SUPERCAPACITOR ELECTRODES BASED ON GRAPHENE MATERIALS

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ABSTRACT

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Graphene is a new type of carbon material with promising potential in energy-storage applications such as supercapacitor electrodes. This paper introduces engineering of graphene, as well as a related material called reduced graphene oxide, as materials for use in supercapacitors. The introduction explains the basic definitions of supercapacitors and graphene materials. Then, the fundamentals of supercapacitors and graphene materials are described in more detail in Chapters 1 and 2, respectively. Chapter 3 covers the synthesis and characterization of graphene-based electrodes.
DEDICATION

To my parents, without whose support this would not have been possible.
I would like to thank Prof. Barbara Murphy-Wesley for a great E200W class. Also, I would like to thank Richard Chung, Bin Chen, and Mike Oye for all the thoughtful advice and help. Finally, I’d like to thank Prof. Tim Hsu of the SJSU Math department for updating and providing the \LaTeX{} thesis style guide.
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CHAPTER 1

INTRODUCTION

Capacitors are energy storage devices similar to batteries, but which use different mechanisms. Namely, batteries store energy chemically, and capacitors store it physically (through dielectric polarization or ionic double-layers). Using chemical storage allows batteries to store relatively large amounts of energy, but there are several disadvantages. In many cases, the lifetime of a galvanic battery is relatively short. Typically, advanced batteries can be completely cycled no more than a few thousand times. Another problem with batteries is the relatively low power density, which means that the device cannot be charged or discharged quickly without overheating and perhaps being destroyed. An general comparison of the energy characteristics of capacitors, electrochemical capacitors (supercapacitors),
batteries, and fuel cells is shown in Figure 1. Generally, fuel cells and batteries can store more energy by weight, but capacitors can charge and discharge faster (lower RC time constants).

Supercapacitors, also known as electrochemical capacitors or ultracapacitors, can overcome some of the limitations of batteries, but generally cannot replace them. Rather, they can be used in certain applications where batteries fail (ex: regenerative braking), and also they can be used as supplements to batteries (ex: hybrid engine-starting modules). Supercapacitors are similar in principle to capacitors, but they use a different mechanism for charge storage. Instead of storing the charge directly in dielectric materials, supercapacitors use electrolyte ions, which create charge storage in electrical double layers. A subclass of supercapacitors, called pseudocapacitors, exploits yet another mechanism for charge storage via faradaic chemical reactions at the anode. The other subclass of supercapacitors is electrochemical double-layer capacitors (EDLC), which use almost entirely double-layer charge storage. In general, supercapacitor performance depends most strongly on the electrode materials engineering.

Ever since the 2009 Nobel Prize in physics was given to Andre Geim and Konstantin Novoselov for their work on single-layer graphite [6], which is usually called graphene, engineers worldwide have attempted to see if graphene can be used for practical applications. A related graphene material is called reduced graphene oxide (RGO), which is similar to graphene but with more structural disorder and more oxygen functionalities. One of the many possible applications of graphene materials is for electrodes, and in particular for supercapacitor electrodes.
2.1 Capacitive charge storage

To understand supercapacitors, it is necessary to understand common capacitors. Some of the first capacitors were built in the mid-1800s by Michael Faraday (1791-1867), and were referred to as “condensers.” The devices had a capacity to store electrical charge, and therefore eventually came to be known as capacitors. The common capacitor is composed of only three parts: two metallic electrodes (ex: aluminum) and one dielectric separator (ex: stretched-out polyethylene).
A dielectric is a material that becomes polarized in an electric field. That is, the material does not (ideally) allow DC charges to pass through it, but rather the material itself becomes electrically polarized. This polarization occurs when, for example, a battery is connected to the capacitor electrodes. The electrode that is connected to the positive terminal of the battery is known as the anode, and the electrode connected to the negative terminal of the battery is known as the cathode. When the battery is connected to the capacitor, electrical charge flows from the battery into the capacitor, but not through it. Instead of passing through the electrodes, the charges accumulate on the electrodes. That charge accumulation, which is proportional to the amount of polarization of the dielectric, is the mechanism for charge storage and therefore energy storage.

Capacitance is defined by the ratio of stored charge, $Q$, over the potential difference between the electrodes, $\Delta V$, as shown in Equation 1. The term $\epsilon$ represents the permittivity of the material between the plates. In a vacuum, $\epsilon \approx 8.85 \times 10^{-12}$ F/m.

Even after the power supply is disconnected from the plates, the charges remain. The capacitor is then said to be “charged,” and it can be used to supply power to other devices. The SI unit of capacitance is the farad, and one farad (F) is defined as 1 coulomb per volt (C/V).

$$C \equiv \frac{Q}{\Delta V} = \epsilon \frac{A}{d}$$  \hspace{1cm} \text{Equation 1}

The potential energy stored in a capacitor can be calculated according to Equation 2.

$$U = \frac{Q^2}{2C} = \frac{1}{2} C \Delta V^2$$  \hspace{1cm} \text{Equation 2}
Often, the energy density, $u$, is a more useful term than just the potential energy, because it allows one to compare relative storage efficiencies between devices of different geometric scales. The energy density of a capacitor is found by dividing 2 by the volume $V$, which for a parallel-plate capacitor is equal to the product of area and distance, $Ad$. In that case, the energy density is given by 3, where $\epsilon$ is the permittivity and $E$ is the electric field magnitude ($[\epsilon] = \text{F/m}$, $[E] = \text{V/m}$).

$$u = \frac{1}{2} \epsilon E^2$$ \hspace{1cm} \text{Equation 3}

Charge storage in supercapacitors can occur via two different possible mechanisms (or some combination of the two). Commonly, both fall under the broader nomenclature of electrochemical double-layer capacitors (EDLC). Such capacitors are typically composed of:

- Two electrodes (ex: activated carbon)
- Porous membrane separator (ex: polyethylene)
- Electrolyte solution (ex: 6 M $\text{H}_2\text{SO}_4$ or KOH)

It should be noted that supercapacitor electrodes based on activated carbon require metallic connectors that can be used for making electrical connections to other devices such as batteries. Such components are known as current-collectors, and their contribution to charge storage is negligible. Therefore, the focus is on the active carbon material, which is where virtually all of the charge is stored.

2.2 Double-layer and pseudocapacitance

The simpler of the two charge-storage mechanisms uses only the formation of an electrical double layer (EDL) at the interfacial area where the electrolyte ions
meet the electrode, as in Figure 2. An electrolyte solution such as potassium hydroxide provides charged ions that form double layers when the electrodes are connected to a power supply such as a battery. Electrolyte choice and optimization is not necessarily trivial, and there is significant research focusing on both aqueous electrolytes and ionic liquids.

Pseudocapacitance, the more complex mechanism of charge-storage, uses chemical (faradaic) reactions on the anode. The anodic chemical charge storage of pseudocapacitors is distinct from that which occurs in batteries, and typically is based on metal oxides (ex: RuO$_2$, MnO$_2$) or specialized polymers. In both cases of “pure” double layer capacitors (EDLC) and pseudocapacitors, the electrode material properties are of fundamental importance.
CHAPTER 3

GRAPHENE

Figure 3: Difference between graphite and graphene structures

3.1 Graphene materials

By far, the most common element used for supercapacitors is carbon. When graphitic carbon is treated for improved properties such as high porosity, it is usually called activated carbon. High porosity is desirable because it implies high surface area for EDL formation (more contact area between electrolyte ions and the plates). Nearly all commercial supercapacitors use electrodes based on activated carbon materials because of its relatively low cost. In the last decade, many attempts have been made to use other, more advanced forms of carbon to build supercapacitor electrodes. In particular, carbon nanotubes have been of primary interest. Carbon nanotubes are very similar to graphene materials; if a single-wall carbon nanotube (SWCNT), taking the shape of a straw, were to be cut down one
edge and flattened out, its wound then be called a graphene sheet or carbon nanosheet. Conversely, if a sheet of graphene were to be rolled up into the shape of a straw, it would then be called a carbon nanotube.

Graphene is simply a single layer of graphite. A single sheet of graphite, however, has properties significantly different from many-layer graphite. Furthermore, bilayer and trilayer graphene also have unique respective properties. Electrical and thermal conductivities, strength, and surface area are all different between graphene and graphite. In many cases, the properties of graphene are more desirable. In practice, conductivity of a single-layer graphene sheet has been measured up to 649 S/cm [7]. This value is similar to that of graphite, but well below the conductivity of copper, which is in the order of $10^5$ S/cm. The most important property of graphene with respect to supercapacitors is, naturally, its high theoretical specific surface area of 2675 m²/g and the corresponding theoretical specific capacitance of 550 F/g [4].

3.2 Reduced graphene oxide

Figure 4: Model of graphite oxide proposed by Szabo et al. [2], illustrated by Dreyer et al. [3]

Another related material, known as reduced graphene oxide (RGO), is
sometimes called graphene. Although RGO is significantly different from graphene, it retains some of the desirable properties such as high surface area. Reduced graphene oxide is made by reducing graphene oxide, which is made by exfoliating graphite oxide. Graphite oxide is made via a Hummers’ reaction in solution [8]. The reduction can be accomplished chemically with sodium borohydride (NaBH₄) or hydrazine (N₂H₄). Alternatively, the graphene oxide can also be reduced thermally or electrochemically. The resulting RGO is sometimes called graphene, although there are some important differences. Firstly, RGO usually has a significant amount of residual oxygen (ex: several percent). Secondly, RGO is highly disordered and distorted compared to pristine graphene. Finally, RGO is rarely single-layer (also called monolayer), but rather it is usually “few-layer,” which usually means about 2 - 10 graphene layers.

3.3 Composites

Both graphene and RGO are frequently made into composites for experimental electrode devices [4]. Composite materials can be simple to make when various materials (ex: conductivity boosters, adhesive binders, etc.) are mixed together. The electrical conductivity of most graphene materials is not exceptional, so conductive additives are often used. Binders are required in order to glue the materials together. There are disadvantages to these types of composites, however, because the high porosity causes pore resistance (impedance), which increases the capacitor time constant. Additives also reduce active surface area for double-layer charge storage. Graphene-based composites can also be made other methods that avoid binders (ex: electrophoretic impregnation). For pseudocapacitive electrodes, metal oxides or polymers can be made into composites with the carbon materials.
4.1 Characterization

Perhaps the most difficult aspect involved in building new materials is characterization, and graphene is no exception. The characterization of graphene and graphene-based electrode materials is an intensive process, requiring state-of-the-art instruments. Some of the most frequently used characterization tools include:

- Scanning electron microscopy (SEM): a visualization tool for imaging on the order of 30 nm to 1 \( \mu m \)

- Cyclic voltammetry (CV): an electrochemical method used to quickly check capacitance and chemical reactivity of potential electrode materials

- Atomic-force microscopy (AFM): a visualization and thickness-measurement tool for very small length scales on the order of 5 - 50 nm

- Electrochemical impedance spectroscopy (EIS): a method used to determine information regarding porosity and equivalent-series-resistance (ESR)

- Raman spectroscopy (RS): a laser-based method that returns structural “fingerprints” of materials

There are at least five different experiments that can be used to estimate the capacitance of an electrode, including galvanostatic charge/discharge, voltage and
current sweeping techniques, self-discharge through known resistance, and ac impedance spectroscopy [9].

Figure 5: Cyclic voltammetry of a graphene-based composite electrode at various scan rates [4]

Most supercapacitor characterization is performed using comprehensive electrochemical workstations that can perform dozens of tests. One can determine the capacitance of an ideally-polarizable electrode according to Equation 4, wherein the capacitance is calculated as the inverse of the slope of the linear portion of the plot of potential as a function of time while the electrode is charged at constant current [9].

$$C = \int i \cdot \frac{\Delta t}{\Delta V}$$  \hspace{1cm} \text{Equation 4}

To determine the capacitance from cyclic voltammetry (CV), one generally uses the area of the either the anodic or cathodic portion. A typical CV plot is shown in Figure 5. In some cases, an average is taken between the two. That case is
shown in Equation 5, where \( \int idV \) is the total area of the CV curve, \( m \) is the mass of the active electrode material (ex: graphene-based composite), \( \Delta V \) is the range of voltage, and \( \frac{\Delta V}{\Delta t} \) is the scan rate.

\[
C = \frac{\int idV}{2m\Delta V(\frac{\Delta V}{\Delta t})}
\]

Equation 5

In the case of thin-film electrode materials, the mass term \( m \) can be very challenging to obtain experimentally, so it is sometimes estimated. This is because the deposited mass may be on the order of micrograms (\( \mu g \)).

Figure 6: Nyquist plot of a graphene-based composite electrode [4]

Impedance is determined from electrochemical impedance spectroscopy (EIS). This is of fundamental importance for supercapacitors, as the equivalent series resistance (ESR) can be calculated if the impedance data are known. The impedance data area usually interpreted via Nyquist plot, an example of which is shown in Figure 6. The ESR can also be determined from galvanostatic
charge/discharge, and the value can be used to estimate the specific power from Equation 6, where $V$ is the cell voltage, $m$ is the electrode mass, and $R$ is the ESR.

$$P = \frac{V^2}{4Rm} \quad \text{Equation 6}$$

In porous supercapacitors, each pore has associated resistance, and if the pore network is extensive enough, the series resistance has undesirable effects. Recent graphene-based electrode materials have been designed specifically to address the ESR problem [5].

4.2 Graphene and electrode synthesis

Graphene-based materials may be obtained many ways. The most common are:

- Exfoliation of graphite (ex: mechanical, thermal, or electrochemical)
- Vapor deposition
- Chemically via graphene oxide

Mechanical exfoliation was the method used by Novoselov et al. [6], who famously used Scotch tape to separate the graphite layers. However, mechanical exfoliation appears better suited for fundamental research rather than scalability.

Vapor deposition, particularly chemical vapor deposition, is an active area of graphene research [5]. Decomposition of a carbon source such as methane can be used to grow thin films of graphene onto various substrates. Plasma processing is often used for improved properties.

The simplest and most common way to make graphene-based electrodes, after the graphene material has been made, is to simply mix the graphene with additives
that improve conductivity and binding [4].

4.3 State of the art

Pure electrochemical double-layer capacitors (EDLC) have been found to support specific capacitances of about 100 - 250 F/g. Pseudocapacitors (PC) typically have about double the specific capacitance of EDLCs, and there have been reports of specific capacitances of over 1000 F/g [10]. A summary of some recent research papers is shown in Table 1. In the table, edlc and pc refer to electrochemical double-layer capacitors and pseudocapacitors, respectively. It should be noted that the specific capacitance $C_s$ of a supercapacitor is only one of several important performance metrics. Other performance parameters of electrode materials include cycling stability, volumetric density, voltage range, frequency response (impedance), among others. Practical considerations for manufacture include cost, toxicity, and material availability.

Typically, the carbon material to be used in a supercapacitor electrode needs to be mixed with other additives such as binders and conductivity boosters. For most researchers working on graphene-based supercapacitor electrodes, this is the case. The Jang group, for instance, has made promising graphene-based supercapacitor electrodes by mixing many sheets of graphene with 5 %$_w$ Super-P (conductivity booster) and 10 %$_w$ polytetraflouroethylene (PTFE) [4]. The graphene-based composite is then typically applied to a metallic substrate, which is known as the current collector. Two such electrodes can then be separated by a porous membrane such as the Celguard-3501, which is what was used by the Jang group [4]. Their fabricated cell was estimated to have a specific energy density of over 80 Wh/kg at room temperature, which is about twice that of an average
lead-acid battery and approaching that of a lithium ion battery.

Many laboratory-scale efforts have been made to grow graphene and carbon nanotubes vertically (perpendicular to the current-collector) in order to achieve high surface area and low porosity. The active carbon materials grown in this fashion are significantly different from traditional porous carbon composites, if only for their relatively low thickness values (ex: < 1 μm) and negligible weights. As such, these more advanced electrodes can be called thin-film electrodes. In principle, thin-film supercapacitors using the spiral geometry could outperform commercial devices. A calculation based on the spiral architecture predicted a capacitance $C > 14,000 \text{ F}$ for a graphene electrode with thickness of 0.6 μm and an overall device length of 13.8 cm [11].

Table 1: Specific capacitances of RGO/graphene-based electrodes

<table>
<thead>
<tr>
<th>material</th>
<th>synthesis method</th>
<th>type</th>
<th>$C_s, \text{ F/g}$</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>RGO</td>
<td>PTFE composite</td>
<td>edlc</td>
<td>205</td>
<td>[12]</td>
</tr>
<tr>
<td>modified graphene</td>
<td>PTFE composite</td>
<td>edlc</td>
<td>135</td>
<td>[13]</td>
</tr>
<tr>
<td>graphene</td>
<td>PTFE composite</td>
<td>edlc</td>
<td>250</td>
<td>[4]</td>
</tr>
<tr>
<td>RGO</td>
<td>ionic liquid composite</td>
<td>edlc</td>
<td>187</td>
<td>[14]</td>
</tr>
<tr>
<td>RGO</td>
<td>electrolytic deposition</td>
<td>edlc</td>
<td>128</td>
<td>[15]</td>
</tr>
<tr>
<td>RGO</td>
<td>LBL self-assembly</td>
<td>edlc</td>
<td>247</td>
<td>[16]</td>
</tr>
<tr>
<td>graphene/polyaniline</td>
<td>drop casting</td>
<td>pc</td>
<td>480</td>
<td>[17]</td>
</tr>
<tr>
<td>graphene/poly(pyrrole)</td>
<td>EPD</td>
<td>pc</td>
<td>1510</td>
<td>[10]</td>
</tr>
<tr>
<td>graphene/MnO$_2$</td>
<td>electrostatic LBL</td>
<td>pc</td>
<td>263</td>
<td>[18]</td>
</tr>
<tr>
<td>graphene/NiO</td>
<td>EPD/CBD</td>
<td>pc</td>
<td>400</td>
<td>[19]</td>
</tr>
<tr>
<td>graphene/MnO$_2$</td>
<td>solution LBL</td>
<td>pc</td>
<td>380</td>
<td>[20]</td>
</tr>
</tbody>
</table>

A leader in supercapacitor applications is John R. Miller, who recently succeeded in growing and characterizing vertically-oriented graphene sheets using plasma-enhanced chemical vapor deposition (PECVD), a thin-film deposition method used frequently in the semiconductor industry [5]. The focus was on the ac
impedance behavior, which appeared, via EIS, to have been optimized (low pore resistance). The target application for such supercapacitors is for ac line filtering. An SEM image of the vertical graphene sheets is shown in Figure 4.7(a), and the corresponding Nyquist plot is shown in Figure 4.7(b). The nearly-vertical orientation is indicative of low pore resistance. For comparison, the curved shape of the Nyquist plot of the composite electrode, shown in Figure 6, is indicative of high pore resistance, and is a more typical of conventional porous electrode materials.

![SEM of graphene sheets](image1.jpg)  
(a) SEM of graphene sheets  

![Nyquist plot](image2.jpg)  
(b) Nyquist plot showing very low ESR

Figure 7: Reduced ESR in a vertically-oriented graphene electrode [5]
Graphene-based materials are attractive candidates for supercapacitor electrodes. Graphene may eventually replace or compliment other carbon materials as sources of high surface area and therefore high capacitance. More laboratory-scale capacitor cells need to be assembled and replicated to verify the technological improvements over cheaper carbon materials, but some laboratory data have looked promising. Cost effective mass production of single-layer graphene has not yet been realized, although it may be possible. Nevertheless, few layer graphene still shows improved performance over other carbon materials, and it is much easier to obtain. In particular, reduced graphene oxide (RGO) materials are very easy to make and could be competitive commercially.

Pristine single-layer graphene is usually made with vapor deposition methods, whereas few-layer RGO is usually made chemically. Once the graphene or composite material is made, there are many methods to synthesize electrodes, including pressing, drop-casting, layer-by-layer (LBL) assembly, and electrophoretic deposition (EPD). Pure electrochemical double layer capacitors made of graphene materials have specific capacitances up to about 250 F/g. Graphene based pseudocapacitors, which are composites with polymers or metal oxides, have specific capacitances of over 400 F/g. Although pseudocapacitors hold more energy than pure EDLCs, they are unstable in some circumstances. Thin-film electrodes, particularly those with vertically-oriented sheets, hold promise for future developments. Ionic liquid electrolytes can be used to extend voltage ranges, and therefore capacitance values.
REFERENCES


