has been further processed, by
adding EMImBF$_4$, and subsequently heat treated in an inert atmosphere. As the details of this composite electrode after heat treatment govern the device performance, we turn our attention to understanding the electrode morphology after it has been fully processed.

Though the effect of heating graphene oxide has been well studied, we do not know how DS behaves when subjected to elevated temperature. Figure 3.8 shows atomic force micrographs of DS on mica before and after heat treatment to 400 °C under nitrogen atmosphere. As can be seen, before heat treatment, the DS feature heights comparable to those previously shown (Figure 3.5). After heat treatment, the DS remain particulate, but the heights of the particles increase significantly. This observation suggests that the DS particles do not melt when heated to moderate temperatures (400 °C), but rather expand, likely due to the liberation of gaseous products, such as carbon monoxide, carbon dioxide, and water, but this has not been confirmed. Therefore, the pore space of the electrode may be larger than expected due to expansion of the DS during heat treatment.

As it is difficult to probe the morphology of the electrode directly, we rely on on EIS to indirectly gather information about the electronic and ionic conductivity of the composites. Figure 3.9 shows Nyquist plots for the two batches of electrodes studied in

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**Figure 3.8: AFM of dehydrated sucrose before and after heat treatment.** Concentrated DS suspension drop-cast onto mica (a) before and (b) after heat treatment to 400 °C under nitrogen.
Figure 3.3. For the electrolyte-lean electrodes, shown in Figure 3.9(a), the slope of the curve at low frequencies for $w_{DS}$ of 0 and 0.4 are nearly identical, indicating similar transport behavior in both of these electrodes. At $w_{DS}$ of 0.5, the slope increases, indicating an improvement in transport despite a decrease in the EMImBF$_4$ content; however, at a $w_{DS}$ of 0.7, the slope of the mid-frequency range follows a 45-degree line, which indicates a Warburg-like impedance associated with ionic transport resistance in porous electrodes.
This result provides evidence for our previous claim that the $C_G$ of the electrolyte-lean electrode for $w_{DS}$ of 0.7 was low due to an insufficient amount of electrolyte per total mass of solids in the electrode. Comparatively, as seen in Figure 3.9(b) for the electrolyte-rich electrodes, the slope of the low-frequency range increases substantially at a $w_{DS}$ of 0.4, likely due to the excess EMImBF$_4$ present in this electrode. Upon further addition of DS, the slope begins to decrease as it approaches $w_{DS}$ of 0.7. At this DS content, the total EMImBF$_4$ content with respect to the mass of FGS is approximately 93 wt%, which is a significant excess of EMImBF$_4$ based on the results of Pope et al.$^6$ Though we expect the ionic conductivity to not be limiting at exceptionally high EMImBF$_4$ content, the EMImBF$_4$ may interfere with the electronic conductivity of the FGS by swelling the composite and increasing the electronic resistance between the sheets.

We can further investigate this hypothesis by analyzing the low-frequency impedance data. In comparing the low-frequency response of the electrolyte-lean and electrolyte-rich electrodes shown in Figures 3.9(c) and (d), respectively, several differences are noted. The semicircles formed at low frequency for the electrolyte-lean electrodes have smaller diameters than do those of the electrolyte-rich for corresponding DS contents. Additionally, the slopes of the curves closer to the mid-frequency regime are larger for the electrolyte-rich electrodes than for the electrolyte-lean. The relatively smaller semicircles of the electrolyte-lean electrodes suggest that the electronic resistance of these electrodes is smaller than that of the electrolyte-rich. This appears counter-intuitive as one may not predict the electronic conductivity to increase upon the addition of an insulating spacer; however, we hypothesize that this behavior is due to a closer packing of the FGSs which
is enabled by the relatively smaller amounts of EMImBF$_4$ in these electrodes. The closer packing of the FGS results in a smaller pore space and more obstructed ionic transport, which also explains why the slopes in the mid-frequency region are smaller than the corresponding slopes for the electrolyte-rich electrode.

Figure 3.10 shows a characteristic cyclic voltammogram for an electrode at 5 mV/s. As can be seen, the waveform is rectangular across the voltage window studied. This shape suggests that pseudocapacitance does not contribute to the capacitance of the electrode as prominent redox peaks are not observed. This is an interesting result given the rather high residual oxygen content present in the electrodes, as one may have expected the oxygen-containing groups to have been redox active species at the voltages investigated ($\pm$ 1.5 V from open circuit potential).

As we have shown, the total EMImBF$_4$ content is an important consideration for the fabrication of FGS-based EDLC electrodes as it influences the electronic and ionic transport in the device. More importantly, in calculating $E$, the total EMImBF$_4$ content is critical as it contributes significantly to the total mass of the electrode, which greatly
impacts $f$. Figure 3.11 shows $E$ calculated using Equation 3.1 for each batch of electrodes as a function of $w_{DS}$. As can be seen, the total EMImBF$_4$ content has a substantial impact on the $E$ of the electrodes. Despite having high $C_G$ at high and low scan rates, the electrolyte-rich electrodes do not outperform the electrolyte-lean electrodes. In fact, at 5 mV/s, we report an $E$ of 13.3 Wh/kg for the electrolyte-lean electrodes at $w_{DS}$ of 0.6, (the DS content at which a maximum $C_G$ was previously shown), a value which is 160% larger than the $E$ for the corresponding electrolyte-rich electrode. The value of $E$ is also 40% higher than the control electrode despite containing $\sim$25% less EMImBF$_4$. Additionally, the $E$ for both the electrolyte-lean and electrolyte-rich electrodes at 500 mV/s are similar despite the apparent gains in $C_G$ afforded by the high EMImBF$_4$ content. These results demonstrate the importance of reporting not only the $C_G$ of the electrode, but also in calculating the true $E$ by accounting for the $f$ of the assembled electrodes.

Figure 3.11: Energy density for the electrodes. Energy density calculated using Equation 1 for both electrolyte-lean and electrolyte-rich electrodes at 5 and 500 mV/s. A maximum energy density is achieved at low scan rates (5 mV/s) of 13.1 Wh/kg for electrolyte-lean electrodes with $w_{DS}$ of 0.6.
3.4.4 High Temperature Heat Treatment of Dehydrated Sucrose

Based on the aforementioned analysis, the value of \( w_{DS} \) in our electrodes essentially indicates the fraction of the total solids content which, in addition to the total EMImBF\(_4\) content, contributes to \( f \). However, if the DS could be converted into an active material in the electrode, its mass would no longer contribute to \( f \), but instead contribute toward \( C_G \). We performed Raman spectroscopy on samples of DS heat treated to temperatures higher than those presently investigated. Figure 3.12 shows that above 500 °C, the Raman spectrum for DS features prominent D- and G-peaks indicating the presence of networks of sp\(^2\) bonds. The C/O of the material at this temperature was measured via EDS to be 5.1 which is comparable to the C/O of the FGS material in our electrodes, as previously measured. Upon extreme heat treatment to 1200 °C, the peaks become much sharper and the material reaches a C/O of 22 ± 4. Additionally, the G’-peak near 2700 cm\(^{-1}\) which is a characteristic peak of graphite begins to emerge at higher temperatures. Furthermore,

![Figure 3.12: Raman spectroscopy and DSC/TGA of heat treated dehydrated sucrose. (a) Raman spectra of DS heated in inert atmosphere from 500 to 1200 °C. (b) DSC/TGA of DS to 1200 °C under inert atmosphere at 20 °C/min. ramp rate.](image)
Figure 3.12(b) shows the TGA and DSC of the DS as a function of temperature. At low temperatures, the broad endotherm is likely the result of the removal of residual water, which accounts for approximately 5% of the total mass of the sample. A significant chemical change likely occurs around 200 °C as evidenced by the sharp exotherm. At temperatures beyond 300 °C, subsequent chemical changes occur, which create volatile species, removing additional mass from the material, as evidenced by the TGA trace. At high temperatures, the mass loss of DS is substantial: at 500 °C only 45% of the mass of the material remains. This significant mass loss may significantly affect the density as well as the mechanical properties of the material, which may compromise its use as a spacer. Currently, we cannot process our electrodes at temperatures much higher than 300 °C as we find that the EMImBF$_4$, at these temperatures, evaporates and, hence, the liquid content is difficult to control. A solution to this problem consists of processing the electrodes in a chamber which is saturated with EMImBF$_4$ vapor to prevent the loss of EMImBF$_4$ in the electrode. Additionally, the heat treatment temperature is limited by the decomposition temperature of the RTIL used, which for the case of EMImBF$_4$ is near 400 °C. Thus, the ability to process the electrodes at higher temperatures would likely transform the currently insulating DS into a conductive spacer for FGS; however, one must consider the morphology and structural stability of the resulting material to determine whether its spacer properties are retained. The latter experiment is non-trivial as it likely involves difficult in situ measurements of the DS structure at the nanoscale. Additionally, to achieve these higher temperatures, RTILs with higher decomposition temperatures will likely be needed.
3.4.5 Dehydrated Sucrose as Dispersant for FGS with High C/O

We have shown that DS adsorbs to graphene oxide in an aqueous environment and can be effectively used as a spacer. In order for the prepared DS-graphene oxide-RTIL composites to be used as EDLC electrodes, we needed to heat treat the material to render the graphene oxide conductive. In this section, we investigate the use of DS as a similar spacer for FGS with high C/O ratio (> 5). This material (as described in Section 2.2) is formed via the thermal reduction and exfoliation of GO powder. By varying the heat treatment temperature and time, we can achieve materials having a C/O between 5 (heated at 300 °C for 60 s) and 400 (annealed at 2200 °C). Also, the $I_D/I_G$ ratio of the material greatly influences the areal capacitance of the FGS with a maximal areal capacitance reported for a material with C/O near 13 (1100 °C heat treatment for 60 s). Therefore, there is much incentive in using FGS with high C/O in EDLC electrodes. However, the FGS powders that are produced via thermal reduction and exfoliation are difficult to disperse in solvents and often require the use of a surfactant, such as sodium dodecyl sulfate or block copolymers (F127, Pluronic), to achieve adequate dispersion in aqueous suspensions. Figure 3.13 shows optical microscope images of FGS suspensions in the presence of DS at various DS weight contents. The FGS used in these experiments was provided by Vorbeck Materials and had a C/O of ~33 (measured by EDS). As can be seen, the addition of DS (and subsequent sonication) helps to disperse large aggregates of FGS in suspension. At a DS content of 40 wt%, the FGS-based particle size is drastically reduced, and remains in this state upon further addition of DS. Thus, we have evidence that DS can serve as a dispersant for FGS. Subsequent dispersion stability studies using UV-
vis have revealed that the suspension of 40 wt% DS retains 60% of its concentration over the course of 8 days. The remaining 40% settled out of suspension.

Figure 3.14(a) shows that the suspension of FGS with DS are electrostatically stabilized as the addition of sodium chloride causes flocculation of FGS, which fall out of suspension. This observation suggests that the DS adsorbs onto FGS, and some evidence is provided for this claim in Figure 3.14(b) as seen in the AFM micrograph. The FGS appeared pocked and the roughness of the FGS is on the order of the size of the nanoparticles. The large circular feature at 10 nm is likely a wrinkle in the sheet, and not a DS particle.

Though the DS adsorbs onto FGS and it appears that the DS disperse FGS well in water, the performance of these composites as materials for EDLCs electrodes assembled via the evaporative consolidation approach is poor compared to those assembled starting with graphene oxide. The electrodes yielded a $C_G$ less than 70 F/g using both EMImBF$_4$ as well as the hydrophobic RTIL 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, both at 70 wt% content (30 wt% total solids). At this time we attribute the poor performance
of the FGS-based electrodes to the low ion-accessible specific surface area of the material, though further experiments are needed to confirm this hypothesis. These results highlight the importance of starting with fully dispersed, single sheets of FGS or graphene oxide.

3.5 Conclusions

DS synthesized via an acid-catalyzed dehydration of sucrose can be used as a spacer to prevent graphene oxide sheets from restacking during evaporative consolidation by showing that DS adsorbs directly onto the graphene oxide. We couple the aqueous suspensions of DS and graphene oxide with a water-miscible RTIL and achieve a $C_G$ of 271 F/g at an EMImBF$_4$ content of 61 wt% and a $w_{DS}$ of 0.6. We report a maximum $E$ of this electrode of 13.3 Wh/kg and show that gains in $E$ are not achieved by increasing the amount of RTIL in the electrode. Future efforts to further transform the DS into a conductive electrode component may offer additional improvements in $f$ and insight into the design of highly energy dense EDLC electrodes. We also show that DS can be used to disperse FGSs with high C/O in aqueous suspension.
References


Chapter 4

4 Anomalous Capacitance Maximum of the Glassy Carbon-Room Temperature Ionic Liquid Interface

This chapter is adapted from work to be submitted to The Journal of Physical Chemistry Letters coauthored with Betül Uralcan, Nicholas Szamreta, Michael Pope and Ilhan Aksay. B. Uralcan assisted with the experimental design, data analysis and provided theoretical insight; N. Szamreta helped with the electrochemical measurements; M. Pope assisted with experimental design and data analysis.

Chapters 2 and 3 of this dissertation presented work that aimed to engineer FGS-based electrodes with high energy density. In this final chapter, I turn my attention away from porous electrodes to study the fundamental physics occurring in the electrochemical double-layer of RTILs. This chapter details measurements performed using a model three-electrode electrochemical system to understand how the double-layer capacitance of concentrated RTIL-based electrolytes is affected by the addition of organic solvents. The insight gained from these model studies can be applied to theories regarding the capacitance of concentrated electrolytes and assist in the design of practical devices.

Specifically, in this chapter, we use electrochemical impedance spectroscopy (EIS) to measure the effect of diluting a hydrophobic room temperature ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMImTFSI), with miscible organic solvents on the differential capacitance of the glassy carbon (GC)-electrolyte
interface. We show that the minimum differential capacitance reported over a 2 V electrochemical window near the open circuit potential (OCP) increases with dilution, and reaches a maximum value at ionic liquid contents near 5-10 mol% (i.e., ~ 1 M). By using a series of three different solvents with drastically different dielectric properties, we further provide evidence that 1,2-dichloroethane (DCE), a low-dielectric constant solvent, yields the largest gains in capacitance near the open circuit potential when compared against two traditional solvents, propylene carbonate (PC) and acetonitrile (AN), each having a higher dielectric constant. Our results provide experimental insight into the electrochemical double-layer (EDL) for RTIL-based electrolytes and reveal the enhancement of double-layer capacitance through dilution.

4.1 Introduction

RTILs are regarded as next-generation electrolytes for EDLCs as their low volatility and wide electrochemical windows (> 4 V) can lead to safer devices with greater energy density.\(^1\)\(^-\)\(^2\) However, their high viscosity and resulting low conductivity compared to that of traditional aqueous or organic solvent-based electrolytes limits the rate performance of EDLCs and yields devices with sub-optimal power density.\(^1\) To overcome this rate limitation, low-viscosity organic solvents have been introduced to RTILs to decrease their viscosity and, hence, increase their conductivity.\(^3\)\(^-\)\(^5\) For example, top-performing RTIL-based EDLCs use a 50/50 wt% mixture of RTIL and AN as the electrolyte.\(^6\)\(^-\)\(^7\) Such mixtures have electrochemical windows up to 4 V and have also shown promise in devices operating at extreme temperatures.\(^8\)\(^-\)\(^9\)
However, the effect of diluting RTILs with organic solvents on the double-layer capacitance of the electrode-electrolyte interface remains unclear.\textsuperscript{10-13} Understanding this behavior is important as such information will assist in the design of RTIL/solvent combinations that maximize capacitance and, correspondingly, improve the energy density of EDLCs. Though a large body of work exists regarding the theory and measurement of the double-layer capacitance of neat RTILs, few studies have focused on RTIL/solvent mixtures, despite the fact that they are often reported in the EDLC literature.\textsuperscript{14} Recently, several computational works have begun investigating this phenomenon and have claimed that the capacitance of the electrode-RTIL interface can, in fact, increase with the addition of non-ionic solvent.\textsuperscript{10-11} This phenomenon has been attributed to the reorganization of the EDL in the presence of solvent molecules, specifically the expulsion of co-ions from the EDL. Herein, we use EIS and a planar glassy carbon electrode to probe the EDL and provide experimental insight into the EDL of RTIL/solvent mixtures.

As we would like our model studies to have practical value, we selected materials relevant to those reported in the EDLC literature. We chose GC as the working electrode as it not only resembles the disordered carbonaceous materials typically employed in EDLCs,\textsuperscript{15} but also because it possesses a large space-charge capacitance (Chapter 1) which allows us to probe the ionic side of the interface with greater sensitivity than if we had used a material such as highly oriented-pyrolytic graphite, which is limited by its low space-charge capacitance.\textsuperscript{16} We also selected the “hydrophobic” ionic liquid EMImTFSI as it remains popular in the EDLC literature due to its moderate voltage window (\(~4.3\) V),
relatively low viscosity (~33 cP at 22 °C) and compatibility with a variety of organic solvents.\textsuperscript{17}

4.2 Experimental Methods

Experimental details specific to this chapter are provided below, including material preparation and the procedure for electrochemical measurements. A background on the EIS technique used to measure the differential capacitance is also provided in Section 4.2.4.

4.2.1 Materials Preparation

AN (99.8%), DCE (99.8%) and PC (99.7%) were purchased from Sigma-Aldrich, uncapped and stored within a glove box (Innovative Technology) filled with ultra-pure argon (99.9999%, AirGas). The water and oxygen content inside the glove box were kept below 1.0 ppm and 0.2 ppm, respectively. EMImTFSI (99.5%, UltraPure\textsuperscript{®}) was purchased from Iolitec at its highest available purity. The as-received EMImTFSI was further purified by washing 5 times with warm, deionized water and drying at 110 °C under vacuum for 2 days on a standard Schlenk line. The purified EMImTFSI was immediately transferred to the glove box for storage until use. Cyclic voltammetry was performed at 10 mV/s to ensure that the EMImTFSI had been properly purified. Mixtures of EMImTFSI and the three organic solvents were prepared in scintillation vials inside the glove box with selected mass ratios. Extreme care was taken not to contaminate the EMImTFSI after purification: only glass materials (vials, pipettes etc.) that had been washed with DI water and baked at
200 °C were used. The mixtures were vigorously stirred with a PTFE stir-bar for 15 min. prior to use. Each mixture was freshly prepared before use.

4.2.2 Electrochemical Measurements

A three-electrode electrochemical cell was used for the electrochemical measurements. A 3 mm GC rod electrode (CH Instruments) was polished with 0.05 µm alumina powder, rinsed with DI water and bath sonicated in ethanol for 20 min. after each polish. The rod electrode was immediately transferred to the glove box where it remained until use. A platinum mesh was used as a counter electrode, while a pseudo-reference electrode was employed consisting of a platinum wire encased in a fritted glass sheath (BASi) and filled with the same electrolyte that was being probed in each measurement. This reference electrode architecture allowed for isolation of the platinum wire from the bulk electrolyte and kept the submerged area of the wire constant, which appeared to help stabilize the potential. The reference electrode was calibrated against a 5 mM ferrocene standard for the same RTIL/solvent composition immediately after each measurement was performed to
ensure a steady and accurate reference potential reading. The ferrocene electrolyte was also used to confirm the exact surface area of the electrode using the Cottrell equation.

Cyclic voltammetry and EIS were performed using a computer-controlled digital potentiostat (VSP, Bio-Logic, USA). All experiments were conducted in the three-electrode electrochemical cell inside the glove box. The measurement protocol consisted of the following: (1) a 60 min rest to allow the reference potential to stabilize, (2) cyclic voltammetry from the OCP, performed 3 times at 10 mV/s to clean the electrode surface, (3) a 30 min rest at the OCP, (4) EIS measurement performed, scanning the potential from OCP to positive potentials in 100 mV increments with a 2 min rest at the potential of interest before the impedance (10 mV perturbation, 10 kHz to 1 Hz) was recorded, (5) a 30 min rest at OCP, (6) EIS measurement performed scanning the potential from OCP to negative potentials. The anodic and cathodic scans were performed from the OCP as suggested by Lockett et al. as experimental artifacts were seen when the scans were conducted from negative to positive potentials. The EIS data were analyzed (Section 4.2.4) following common protocol in the literature and reported at 46 Hz as that was deemed an appropriate frequency for all EMImTFSI/solvent mixtures studied.

4.2.3 Bulk Property Measurements

The conductivity of EMImTFSI/solvent mixtures was measured using a conductivity meter with a compensation probe (CDM83, Radiometer Copenhagen) at 22 °C. The measurements were performed outside the glove box. The organic solvents were added
dropwise into a sample of EMImTFSI (5 mL) that was constantly stirred with a PTFE stir-bar. Select mixtures were prepared independently and sheared on a rheometer (Anton Parr MCR 501, U.S.A.) in a Couette cell to measure the viscosity of the mixtures.

4.2.4 Differential Capacitance via EIS Measurements

EIS techniques have been used to measure the capacitance of the electrode-electrolyte interface using carbonaceous surfaces. EIS measures the sum, or aggregate, impedance response of a system by applying a small, frequency-dependent alternating-current (AC) perturbation. In order to separate the aggregate impedance response of a system into its resistive and capacitive components, one must interpret the impedance data based on the behavior of model scenarios, referred to as equivalent circuits, where the theoretical impedance response is known. Thus, to measure the differential capacitance of the electrode-RTIL/solvent interface, we first construct a simple circuit model for our electrochemical system. A popular model used in the literature consists of an electrode in contact with an electrolyte, as shown in Figure 4.2. The corresponding equivalent circuit of this system consists of a resistor, which represents the bulk electrolyte resistance, in
series with a capacitor, which represents the double-layer capacitance at the electrode-electrolyte interface. The complex impedance ($Z$) of these circuit elements are well known. The impedance of a resistor is equal to its resistance ($Z = R$) and this quantity is entirely real; it does not have an imaginary component. The impedance of a capacitor is entirely imaginary, and is expressed as $Z = -j/C\omega$ where $j = \sqrt{-1}$, $C$ is the capacitance and $\omega$ is the frequency of the AC perturbation. As the resistor and capacitor are connected in series, the impedances add as

$$Z_{eq} = R - \frac{1}{C\omega}j$$  \hspace{1cm} (4.1)

where $Z_{eq}$ is the equivalent impedance of the circuit. By inspection of Eqn. 4.1, it is evident that for a simple serial $R$-$C$ model, the capacitance can be calculated from the imaginary component of the total impedance response, $\text{Im}(Z_{eq})$, as

$$C(\omega) = \frac{1}{-\text{Im}(Z_{eq})\omega}$$  \hspace{1cm} (4.2)

The capacitance term in Eqn. 4.2 is known as the *differential capacitance* and is typically reported as a function of $\omega$. One would expect the capacitance of an AC system to be a function of the frequency of the AC perturbation. At very low frequency, the capacitor will be charging and the current will be increasing at a decreasing rate as predicted by the circuit’s RC time constant. However, as the frequency of the AC perturbation increases, the capacitor element acts as a short and the resistance dominates the system. This behavior is shown schematically in Figure 4.3(a). We refer to the inflection point of the decreasing capacitance at high frequency as the “knee frequency.”
However, the capacitance-frequency behavior sketched in Figure 4.3(a) is an idealized case and is rarely observed in actual experiments. More commonly, a behavior sketched in Figure 4.3(b) is observed in which the capacitance does not remain constant at low frequency, but begins to increase. This phenomenon is referred to as *capacitance dispersion* and is a feature of real electrodes which occurs upstream of the knee frequency. The exact cause of capacitance dispersion has not been agreed upon in the literature. Capacitance dispersion has been attributed to physical inhomogeneities on the electrode surface (*i.e.*, roughness), inhomogeneous charge distribution on the electrode surface and the physical construction of the electrode-electrolyte interface.\textsuperscript{20-22} Therefore, due to real limitations of the impedance technique it is important to note that the true value of the thermodynamic double-layer capacitance can only be approximated using EIS. Thus, *the differential capacitance measured using EIS serves only as a proxy for the true double-layer capacitance of the interface.*

In order to gather meaningful information with the EIS technique, we must carefully select a frequency at which to report our differential capacitance values. The selected
frequency should lie somewhere in the constant capacitance region highlighted in Figure 4.3(b), that is, sufficiently upstream of the knee frequency and downstream of the steep increase in capacitance observed at low frequencies. Once a frequency is selected, all differential capacitance values are reported at that frequency for purpose of comparison. As mentioned, a frequency of 46 Hz was sufficient for all EMImTFSI/solvent mixtures used in our study.

4.3 Results and Discussion

The minimum differential capacitance ($C_{\min}$) of the GC-electrolyte interface for mixtures of EMImTFSI diluted with AN, DCE and propylene carbonate (PC) is shown in Figure 4.4 as a function of EMImTFSI content. (Note: Though the EMImTFSI content is typically reported in units of molarity [mol/L] in the EDLC literature, due to the high molar EMImTFSI content of some of our EMImTFSI/solvent mixtures, the low volumes of mixtures prepared [~4 mL], and our desire to minimize contamination via transferring

![Figure 4.4: $C_{min}$ versus EMImTFSI molar content for EMImTFSI/solvent mixtures. $C_{\min}$ for mixtures with AN, DCE and PC is reported as a function of EMImTFSI molar content over a 2 V window near the OCP. 100 mol% EMImTFSI corresponds to 3.85 M. A maximum $C_{\min}$ is observed near 5-10 mol%.

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EMImTFSI into multiple containers [i.e., graduated cylinders], we find that reporting EMImTFSI content in terms of molar composition [mol\%] to be more useful and accurate. We do make an effort to correlate such compositions to molarity, and we provide an estimate where necessary assuming additive volumes.) The $C_{\text{min}}$ for neat EMImTFSI (100 mol\%) is 9.5 $\mu$F/cm$^2$, a value comparable to what has previously been reported in the literature. As can be seen, when EMImTFSI is diluted to 20-40 mol\% with each solvent (~2.5 M), $C_{\text{min}}$ increases. Upon further dilution, $C_{\text{min}}$ reaches a maximum and begins to decrease at EMImTFSI contents below 5 mol\%. We found evidence for this capacitance maximum only in two publications. Although Siinor et al. showed that the differential capacitance of neat 1-butyl-1-methylpyridinium tetrafluoroborate was less than that of a 0.5 M solution in AN, the presence of a maximum was overlooked, and no discussion was provided. Additionally, Liu et al. show a maximum capacitance at 2.0 M 1-ethyl-3-methylimidazolium tetrafluoroborate in AN, but, as they use porous electrodes, they are unable to extract information about the double-layer capacitance due to complicating transport effects. As we observe a maximum $C_{\text{min}}$ for mixtures of EMImTFSI with three different solvents, we show that this behavior is not exclusive to mixtures with AN, and may generally hold for diluting RTILs with any miscible solvent. In addition to the observation of a maximum $C_{\text{min}}$ with dilution, we note that the values of the maximum $C_{\text{min}}$ for each solvent are quantitatively different. Mixtures with DCE display the largest maximum $C_{\text{min}}$ of 23.4 $\mu$F/cm$^2$ at 5.3 mol\%, while dilutions of EMImTFSI with AN or PC display maxima of 20.1 and 17.6 $\mu$F/cm$^2$, respectively.
In addition to the quantitative differences in the maximum $C_{\text{min}}$, we find that the shape of the differential capacitance-potential ($C$-$V$) curves of the EMImTFSI/solvent mixtures are remarkably different. Figure 4.5 shows the $C$-$V$ curves for neat EMImTFSI and for EMImTFSI diluted with each solvent. As seen in Figure 4.5(a), the shape of the $C$-$V$ curve for neat EMImTFSI is concave up within the 2 V potential window studied, which is in agreement with the shape predicted by models of non-spherical RTIL ions. When EMImTFSI is diluted with DCE to 75 mol%, the capacitance increases globally as shown by the vertical shift in C-V curve and features a shallow “U”-shape, with a pronounced $C_{\text{min}}$. As EMImTFSI is diluted to 36 mol% with DCE, the slopes of the anodic and cathodic branches of the C-V curve increase and the curve assumes a sharper “V”-shape, which is retained down to 0.8 mol%. Similar behavior is observed in Figure 4.5(b) for mixtures of EMImTFSI/AN as the slopes of the anodic and cathodic branches increase as EMImTFSI is diluted to 0.5 mol%; however, the increase in the slopes is not as large as that observed for the EMImTFSI/DCE mixtures. For EMImTFSI/PC mixtures shown in Figure 4.5(c), the increase in the slopes is minimal up to 21 mol%, and only at 5.7 mol% does a shallow “U”-shape begin to appear. Thus, we find that the gains in differential capacitance of EMImTFSI/solvent mixtures near the OCP increases in the order of PC < AN < DCE. This result is remarkable as it suggests that a low-dielectric constant solvent, such as DCE ($\varepsilon \sim 11$) can afford greater enhancement in the double-layer capacitance than AN ($\varepsilon \sim 34$). Materials with low-dielectric properties are not often associated with high capacitance as the expression for the capacitance of a simple parallel-plate capacitor shows that capacitance is directly proportional to the dielectric constant. However, the behavior of the
EDL in concentrated electrolytes is complex, and interactions between the EMImTFSI and both solvent molecules and electrode surface play an underappreciated role in determining the double-layer capacitance, as discussed below.

Figure 4.5: Differential capacitance versus potential profiles for EMImTFSI/solvent mixtures. Differential capacitance-potential curves for the GC-EMImTFSI interface using neat EMImTFSI and EMImTFSI diluted with (a) DCE, (b) AN, and (c) PC.
Highly concentrated electrolytes, such as RTILs, have been shown both theoretically and experimentally to consist of alternating layers of counter- and co-ions which oscillate and dampen into the bulk as a result of overscreening.\textsuperscript{27-29} The differential capacitance has been shown to be inversely proportional to the center of mass of this excess charge distribution in the EDL ($\delta$), and can be represented mathematically as an analog to the Helmholtz layer capacitance as

\[
C = \frac{\epsilon^*}{\delta}
\]

(4.3)

where $\epsilon^*$ is the effective dielectric constant between the electronic and ionic charges.\textsuperscript{14} The oscillating charge density in a RTIL electrolyte effectively distributes the ionic charge over several ionic layers, resulting in a $\delta$ which is larger than if the counter charge were confined to a single ionic layer. The large $\delta$ and correspondingly low $\epsilon^*$ of RTILs explain the relatively low differential capacitance observed when RTILs are employed as electrolytes.\textsuperscript{30} Studies have shown that the addition of solvent dampens the ionic oscillations in RTILs.\textsuperscript{31} This dampening is due to two effects: the physical separation of the counter- and co-ions and the screening of the ionic charges due to polarizability.\textsuperscript{11} These effects allow the counter-charge to be concentrated closer to the electrode interface and enable the expulsion of co-ions from the EDL, as reported in the literature.\textsuperscript{11, 13} We hypothesize that the aforementioned phenomena decrease the $\delta$ of the neat RTIL electrolyte, which can explain the initial increase in $C_{\text{min}}$ observed upon diluting EMImTFSI with organic solvents (Figures 4.4 and 4.5). However, the capacitance gains achieved at moderate dilution (to $\sim$10 mol\%) in reducing $\delta$ are offset at higher dilution
(< 5 mol%) by additional phenomena, which cause the maximum in $C_{\text{min}}$ to occur. These additional effects include the competition between solvent molecules and the ions of EMImTFSI at the electrode surface, as well as the domination of the diffuse double-layer capacitance due to an increasing Debye length, consistent with the Gouy-Chapman-Stern (CGS) treatment of the EDL for dilute electrolytes.\textsuperscript{32-35} Qualitatively, the decrease in capacitance from ~5 mol% to ~0.5 mol% is predicted by the GCS treatment as the diffuse double-layer capacitance is proportional to the square root of the bulk electrolyte concentration.\textsuperscript{32} Therefore, as EMImTFSI is diluted, the resulting differential capacitance progression can be summarized as follows:

- The neat EMImTFSI exhibits a “swollen” EDL in which the $\delta$ is large due to the ionic correlations in the concentrated electrolyte.
- As neat EMImTFSI is diluted with organic solvent to moderate dilutions (~10 mol%), $\delta$ decreases due to the disruption of ionic correlations, which had reduced the effective ionic charge per EMIm$^+$ and TFSI$^-$ ion. Now, a larger amount of counter charge can be concentrated closer to the electrode surface.
- At high dilution, competing effects such as solvent-EMImTFSI competition for space at the electrode surface as well as the increasing diffuse double-layer lower the capacitance contributions of both the first-layer of ions (Helmholtz layer) as well as the subsequent layers (diffuse double layer).
- Finally, the electrolyte enters the concentration regime which is governed by the GCS treatment of the EDL and can be considered a “dilute electrolyte.”
Furthermore, we attribute the discrepancies in both the maximum $C_{\text{min}}$ and the $C$-$V$ curves among the three solvents investigated to solvent-specific interactions between the solvent molecules and both GC and the constituent ions of EMImTFSI. We expect both specific adsorption of solvent at the GC surface as well as the formation of a solvation shell to influence the structure of the EDL and hence, the differential capacitance. Of the three solvents studied, PC has been shown to adsorb strongly onto carbonaceous surfaces and this behavior has contributed to the lower capacitance of PC-based electrolytes when compared to AN-based electrolytes in simulations. Additionally, the formation of a solvation shell around the ions has competing effects in the EDL as it not only acts to separate ionic charges, and decrease ionic correlations, but also reduce the planar density of ions packed in the EDL. The latter would negatively affect the differential capacitance as previous experimental studies have noted that the differential capacitance decreases as the size of the RTIL ions increase. Thus, differences in size, shape and polarizability are expected to have complex effects in the EDL. Though we expect the specific solvent-GC and solvent-EMImTFSI interactions to largely influence the structure of the EDL, at this time we cannot ascertain which interactions are dominant in the EDL.

Though we are unable to isolate the exact mechanisms which account for the discrepancies in $C_{\text{min}}$ for DCE-, AN- and PC-based mixtures with EMImTFSI, we speculate that solvent polarizability may play an important role. As can be seen in Table 4.1, we report an increasing trend in maximum $C_{\text{min}}$ with decreasing solvent dipole moment and dielectric constant. The polarizability of the solvent is expected to not only impact the structure of the solvation shell, but also influence the specific adsorption of the
molecules at the electrode surface. The molar volumes of neat DCE and PC at room temperature differ only by 8%, suggesting that the molecules are of similar size. (Note: We understand that a more established and accurate way of gauging molecular size would be to calculate the van der Waals radius for each solvent molecule. However, as the van der Waals radius of these polarizable molecules will be highly dependent on the force field used, we feel that the molar volume of the solvent provides an adequate estimation of molecular size, for comparison purposes here.) However, both the maximum \( C_{\text{min}} \) (Figure 4.4) and the C-V curves (Figure 4.5) for EMImTFSI/DCE and EMImTFSI/PC mixtures are significantly different, suggesting that molecular size alone likely cannot account for our observations. Weakly polarizable solvents, such as DCE, are not expected to interact as strongly with the ionic charge as more polarizable solvents, such as AN or PC. Thus, DCE molecules may function primarily as void spaces within the electrolyte which can disrupt the EMImTFSI oscillations at the electrode surface. The more polarizable solvents also function as void spaces, but are also expected to solvate the ions and partially screen their formal charges. Such interaction would result not only in a lower effective charge per ion, but a larger molecular radius due to solvation, two effects which we hypothesize could contributed to the observed decrease in \( C_{\text{min}} \) with increasing solvent

<table>
<thead>
<tr>
<th>solvent</th>
<th>( \text{maximum } C_{\text{min}} ) (( \mu \text{F/cm}^2 ))</th>
<th>( \varepsilon ) (^a)</th>
<th>Dipole moment (^a) (D)</th>
<th>( V_m ) (^b) (cm(^3)/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCE</td>
<td>23.4</td>
<td>11</td>
<td>1.80</td>
<td>79</td>
</tr>
<tr>
<td>AN</td>
<td>20.1</td>
<td>36</td>
<td>3.44</td>
<td>52</td>
</tr>
<tr>
<td>PC</td>
<td>17.6</td>
<td>65</td>
<td>4.98</td>
<td>85</td>
</tr>
</tbody>
</table>

\(^a\) Reported from Aurbach, D. *Nonaqueous Electrochemistry*, 1999
\(^b\) Calculated from physical property data at rm. temperature
dielectric constant. We emphasize that our hypothesis does not suggest that polarizability effects are dominant in the system, as experimental measurements on porous electrodes suggest that other effects which we mentioned, such as specific adsorption, may play a significant role. Studies have shown that the surface of GC electrodes can be made more hydrophilic by electrochemical pre-treatment in aqueous electrolytes. Though there is very little water in the EMImTFSI/solvent mixtures, the stability of the surface chemistry of GC as a function of potential has not been thoroughly investigated and may be altered during the “cleaning” voltammetry cycles conducted prior to the impedance measurements.

In changing the composition of the RTIL/solvent mixture, we note that we are also altering the bulk conductivity of the electrolyte. As mentioned, this fact has been the primary motivation for using RTIL/solvent mixtures as electrolytes. Conductivity data for mixtures of EMImTFSI diluted with AN, DCE and PC are shown in Figure 4.6(a) as a function of EMImTFSI content. The EMImTFSI contents at which a maximum in conductivity is observed appear in a regime of EMImTFSI contents (> 20 mol%) similar to those at which a maximum $C_{min}$ is observed, especially for the case of AN. This correlation is unexpected as the double-layer capacitance is a quantity defined at thermodynamic equilibrium, while bulk conductivity is a kinetic measurement based on dissipative losses in the system. We do not suppose that the trends seen in Figures 4.4 and 4.6 are an artifact of conductivity as quantitative discrepancies exist between the maximum conductivity and maximum $C_{min}$ reported for each solvent series. Mixtures with AN yield the largest values of conductivity, with a maximum of 36.1 mS/cm observed at 10.8 mol% EMImTFSI. This value is nearly three times larger than the conductivity
maxima observed for mixtures with DCE and PC, yet mixtures with DCE yield the largest $C_{\text{min}}$. Furthermore, despite having similar conductivity at similar molar EMImTFSI content, mixtures with DCE and PC result in notably different $C-V$ curves (Figure 4.5).

Figure 4.6(b) shows the viscosity of the EMImTFSI/solvent mixtures as a function of EMImTFSI content. As can be seen, the viscosity decreases with dilution for each solvent studied. However, upon inspection, one can see that the quantitative trends in maximum $C_{\text{min}}$ (Figure 4.4) do not follow the trends in viscosity as mixtures with AN have the lowest viscosity for mixtures with similar EMImTFSI molar content, providing further evidence that bulk mixture properties are not entirely responsible for the observed phenomena.

Interestingly, a similar increase in the differential capacitance of the electrode-electrolyte interface with RTILs has been reported in the literature as the temperature of the RTIL is increased. Though no explanation for this behavior has been agreed upon in the literature, Holovko et al. asserted that the improvement may be caused by a disruption of the ionic liquid’s structure as a result of weakening the intermolecular forces...
between the ions of the RTIL due to increased thermal motion. Any correlations between the increase in differential capacitance due to increased temperature and that due to moderate dilution with organic solvents is predominantly speculative at this time.

**Conclusions**

Our experimental results show that the differential capacitance of the GC-electrolyte interface can increase through diluting EMImTFSI with a miscible organic solvent to EMImTFSI contents between 5 and 10 mol%, depending on the solvent used. Additionally, we demonstrate that of the three solvents studied, DCE, a low-dielectric constant solvent, affords the greatest gains in capacitance for EMImTFSI/solvent mixtures at potentials near the OCP. Further computational work accounting for the size, shape and polarizability of the added solvent and the RTIL ions can help elucidate the structure of the EDL of highly concentrated RTIL-based electrolytes. Such knowledge may ultimately prove useful in engineering new RTIL-solvent mixtures for EDLCs to maximize both energy and power density.

**References**


CHAPTER 4


5 Concluding Remarks

5.1 Summary of Conclusions

The purpose of this thesis was to investigate both the construction and properties of functionalized graphene-ionic liquid interface with the ultimate goal of creating high energy density EDLCs. After completing my Ph.D. work, I acknowledge that there is still much work to be done to realize this goal; however, my investigation has provided insight into how this can be best achieved. Engineering the nanometer-scale spacing of FGSs is critical in achieving the highest energy density electrodes and starting with high surface area FGSs is critical in achieving this goal. For this reason processing routes starting with graphene oxide were explored. I found that EDLC electrodes could be simply assembled by drop casting mixtures of graphene oxide, alcohols and RTILs and heat treating the material to produce conductive FGS. With this approach, I was able to achieve thin electrodes (0.5 mg/cm$^2$) with energy density of 6.3 Wh/kg, accounting for the total mass of the electrode (FGSs and RTIL), a consideration which is often not taken in the literature.

However, this approach is difficult to optimize as it requires the RTIL to perfectly wet the FGSs in the material; selecting a RTIL to accomplish this task is difficult considering that the hydrophilicity of the graphene-material changes during processing. To prevent the sheets from restacking I next investigated the addition of carbonaceous nanoparticles to the graphene oxide-RTIL mixtures and found that sucrose-derived nanoparticles could be used as spacers for graphene oxide to prevent the sheets from restacking. Using this approach, I
was able to achieve an energy density of 13.1 Wh/kg (with respect to the total mass of the electrode). However, my work revealed that the amount of nanoparticles needed to achieve this benefit was substantial (~60 wt% of the total solids content) and that the gains in capacitance only slightly outweighed the losses incurred by the additional mass of the spacers. This approach, however, was not optimized, and further studies performed at higher reduction temperatures are needed to fully realize the potential of this approach.

Lastly, my attention turned to the electrolyte. As mixtures of RTILs and organic solvents are reported in the literature for top-performing EDLCs, I investigated the fundamental effect of solvent addition on the double-layer capacitance of the electrode-electrolyte interface. I found that a maximum in the differential capacitance is achieved with the addition of common organic solvents to neat RTILs. The benefits of solvent addition must be weighed against the reduction in voltage window which occurs due to the electrochemical decomposition of the solvent molecules. In summary:

- Graphene oxide can be effectively co-assembled with sacrificial polymer-based colloids to create thin films, with sub-micron-scale porosity. After heat treatment to reduce the graphene oxide to conductive FGS, the films retain the shape imparted by the template; the sheets do not collapse.
- The $d_{0002}$ spacing of GO increases from 8 to ~15 Å in suspensions with ethanol, suggesting that alcohols can serve as intercalants for GO at room temperature.
- Water-free mixtures of graphene oxide-alcohol-RTIL can be processed into EDLC electrodes by simply drop-casting and can exhibit a $C_G$ of 134 F/g and energy density of 6.3 Wh/kg after mild heat treatment to 300 C.
Nanoparticles synthesized via the dehydration of sucrose adsorb onto graphene oxide and prevent the sheets from re-stacking during evaporative consolidation.

Electrodes assembled from nanoparticle-decorated FGSs can exhibit a high energy density of 13.3 Wh/kg at a high loading of nanoparticles (> 50% of solids content), despite the nanoparticles showing little evidence of being an active component.

The minimum differential capacitance of the glassy carbon-RTIL interface reaches a maximum value as the RTIL is diluted with organic solvents. The gains in capacitance are largest for mixtures with 1,2-dichloroethane, a low dielectric constant solvent.

These results offer a promising strategy for the bottom-up assembly of EDLC electrodes using both FGSs and RTIL electrolytes as well as offer insight into the fundamental processes governing the double-layer capacitance of the electrode-RTIL interface. However, though these results are scientifically intriguing, more work is needed before these efforts can be translated into electrodes suited for a commercial device. The following sections outline future research directions for my work.

5.2 Future Directions

5.2.1 High Voltage Studies

The EDLC community, including myself, is currently performing measurements with RTILs at voltages between 3 and 4 V. However, if the goal of EDLC research is to generate electrodes with high energy density, then research efforts must be directed toward performing measurements at higher voltages, beyond 4 V. Figure 5.1 shows the projected
energy density of EDLC electrodes as a function of the gravimetric capacitance. Six trajectories are shown at two different voltages (3 and 5 V) and three different active material loadings of 20, 30 and 40%. Back of the envelope calculations reveal that the minimum amount of EMImBF$_4$ required to coat each FGS (two monolayers of RTIL per sheet, one on each side) is approximately 70 wt%. Assuming that the RTIL and FGS are the only two components in the electrode, this scenario corresponds to an active material loading of 30% \((i.e., f = 0.3)\). Furthermore, this RTIL is likely not ideal for a high-rate EDLC as the electrodes will be transport limited due to the densely confined porosity; therefore, one may look at this scenario as a “best case” for energy density of FGS-EMImBF$_4$ electrodes as the addition of more electrolyte will only lower the energy density.

In order to compete with a lead acid battery, at an active material loading of 30%, gravimetric capacitances near 350 F/g will be needed as seen in the figure. However, the typical gravimetric capacitances achieved for FGS-based electrodes are highlighted in blue. If we were to maintain current levels of gravimetric capacitance, but operate the devices at

**Figure 5.1: Projected energy density of FGS-RTIL electrodes at 3 and 5 V.** Typical literature values for the gravimetric capacitance are highlighted in blue. The yellow area indicates that in which the majority of the EDLC is actually working. Benchmark values for energy density are indicated for commercial EDLCs, lead-acid batteries and lithium-ion batteries.
5 V, the community may be able to develop devices that compete with lead-acid batteries relatively soon. Figure 5.1 also highlights the difficulty in achieving an EDLC which rivals the energy density of lithium-ion batteries. (The benchmark value for lithium-ion batteries shown is the ultimate low-end of the range of energy density of state-of-the-art technology. Typical energy densities are around 200 Wh/kg).

On this front, studies which investigate the degradation of FGS and RTILs at high voltage are needed. Model systems using planar electrodes may be sufficient for a first-pass, but specific attention should be given to model studies that can be performed under RTIL confinement, representative of the RTIL arrangement in nanoporous electrodes. These studies will require the use of RTILs with higher electrochemical stabilities; these RTILs are expected to be larger than previously used RTILs. To further analyze the trade-off between capacitance and high voltage operation, due to the size differences, the differential capacitance of these the electrode-electrolyte interface should be measured over their entire voltage window. Additionally, RTIL purity, including oxygen and water content will be critical considerations in ensuring high voltage operation.

5.2.2 Understanding Energy and Power Trade-Off

The majority of the samples investigated in this thesis, and the scientific EDLC literature, involve thin electrodes of low active mass loadings (~1 mg/cm²). Proper scan rate dependence studies should be paired with energy density calculations and presented as a function of the electrode’s thickness. This information can provide insight into the length scale of porosity needed to ensure adequate rate performance for energy dense electrodes.
Modeling studies are also needed in these efforts. High energy density electrodes require the dense stratification of ionic and electronic charge. However, the transport of ions within a monolayer or two of ions in the presence of an orthogonally oriented electric field is not well understood or studied, but is critical to fully understand the extent of energy and power trade-off in EDLC electrodes.

5.2.3 Improving the Bottom-Up Assembly with Nanoparticles

The electrodes prepared from graphene oxide and DS in the presence of EMImBF$_4$ were heat treated to 300 °C. As mentioned in Chapter 3, the electronic resistance of the electrodes can be improved if the electrodes were heat treated further, perhaps to 400 °C. Such a heat treatment is expected to also reduce the DS and, perhaps, increase their activity in the electrode. Investigating the energy density of the electrode as a function of the heat treatment temperature would allow one to realize the full potential of this processing strategy. In order to accomplish this, one will have to prevent the evaporation of the RTIL as the vapor pressure of the electrolyte can be significant at elevated temperatures.

5.2.4 Improving Electrode Characterization

Insight into how the spacing of graphene oxide or FGSs changes with the addition of RTILs will be useful understanding the morphology of FGS-based electrodes. Though our XRD instrument could only explore scattering angles down to 5° (~2 nm), measurements performed at lower scattering angles could help elucidate the structure of the FGS-RTIL composites. Small angle X-ray spectroscopy studies can be used to study sheet spacing up to ~20 nm, which will be especially useful as the size of the RTIL typically increases with electrochemical stability.