Making Scalable Inexpensive High Power and Energy Density Graphene Supercapacitors with the LightScribe Method

Abstract

Improvements in energy storage devices can help facilitate the implementation of renewable energy resources in collecting energy, energy storage, and using the energy efficiently. Most energy storage devices today face similar problems: slow charging time, low power and energy density, safety, and cost. The goal of this research was to address these issues with graphene supercapacitors.

Graphene supercapacitors have fast charging and discharging rates, which not only reduce charging time but also enable better performance. The improvements in the electrolytes and the pattern design can further increase graphene supercapacitors’ power and energy density. Inexpensive graphene supercapacitors can lower the cost of energy storage in solar and wind farms. They also have many more applications on a smaller scale. Graphene’s flexibility and transparency give graphene supercapacitors many potential applications in electronic devices like
phones and wearables. Driving down the cost of LSG (laser scribed graphene) and scaling up the production will help make graphene supercapacitors commercially available.

Although some lithium-ion batteries can achieve fast charging rates, graphene supercapacitors have many more benefits thanks to graphene’s physical properties. A gelled electrolyte allows more flexibility and does not have the safety hazard of leakage while a reliable solid electrolyte in batteries is yet to be invented. Despite the low-cost associated with sodium-based batteries, the comparative performance of graphene supercapacitors may still be superior.

This research focused on scalable inexpensive graphene supercapacitors from graphite oxide exfoliated with LightScribe DVD burners. This research demonstrated the feasibility of an inexpensive scalable high energy density graphene supercapacitor. The graphene capacitor made with the LightScribe method has a capacitance of about 200 $\mu F$. It would take approximately four kilograms of those capacitors in parallel to have one Farad of capacitance. Although my graphene supercapacitors did not achieve high energy density, they have the potential to with further improvements. The inexpensive and scalable method could be helpful for manufacturers as well.

*Keywords: energy storage, graphene, capacitor, LightScribe*

**Introduction**

Improvements in charging and discharging rates, number of charging cycles, energy density, safety, efficiency, and cost in energy storage devices can help stimulate the implementation of renewable energy resources. This research project aims to create an inexpensive scalable method to fabricate high energy and power density graphene supercapacitors using laser scribing methods. Some variables in the experiment include the concentration of the graphite oxide solution, the volume of the graphite oxide, the capacitor
pattern, the substrate, and the laser intensity. Factors such as the working voltage window, discharge rate, mass, and conductivity determine the performance of the graphene supercapacitors. The LightScribe method has the potential to make high energy density graphene supercapacitors. 

Background Information

**Energy Storage**

While lithium-ion batteries can hold a relatively large amount of energy, giving some Electric Vehicles (EVs) a range comparable to that of a gas car, they also have many problems. The electrolyte inside lithium-ion batteries is flammable, making them a safety hazard (Geere, 2016). It can deteriorate over time and use, giving these batteries a limited charging cycle (Zhu et al., 2011). Furthermore, lithium mining emits greenhouse gases and leaves toxic chemicals at mining sites, causing health issues (Kaiser, 2013).

One alternative to batteries is a hydrogen fuel cell system. Also storing energy in the form of chemical potential energy, a Polymer Electrolyte Membrane (PEM) fuel cell collects the energy in a reversed electrolysis process between hydrogen and oxygen gases (Promislow & Wetton, 2009). Although hydrogen is an excellent way to store energy, the low efficiency and high cost of fuel cells limit their applications (Behling, 2013).

Capacitors are the counterpart to batteries for energy storage: they charge and discharge quickly and have many more charging cycles while they store much less energy per unit mass. Supercapacitors are electric double-layer capacitors (EDLCs) with two electrodes separated by an ion porous medium in an electrolyte (Aung & Sherman, 2013). They can not only store more electric potential energy than regular capacitors but also charge faster than batteries. On the other hand, the capacitance of a regular capacitor increases directly proportional to the surface area of
the positive and negative electrodes. It also increases when the distance between the two electrodes decreases.

**Graphene**

Graphene is “a single layer of graphite with a honeycomb lattice of carbon atoms.” Graphene’s carrier mobility — how quickly electrons can move through it — is 10 times higher than that of silicon. Graphene's incredible conductivity makes it ideal for electronics such as transistors and capacitors. Because it is only one atom thick, graphene has excellent transparency and flexibility. It is also two hundred times stronger than steel (Lee, Salleo, Bao & Brongersma, 2012). Graphene’s Specific Surface Area (SSA), the surface area per unit mass, is extremely high (Zhu et al., 2011). The physical properties of graphene give it many applications. Notably, graphene supercapacitors have the potential to achieve high energy density. The high SSA of graphene leads to a high surface area of the electrodes, which results in higher capacitance. Because of its high electrical conductivity and high surface area, graphene can serve as both the electrode and current collector, which simplifies the building process of supercapacitors (El-Kady & Kaner, 2013). Graphene supercapacitors also have many more charging cycles than lithium-ion batteries.

**Graphene Production**

Some major problems with graphene supercapacitors include the production process, working voltage, and power and energy density. Some researchers claim that graphene can be produced efficiently and inexpensively through physical and chemical exfoliation of bulk graphite (Cai et al., 2015). Chemical graphite exfoliation methods yield good quality graphene but produce random deposition of graphene flakes or ribbons. The thermal decomposition of
Silicon Carbide with high synthesis temperature takes too long, is hard to integrate with other materials, and cost too much. The chemical vapor deposition on transition metals requires high temperature and has a low yield. The unzipping of carbon nanotubes also has low yield and produces randomly oriented geometries. Some researchers have found growing epitaxial graphene (EG) on silicon carbide substrates effective (Lee, Salleo, Bao & Brongersma, 2012). Others have found that X-ray can break the carbon into carbon bonds (Zhou et al., 2010).

The goal of the materials scientists and engineers is to find a scalable process to obtain one layer of carbon atoms from an inexpensive material. Each scientist may have their own findings on what that “inexpensive material” may be, and Graphite Oxide (GO) is certainly one of them. GO can be produced from the oxidation of graphitic powders, and graphite is the most common allotrope of carbon (Strong et al., 2012). GO’s availability, as they are already manufactured on the ton scale, ensures the inexpensive raw material for graphene production (El-Kady et al., 2012). When the GO entraps enough water, it becomes an anisotropic ionic conductor while maintaining its other physical properties (Gao et al., 2011). Therefore, hydrated GO is both a good ionic conductor and an electrical insulator, simplifying the supercapacitor structure (El-Kady, & Kaner, 2013). However, electrical capacitors (ECs) made with graphene derived from GO yield low values of specific capacitance, energy density, and power density. The van der Waals force between the graphene sheets causes them to restack, leading to these performance issues. In addition, these ECs have relatively low charge and discharge rates, which hinder their implementation in EVs (El-Kady et al., 2012).

**Laser Exfoliation**

Laser irradiation can exfoliate GO sheets to laser-scribed graphene (LSG) (El-Kady et al., 2012). The laser reduction conversion of GO into reduced-GO (RGO) has better electrical
conductivity than the ones made with the previous chemical and physical exfoliation methods. The laser converts the initially stacked GO sheets into exfoliated LSG sheets. Graphene’s excellent mechanical flexibility allows the LSG sheets to be directly used as EC electrodes without additional structural support. More importantly, LSG can act as both the electrode and the conductor in the EC. Thus, a graphene supercapacitor can consist of only two identical LSG electrodes separated by an ion porous resistor (El-Kady et al., 2012).

**LightScribe**

LightScribe is a commercially available program that uses a laser to print labels on the top side of LightScribe-enabled CD/DVD disks. The LightScribe program uses a computerized grayscale algorithm to generate different levels of contrast of a pattern. The grayscale “darkness” levels determine the laser intensity needed to selectively print patterns on a dye matrix on the disk. To control the laser intensity on the LightScribe burner, the program pulses an objective lens assembly periodically, focusing and defocusing the laser (Strong et al., 2012).

To print graphene supercapacitors, a thin layer of graphite oxide takes the place of the original dye matrix on LightScribe-enabled disks. Prior to laser exfoliation by the LightScribe burner, the graphite oxide film is deposited on a thin flexible substrate, polyethylene terephthalate (PET). The LightScribe program then effectively and controllably reduces the GO and makes the designed pattern (Strong et al., 2012). Using a consumer-grade LightScribe DVD burner to exfoliate graphene from GO is a readily scalable process. The graphene supercapacitors can potentially be fabricated on large substrates at a fraction of the cost of traditional microfabrication methods (El-Kady & Kaner, 2013).

**Structure**
With the LightScribe method, it is possible to pattern any GO surface into GO–GO–RGO structures in various geometries with precision (Gao et al., 2011). Regular supercapacitors consist of a separator sandwiched between two electrodes with an electrolyte.

On the other hand, thanks to its near insulating properties, GO can serve as the separator between the positive and negative electrodes. Therefore, the laser scribed RGO pattern, after receiving an electrolyte overcoat, can directly function as a supercapacitor in an interdigitated structure. Graphene supercapacitors with the interdigitated structure have higher capacitance than those with the sandwich structure because the unique porous network structure of the LSG electrodes helps minimize the pathway for ion diffusion from the electrolyte to the electrode material. Furthermore, more interdigitated electrodes per unit area lead to higher power and energy density of the device. This allows for maximizing the available electrochemical surface area and results in increased capacitance and the faster charge/discharge rates. (El-Kady et al., 2012).
Recently, researchers have achieved even higher energy density with electrodes based on the ingenious fractal structures. The Hilbert Fractal attains the highest dimension (fills the most space on the LSG), leading to high SSA. The fractal structure has higher surface area and shorter distance between the electrodes, which enhances the performance of graphene supercapacitors.
Electrolyte

EDLC’s electrical double layer effect, which gives them higher capacitance than regular capacitors, comes from an electrolyte that allows ion diffusion between the two electrodes. The polarity caused by the electric potential between the electrodes needs to be balanced by the redistribution of ions close to the electrode surface through the electrolyte. The attracted ions’ movement towards the electrode surface forms the electrical double layer effect. (“The Electrical Double Layer,” 2013).
In EDLCs, electrical energy storage is achieved by both the electric potential difference like regular ECs and the ion separation between the electrodes and the electrolyte. Although some researchers have claimed that their laser-patterned devices in the sandwich structure exhibit good electrochemical performance without the use of an electrolyte, external electrolytes can further improve the performances of the devices (Gao et al., 2011). The LSG surface’s high accessibility to the electrolyte with little impediment to ion transport leads to high capacitance even when the graphene supercapacitor is operating at ultrahigh charge/discharge rates (El-Kady & Kanner, 2013).

Graphene supercapacitors with liquid electrolytes, however, are vulnerable to harmful leakage of the electrolyte and have low operating voltages. Thus their implementation in electronic and energy storage devices is limited. Fortunately, liquid electrolytes can be replaced by gelled or solid electrolytes. The porous structure of the LSG electrodes can effectively absorb the electrolytes, help facilitate ion transport, and minimize the diffusion distance to the interior surfaces. Moreover, the gelled or solid electrolyte can improve the mechanical integrity and increase the cycle life of the graphene supercapacitors. (El-Kady et al., 2012).

Unlike water-based electrolytes, ionic liquids (ILs) have a wide electrochemical window, high ionic conductivity, good thermal stability, and non-volatility. ILs can be mixed with another solid component, such as a polymer or a silica, to form gelled electrolyte called an ionogel. The combination of a solid matrix and ILs allows more flexibility of the device without leakage problems of liquid electrolytes. Moreover, the graphene supercapacitors with an ionogel have ultra-high charge/discharge rates comparable to those with a liquid electrolyte. They also operate at a higher voltage. The integration of ionogel into solid state graphene supercapacitors can lead to promising applications. (El-Kady & Kanner, 2013).
Methods

Materials

- Graphene Oxide Water Dispersion 4 mg/mL (Graphenea, n.d.).
- Wintale USB 3.0 External Slim DVD Drive with LightScribe (Wintale, n.d.).
- Verbatim LightScribe DVD for this experiment (Verbatim, n.d.).
- SureThing Labeler 6 Gold (SureThing, 2014).
- Clear Craft Plastic .007 Thickness 12-Inch by 12-Inch (Rafix, n.d.).
- Repositionable Mounting Spray Adhesive, 10 Oz, Clear (Elmer, n.d.)

Procedures

1. Cut the plastic film into the shape of the DVD disks. Trim the plastic so it does not cover the center rim of the disk, which is important for the LightScribe process.
2. Glue the plastic film temporarily onto the disk.
3. Dilute the graphite oxide solution to 2 mg/mL. Mix 8 mg/mL of the solution with 8 mg/mL of distilled water (Figure 3).
4. Drop cast 16 mL of the solution onto the plastic film substrate with a pipet and let it dry in a fume hood. Be careful not to spill or touch the surface of the disc.
5. Design a capacitor pattern. There need to be two electrodes that do not touch one another. The pattern should be black. Save the pattern as an image file (Figure 4).
6. Place the coated DVD disk into the LightScribe DVD burner. Use the capacitor pattern image with a LightScribe software to reduce the GO. This process converts the brown dried GO to graphene capacitor circuit and takes about 30 minutes (Figure 5).
7. Remove the plastic film substrate from the disk and cut out the capacitor.
8. Glue copper wires at the end of the positive and negative electrodes for testing.

9. Cover the capacitor surface with tape to prevent scraping and damage (Figure 6).

Figure 3. | Image of the graphite oxide solution

Figure 4. | The interdigitated planer structure of the capacitor
Figure 5. | The laser scribed graphene capacitor on the DVD disk

Figure 6. | Image of the finished graphene supercapacitor

Results
After the LightScribe process, the conductive reduced graphite oxide becomes black while the insulative graphite oxide remains dark brown. The reduced graphite oxide exhibits electrical conductivity close to that of graphene.

In this experiment, the capacitance of the capacitor is measured in an RC circuit (Figure 7). The circuit uses a 1.5 V AA battery as the power source and a 0.5-megaOhm resistor. With the capacitor and the resistor in series, electrons can only flow through the resistor. Ignoring the internal resistance of the capacitor, the voltage \( V \) at time \( t \) of the circuit \( V(t) \) can be derived from the equation \( V(t) = V \times e^{-\frac{t}{RC}} \) whereas \( R \) is the resistance of the external resistor, \( V \) is the voltage of the power source, and \( C \) is the capacitance of the graphene capacitor (“RC circuit,” 2017). The Logger Pro voltage sensor produces a graph of the voltage drop over time (Figure 8). With the voltage over time data, I then plotted a natural log plot of voltage and time, with the slope of the plot being \( \frac{1}{RC} \). Hence, the capacitance is the negative reciprocal of the time constant divided by the resistance of the external resistor (Figure 9).

![Figure 7. | Circuit diagram of the RC circuit for testing the capacitance](image-url)
Figure 8. | RC circuit setup for testing the capacitance
Figure 9. | The natural log plots of voltage versus time of the capacitor

Since the RC time constant is the slope of the natural log plot, we can measure it. The time constant is $0.01 \pm 2.4 \times 10^{-3}$. Since the time constant is equal to $\frac{1}{RC}$, the capacitance is therefore $209 \mu F \pm 25\%$. 
As shown in the graph below, the capacitor is instantaneously charged to 1.5 volts. Then once disconnected from the power source (the 1.5 V battery), the voltage drop is also almost spontaneous (Figure 10). After that, the voltage drops at a logarithmically slower rate over time. In comparison, another trial is performed without the external resistor. The difference between the trials with and without the resistor in the RC circuit is so insignificant that the electrons directly flowing through the circuit is negligible. Thus, this capacitor does not retain a charge very well.

Figure 10. | The graph of the voltage versus time

To demo the performance of the graphene supercapacitor, the capacitor can light an LED in a circuit. However, the low voltage due to the instantaneous voltage drop makes it hard for the LED, which has a higher working voltage, to stay lit. I used a self-oscillating voltage booster to increase the working voltage of the capacitor, hoping to light the LED in the circuit (Figure 11). Unfortunately, the 200 µF capacitor could not provide enough energy to keep the LED lit.
Furthermore, the mass of the $200 \mu F$ graphene supercapacitor is 0.83 grams (Figure 12). Hence, it will take approximately four kilograms of those capacitors in parallel to have one Farad of capacitance.
Discussion

As the experiment shows, graphene supercapacitors have good electrical conductivity and fast charging rates. Without a flammable electrolyte or lithium, they are safer and more environmentally friendly. They are lightweight and flexible, giving themselves many applications for energy storage in small-scale electronic devices. Furthermore, the LightScribe method proves to be inexpensive and relatively easy to manufacture. On the other hand, the fast discharging rate and graphene supercapacitors’ inability to retain a charge long enough hinder their implementation as a larger scale energy storage device in places like electric vehicles and solar farms. Nevertheless, graphene’s high electrical conductivity, physical strength, flexibility, and transparency make it a great material for various electronics applications. The simplicity of LightScribe laser scribing technology demonstrates the feasibility of a low-cost approach to making reduced graphite oxide, which exhibits similar physical properties to graphene. This research project has successfully demonstrated the feasibility of an inexpensive scalable approach to making graphene supercapacitors.

Some limitations of this experiment include the quality of the substrate, the LightScribe burner, and demonstrating the energy storage capabilities in a simple circuit. With the plastic substrate glued onto the disk, sometimes the LightScribe burner cannot recognize the disk. Most of the “printed” capacitor patterns have printing gaps that make them incomplete circuits. The disk space is very limited, resulting in small capacitor dimensions, although small capacitors can be arranged in parallel. The voltage drop of the capacitor is almost spontaneous, so the supercapacitors need a voltage booster to supply energy to an external circuit.

For further improvement of this project, the graphene supercapacitor needs to be encapsulated inside a more insulative material. Using better substrate will help insulate the
capacitor and prevent electrons from escaping, hence retain a charge longer. On the other hand, although it takes approximately four kilograms of those supercapacitors to make up only one Farad of capacitance, most of the mass come from the plastic substrate. We can reduce a lot of the redundant weight by using thinner and lighter substrate than the crafting plastic. I can also experiment with different fractal patterns such as the Hilbert curve to improve the capacitance by increasing the specific surface area. Moreover, since the LightScribe method has demonstrated the feasibility of graphene exfoliation with a laser, a CNC laser cutter with modified laser intensity can “print” larger graphene capacitors on an industrial scale.

**References**


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