Carbon electrodes for supercapacitors

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Abstract

Supercapacitors play a vital role concerning renewable energy storage, due to the energy density, high power density and the fast charge/discharge cycles. Generally, supercapacitors are used in applications where fast charging or discharging are necessary and small power devices are utilized (for instance, in computers). Currently, different allotropes of carbon are used to manufacture electrodes, where different demands such as shape, stability, and conductivity can be met by varying the polymer precursor. Research conducted on carbon materials (such as carbon nanotubes, glassy carbon, and carbon aerogels) used as electrodes in supercapacitors has yielded exciting results in multiple studies. This study focuses on the fabrication of carbon electrodes using pyrolysis of organic compounds (SU-8, AZ, and PLLA). To further enhance understanding of carbon electrodes, this study includes additional samples, made from other methods, such as CNT (carbon nanotubes) and carbon aerogels. Overall, the goal of this study is to construct electrodes with exceptional conductivity, electrochemical stability, and ion diffusion rate.

The thesis provides the reader with an introduction and state-of-the-art for supercapacitors together with a review of multiple simple experiments. Different types of carbon electrodes are compared in terms of their basic characteristics—capacitance and resistivity. Methods for further improvement of supercapacitors are assessed: a composite supercapacitor consisting of both metal oxide and carbon is presented as a candidate in order to realize the fabrication of a supercapacitor with high energy density and power density.
1 Work-sharing

Charles has contributed with the following:

• Chinese Ink
• All self-made figures
• Proofreading
• EIS theory
• Conclusion

Niels has contributed with the following:

• Pyrolysis
• State of the art
• Abstract
• Motivation

Sebastian has contributed with the following:

• Experiments and Results
• Capacitors and supercapacitors
• Outlook
• Carbon materials

Kristoffer has contributed with the following:

• SEM-imaging
• Introduction
• Motivation
• Conclusion

Connor has contributed with the following:

• Pyrolysis
• State of the art
• Proofreading
2 Introduction

There is an ever increasing need to charge devices fast at a power outlet and use them for a long time away from a stationary power supply. Handheld devices are getting more and more energy efficient but are always forced to balance the power of the device with the specifications of the power supply. Furthermore, a lot of research is being done on how to replace fossil fuels with renewable energy sources, and doing so requires an efficient way to store and reuse the energy created by e.g. solar cells or windmills so that an efficient energy supply is provided at all times. Batteries and supercapacitors are electrochemical energy storage systems. Modern day batteries exhibit a high energy density but a low power density, which means that they are able to store a large amount of energy but are limited in how fast they are charged or discharged. For the capacitors currently available, the story is the opposite; capacitors exhibit a low energy density but a high power density, which means that they can charge and discharge very fast but are limited in the amount of energy that can be stored. Supercapacitors bridge the gap between the two groups, promising energy densities slightly lower than batteries but greater than capacitors and power densities slightly lower than capacitors but greater than batteries. While systems that utilize both batteries and supercapacitors in order to enable long periods of low power output usage and shorter periods with a high energy output is currently being researched, engineering supercapacitors with a high energy density as well as a high power density could replace batteries altogether. This is especially useful in handheld devices that even now burn through the battery in a day’s time and take a long time to recharge. In this example situation, supercapacitors could be used to their full extent as recharging them will be in a much shorter time frame and they could deliver a high power density for short periods. A supercapacitor consists of two electrodes in close proximity saturated with an electrolyte. The supercapacitor differs from an ordinary electrolyte capacitor in which the electrolyte acts as the cathode and in the supercapacitor the electrolyte is the conductive medium between the two electrodes. Supercapacitors store energy via two mechanisms using an electrolyte medium:

In the electric double layer capacitor (EDLC) charge is separated in an electrical layer created by negative and positive charged and formed at the interface between to materials, called a Helmholtz double layer. Pseudocapacitance is achieved by redox reactions at the surface of the electrode. During this Faradaic process the electrons created in the redox processes are transferred from the electrolyte into the electrode. Both of the mechanism can be separately or together to create a supercapacitor with high energy and power density.

3 Motivation

A key part of the supercapacitor is the electrode. It is at the surface of the electrode all the reactions in the supercapacitor happens and through the electrode the charge is transferred when charging or discharging the capacitor. The ideal electrode should possess the following:

- A high specific surface area. The mechanisms storing and releasing the energy are happening at the surface of the electrode, an electrode with a larger surface area will be more active.
- Controlled porosity. Controlling the porosity allows for optimization of surface area, ion diffusion, conductivity and the weight of the electrode.
- High electronic conductivity. When charging and discharging the supercapacitor charges needs to move through the electrode with low losses.
- Desirable electroactive sites. Having the right electroactive sites enables the pseudocapacitance.
- High thermal and chemical stability. The electrode must be stable under different working conditions to function in different thermal environments. The electrode must be chemically stable to ensure it doesn’t decompose or becomes inert over time, to ensure outcome stability and a long life time.
Lightweight. For uses in transportable devices the weight as well as size has a huge impact. As an example supercapacitors are being applied to store braking energy in trains and large trucks, but unless they are lightweight the energy saved in breaking is used for transporting the additional weight.

Low cost of raw materials and manufacturing. For any mass production method the electrodes should consist of raw materials that are cheap and abundant. Processing the raw materials to form a final product should also be cheap.

This is where carbon electrodes comes into the picture. Carbon with all its different allotropes shows promise to deliver on these parameters since it is abundant and cheap, conductive and very thermally and chemically stable. There are many ways to fabricate different types and structures of carbon, here the focus is primarily on carbon produced from pyrolysed polymers but electrodes from Chinese ink and carbon aerogels are also investigated. Using known resists such as SU-8 and AZ as polymers enables the use of photolithography and nanoimprint lithography. These are well developed techniques that allows the fabrication of many different, well-defined patterned structures in the micro- and nanometer scale. This way it is possible to engineer lightweight structures with a high surface area and controlled porosity.

4 Project goals

The goal of this 3-week project is to investigate different carbon electrodes for use in supercapacitors. Carbon electrodes produced by pyrolysis of the photoresist SU-8 and AZ and the polymer PLLA together with carbon electrodes made of carbon aerogels and Chinese ink are investigated. Using pyrolysis to create the carbon electrodes for supercapacitors is a new approach and their usage in supercapacitors must be thorough tested. The first simple test is the conductivity of simple flat structures of pyrolysed resist. If the flat structures are conductive patterned structures can be produced and they should also be tested for their conductivity.

Secondly the capacitance of the samples should be investigated. This can be done by performing cyclic voltammetry and electrochemical impedance spectroscopy. A model setup can be used to get an idea of the performance but ultimately the samples should be tested under real conditions. Additionally a scanning electron microscope is used to image and measure the produced patterned structures to investigate the increase in surface area. The polymer is expected to shrink during pyrolysis and the effective shrinkage is also measured.

The reader should note that performing all of the above mentioned measurements and characterizations are beyond the time frame of this 3-week project. They are listed if future studies will pick up where we have left.

5 Theoretical background

This section will provide a brief description of capacitors, supercapacitors and the pyrolysis process used to create carbon structures from polymers.

5.1 Capacitors

A capacitor is a device that can store energy by charge separation. The capacitor consists of two electrodes, and charge is built up on each electrode by applying a voltage difference across the electrodes, thus producing an electric field between them. The accumulated charge $Q$ per volt $V$ is defined as the capacitance $C$

$$C = \frac{Q}{V}$$

(1)

Capacitors allow for a rapid discharge of the stored energy, which gives them a higher power density compared to batteries. Batteries are limited by the electrochemical reaction rates while capacitors
are limited by ion diffusion rate, and total ion absorption. However conventional capacitors cannot store as much charge as batteries, giving batteries a higher energy density. This can be seen in the Ragone chart in figure 1.

Figure 1: Ragone chart from [1]. Supercapacitors are also referred to as ultracapacitors.

5.1.1 The parallel plate capacitor

The basic model of a capacitor is the parallel plate capacitor, where two parallel, conductive plates with the same area $A$ are separated by a dielectric with the permittivity $\epsilon$ at a distance $d$. The capacitance is then given by [2]:

$$ C = \frac{\epsilon A}{d} \quad (2) $$

Thus to get a high capacitance, a high surface area and a small distance between the electrodes are important. The energy stored in the capacitor is given by [2]:

$$ E = \frac{1}{2} CV^2 \quad (3) $$

and the maximum power delivered is [4]:

$$ P = \frac{V^2}{4R_s} \quad (4) $$

where $R_s$ is the equivalent series resistance of the circuit. To get a high power output, the resistance in the capacitor must be as low as possible. This can also be seen in the characteristic time constant $\tau = RC$, which gives an indication of how long it takes to charge and discharge the capacitor - in order to get a high power device, $\tau$ needs to be as low as possible. It can also be seen that a higher capacitance also increases the charge or discharge time.

The parallel plate capacitor is much simpler than the supercapacitors in this report, but some of the basic principles still apply - the surface area and distance between the stored charges are still important parameters of the supercapacitor.

5.1.2 Supercapacitors

Supercapacitors differ from conventional capacitors in several ways. They don’t have a dielectric between the electrodes but instead use an electrolyte, a medium in which ions can flow, carrying a
current. The electrodes are usually separated by a dielectric membrane that allows transport of the electrolyte ions but keep the electrodes electrically separated [5]. The electrodes in supercapacitors are highly porous, which gives them a much larger specific surface area (SSA, surface area per unit volume or mass) than conventional capacitors. This increases the surface for charge storage and surface where redox reactions can take place resulting in improved supercapacitors. The capacitance of a supercapacitor can consist of two parts: the electric double layer (EDL) and pseudo-capacitance.

**Electric double layer**

The electrolyte consists of positively and negatively charged ions. When a potential difference is applied to the electrodes, the positively charged ions will move towards the negatively charged electrode and vice versa. The ions and electrode will be very close to each other, only separated by the Helmholtz monolayer of polarised water molecules (in this case) as seen in figure 2. This electric double layer is created on both electrodes, which practically means that the supercapacitor consists of two capacitors connected in series. Because of the very small distance between the charges and the huge surface area of the electrodes, the EDL gives the supercapacitor a big capacitance compared to ordinary capacitors.

![Figure 2: The electric double layer is formed by electric attraction of the charged ions. The ions and electrode are separated by a monolayer of polarized water molecules called the Helmholtz layer [3].](image)

**Pseudocapacitance**

The second method of creating a big capacitance in a supercapacitor comes from the “pseudocapacitance”, implying that this capacitance is not real. In pseudocapacitance, the charge is stored electrochemically instead of electro statically. Pseudo-capacitance comes from reversible faradaic redox reactions, where the charged electrodes are used to oxidise or reduce compounds such as RuO$_2$. The oxide is adsorbed to the surface of the electrode so the charge transfer can take place. When a molecule is adsorbed in a pseudocapacitor an electron is transferred but for a molecule adsorbed in a EDL there is no real charge transfer and you effectively only get part of the electron per molecule adsorbed. Therefore the pseudocapacitance is typically 10 to 100 times higher than the EDLC (EDL capacitance).

Some supercapacitors use both the EDLC and pseudocapacitance to get a high capacitance, these are called hybrid supercapacitors. Capacitors where two different electrodes are used, in order to further benefit from both EDLC and pseudocapacitance, are called asymmetric capacitors. The supercapacitors to be investigated in this report creates an EDL, since the electrolyte used in measurements doesn’t react with the carbon to form a pseudocapacitive layer.
5.2 State of the art

5.2.1 Electrode Materials

Several significant factors for capacitors have been improved, which include energy storage density, cyclic stability, and rate capability. Currently, supercapacitors that utilize carbon as the electrode have energy densities lower than 10 W h kg$^{-1}$. Electrochemical batteries, however, have larger energy densities of 20-35 W h kg$^{-1}$ for a lead acid battery and 120-170 W h kg$^{-1}$ for a lithium-ion battery [22].

In order to improve different parameters for different applications of supercapacitors, a large number of materials have been investigated. The many different allotropes of carbon allow for varying properties of the supercapacitor electrodes which enable manipulation of the carbon composition for different applications [8]. Some examples of these allotropes are graphene, diamond, boron-doped diamond, graphite, glassy carbon, onion-like carbon, activated carbon, fullerenes, and carbon nanotubes (single-walled and multi-walled). See figure 3 for drawings of some of the allotropes. Applications that require a high power density utilize the good conductivity supported by graphene, while applications that require a hard and strong electrode utilize diamond. In addition, glassy carbon has been shown to be an exceptional electrode material due to the high density of electronic states caused by the disordered structure of graphitic regions [?].

In order to obtain high performance for the supercapacitors, the electrodes should have high electrical conductivity, be electrochemically inert, and have a highly porous structure and high specific surface area (SSA). The carbon is electrochemically inert, since the carbon is present even after releasing of an electron when a pseudocapacitance layer is formed. Porosity partially determines the amount of SSA, but also reduces conductivity. This fact leads to the necessity of achieving an optimum between electrical conductivity and porosity. In addition, the pore size of the electrode material must be adequate for electrolyte penetration, or else the effective surface area is drastically reduced. The electrochemical reactivity of the electrode will depend on the atomic structure obtained via the allotrope of carbon used.

![Figure 3: Some of the different allotropes of carbon [17]](image)

5.2.2 Electrode manufacturing

The current use of pyrolysis utilizes the versatility of organic photoresist films. A commonly used polymer is the SU-8 photoresist. The photoresist is spun coated on a substrate that is generally made of silicon. As the pyrolytic carbon precursor is a photoresist, a mask may be applied and the photoresist may be subjected to UV-exposure via electron beam and nanoimprint lithography, as
seen in figure 4. This process can be used to create desired nanoscale interdigitated structures out of the photoresist which increase surface area and enhance possibilities for alternative applications of carbon electrodes.

The acquired small size increases performance of mass transport and thus electrochemical reactions, which can result in faster response time for sensors. In addition, nanoscale dimensions may result in unusual new electrochemical reactions which have to be investigated in order to understand and further improve the technology of carbon electrodes. The current trend is to minimize the size of the electrode without loss of significant parameters such as conductivity, porosity and electrochemical reactivity [25]. Dimensions of the nanoscale may result in unusual new electrochemical reactions, which have to be investigated in order to understand and further improve the technology of carbon electrodes.

![Figure 4: Pyrolysis process with a photoresist structures created via a mask][10].

### 5.2.3 Electrolytes

Electrolytes are the material that makes regular capacitors into higher power-dense supercapacitors. Electrolytes with good ion mobility and a low solution resistance are preferred. There are three different types of electrolytes used in practice. Ionic liquids, aqueous electrolytes, and organic electrolytes each have their own advantages and disadvantages [9]. The electrolyte type of choice in the fabrication of conventional supercapacitors is liquid-based. Due to difficulties in applying these liquid electrolytes to on-chip applications, recent advances have been made in creating supercapacitors with gel-like electrolytes. Gao et al. succeeded in creating a comparable supercapacitor while using an alkaline polymer gel as the electrolyte substance in place of conventional electrolyte liquids [21].

### 5.3 Pyrolysis

The word pyrolysis originates from the Greek words *pyro* meaning fire and *lysis* meaning separating. The process consists of heating organic materials and simultaneously separation of the chemical structure. As high temperatures are reached in an inert environment, the bonds of the
non C-C covalent bonds break and only the carbon backbone of the organic polymer is retained [6]. Pyrolysis must be performed in an inert atmosphere, which prevents chemical reactions between the polymer and atmosphere. In this project, pyrolysis of different organic polymers (called precursor polymer) containing carbon and other chemical substances such as oxygen, nitrogen, hydrogen, etc. are explored, due to the creation of carbon materials via pyrolysis.

The outcome of the pyrolysis process is not always pure carbon. Some polymers will decompose entirely, while others will pass through a liquid or liquid-crystalline state producing coke and create crystalline graphite after additional heating as seen in Figure 6(A). In the polymer precursors of interest here, the carbon backbone of a polymer string will maintain its geometry without moving through a liquid state, resulting in a network of non graphitized interlinked carbon strings as seen in Figure 6(B). The result is carbon that has retained its carbon regions but shrunken in size as other material has left the polymer string during pyrolysis and the remaining carbon strings can interlink which could further reduce the size. The strong C-C bonds protect the carbon backbone from decomposition and the result is a product consisting solely of carbon in a homogeneous distribution of disordered graphitic regions. The pyrolysis process consists of polymer preparation followed by four heating phases shown in Figure 3:

Figure 5: Schematic overview of the different steps during pyrolysis. Notice when the different substrates dissolves. [6]

Polymer precursor preparation phase: Initially, a silicon wafer is spincoated with a photoresist (the polymer precursor), resulting in a layer of a few microns. The negative resist is then hardened by UV-exposure. Finally, the wafer is heated using a hot plate in order to improve the bonding by cross-linking the polymer precursor before pyrolysis.

Pre-carbonization phase (< 300°C): Substances such as monomers and molecules present in the solvent are removed from the precursor due to initial heating and ventilation.

Phase I (300-500 °C): The additional heating results in removal of halogens (Cl) and heteroatoms (oxygen and nitrogen), which decreases the total mass of the polymer. The heating also produces a system of aromatic carbon structures.

Phase II (500-1200 °C): Remaining substances such as oxygen, nitrogen, and hydrogen are removed. The removal of hydrogen (dehydrogenation) is initiated due to an increase in temperature, and the aromatic structure is changed to an interconnected structure (i.e. stronger bonding). Per
consequence of the removal of the aforementioned substances, the oxygen/carbon ratio (O/C) is lowered.

Annealing phase (> 1200°C): The last impurities are removed, and the final temperature controls the properties of the residual layer (i.e. carbon content, conductivity, etc.). Generally speaking, the higher the final temperature, the better the electrochemical behaviour (lower resistivity), which is due to the increasing number of conductive graphitic regions (graphitization). These regions are approximately parallel to each other whereas non-graphitic regions are distributed randomly, as seen in 6.

By choosing a suitable photoresist polymer precursor, it is possible to create several different structures using UV-lithography and stamps. This ability enables production of several carbon structures that increase the usefulness of applying carbon for electrode fabrication.

![Figure 6: Schematic representation of the structure of (A) a graphitizing carbon - the graphitic regions are approximately parallel to each other; (B) non-graphitizing carbons - the graphitic regions are oriented randomly, and their cross-links are sufficiently strong to impede movement of the layers into a more parallel arrangement [6].](image)

6 Carbon materials

In this report, several different types of carbon electrodes have been investigated, these include pyrolysed SU-8 and AZ photoresist, pyrolysed PLLA, carbon aerogels and a carbon compound, formed chemically through MWCNT (multi-walled carbon nanotubes), chinese ink and PVA (polyvinyl alcohol). The following section will give a brief overview of the properties of these materials as well as how to fabricate them.

6.1 Pyrolysed photoresists

Two types of photoresists have been used in this report; SU-8 and AZ. For completeness it should be mentioned that SU-8 is a negative photoresist and AZ is a positive resist, which would require two sets of masks to create the same pattern in both resists. However we are only making structures in the SU-8 resist so there is no need to further differentiate. Both are polymers that can be carbonized by pyrolysis, and it is possible to create nanostructures by photolithography with these materials. The following types of electrodes have been created:

- **Flat resist electrodes**
  These electrodes were created by spin coating the resists on silicon wafers and then putting them into the pyrolysis furnace (the negative resists should be exposed to UV light first in order to strengthen the bonds). It is expected that the capacitance of these samples is low because of the low surface area compared to some of the more porous structures. Hence, we concluded that these samples will primarily serve as references to investigate the impact of
creating 3D structures on the wafers, which will increase the surface area. The chosen resists were used because they are popular and reasonably cheap polymer resists, and it is possible to fabricate stable microstructures with them relatively easily.

- **Structured SU-8 electrodes**
  Two different kinds of SU-8 3D structures were fabricated. For the first 3D structure, AZ resist was spin-coated on Si, cured and pyrolysed. Then a layer of SU-8 resist was spin-coated on top. With UV lithography the SU-8 was formed into 3D pillars. This is seen in Figure 7(a).

  This wafer was then broken in half. One part was pyrolysed (3D pillars on the upper layer are now pyrolyzed SU-8), resulting in a carbon electrode with a higher surface area than a completely flat (2D) electrode. On the other part, the polymer pillars on top of pyrolysed AZ were left as polymer. A sample like this could be used in close contact with a flat pyrolysed AZ electrode. This would utilize the SU-8 pillars as very small spacers and bring the two electrodes very close to each other. The entire system could then be submerged in electrolyte. The effect of varying the spacing between the electrodes have not been tested here, but in any case bringing the electrode in close proximity will diminish the physical space occupied by the capacitor.

  For the second 3D structure, SU-8 resist was spin coated on Si and cured. Then a layer of SU-8 resist was spin-coated on top. Using UV lithography the top layer of SU-8 was formed into 3D rings. The entire structure was then pyrolysed. This is seen in Figure 7(b).

![Figure 7: The two kinds of structures created on Si wafers.](image)

6.2 Poly(lactic acid) (PLLA)

PLLA is a biodegradable polymer derived from renewable resources containing starch, e.g. potatoes, corn or rice [19], and is therefore an interesting material to use in a supercapacitor. The PLLA was diluted in dichloromethane and then spincoated onto a silicon wafer before being pyrolysed. This didn’t go as well as hoped though, as the PLLA at some places on the wafer had been turned into little bits of carbon, leaving behind areas of exposed silicon as seen on figure 8. This may have been caused by the low glass temperature of PLLA (45°-65° [19]), above which the PLLA becomes plastic and deformable which allows it to flow out and accumulate in certain areas. A uniform surface would be preferred, so further experiments with pyrolysis of PLLA should be performed if pyrolysed PLLA is to be used as electrodes in supercapacitors.
6.3 MWCNT-ink-PVA

Chinese ink has been commonly used as a black pigment in calligraphy and paintings since the Tang Dynasty. Carbon particles found in the ink are classified as soot or lampblack. These are by products due to incomplete combustion [12]. Since they are produced from incomplete combustion, they have lower carbon purity and the particles have significant variance in their shape and sizes [14]. This is because the particles may join to form large clusters. Glue from organic origins, such as egg white, hide glue and even plant gum can function as a dispersant [11],[13].

The conductivity of the Chinese ink can be improved by adding multi-walled carbon nanotubes (MWCNTs) and polyvinyl alcohol (PVA) to the ink as can be seen from table 1. This can be explained as the carbon particles in the ink provide additional connecting sites while the PVA binder ensures a robust conducting network. However, it is pertinent to note that the ingredients used for the experiment were all commercial based products and further understanding of these chemicals should be conducted to properly understand the chemical reactions taking place on a micro-scale.

<table>
<thead>
<tr>
<th>Samples</th>
<th>MWCNTs [g]</th>
<th>Chinese Ink [g]</th>
<th>2.5 wt% PVA [g]</th>
<th>Conductivity [S cm⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/o MWCNTs</td>
<td>-</td>
<td>2.0</td>
<td>5.0</td>
<td>0.80</td>
</tr>
<tr>
<td>w/o Chinese Ink</td>
<td>0.10</td>
<td>-</td>
<td>5.0</td>
<td>0.61</td>
</tr>
<tr>
<td>w/o PVA</td>
<td>0.10</td>
<td>2.0</td>
<td>-</td>
<td>3.40</td>
</tr>
<tr>
<td>Ternary composite</td>
<td>0.10</td>
<td>2.0</td>
<td>5.0</td>
<td>8.17</td>
</tr>
</tbody>
</table>

Table 1: The conductivity and ingredients in different samples of Chinese ink.

The contents of the Chinese ink used in our experiments differ slightly from the values above. The PVA used is 5 wt% and the ratios are a bit different. This is illustrated in table 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>MWCNT</th>
<th>Ink</th>
<th>PVA</th>
</tr>
</thead>
<tbody>
<tr>
<td>G-18</td>
<td>0.04 g</td>
<td>2 g</td>
<td>5 g</td>
</tr>
<tr>
<td>G-20</td>
<td>0.08 g</td>
<td>2 g</td>
<td>5 g</td>
</tr>
<tr>
<td>G-0</td>
<td>0.2 g</td>
<td>4 g</td>
<td>10 g</td>
</tr>
</tbody>
</table>

Table 2: The contents of the Chinese ink used in our experiments

The Chinese ink is a very flexible material, allowing for different types of supercapacitors than the hard pyrolysed surfaces and the brittle aerogel.
6.4 Carbon aerogel

The final material to be characterised was a carbon aerogel created from graphene oxide mixed with carbon nanotubes by Nugroho and Stassen [20]. This is a very light and porous material, giving it a high surface area and thus potentially high capacitance. The aerogel is very bulky compared to the “flat” structures on the silicon wafers, which opens up for some different application possibilities. The aerogel is very brittle however.

7 Experiments and results

This section gives an overview of the experiments conducted and the results will be presented and discussed.

7.1 Experimental setups

The aim of this project was to test various carbon based electrodes for use in supercapacitors. First of all the resistivity was measured, as the electrodes need to have good conductivity in order to obtain a high power output. Secondly a high capacitance is needed - for this, the electrodes need to be porous in order to obtain a high surface area, as this will increase the capacitance of the supercapacitor. Our different electrodes were studied in a SEM to see this porous structure on a micro-scale. Finally cyclic voltammetry and electrochemical impedance spectroscopy were used to determine the capacitances of the electrodes.

7.1.1 Resistivity

An important parameter for the electrodes is the resistivity, as a high resistance in the electrodes will increase the charge/discharge time and reduce the power output of the capacitor. To calculate the resistivity, the resistance of the electrodes were measured using a simple two-point probe ohm-meter across various distances. The resistivity could then be calculated as

\[ \rho = \frac{\pi d R}{2} \]  

where \( d \) is the distance between the probes [24]. This is a very rough and inaccurate measurement, and a 4-point measurement would be preferred, but it should still give a rough estimate of the resistances of the various electrodes.

7.1.2 SEM images

The electrodes were investigated with a Scanning Electron Microscope (SEM). In the SEM, secondary electrons are excited in the sample and detected. This gives information about the topography of the sample. As mentioned earlier the specific surface area of the electrode is very important for the performance of the electrode. Using SEM gives an indication of how porous the structure is, and for well defined structures also enables you to calculate the surface area of a sample. However, because of the limited resolution of the SEM images, nanopores can’t be detected by this method. An alternate solution could be to do precise density measurements of the samples and compare them to solid carbon, or to use a BET-measurement to calculate the total surface area.
7.1.3 Cyclic voltammetry

To measure the capacitance of the different carbon electrodes, cyclic voltammetry was performed. Cyclic voltammetry consists of applying a potential difference across the electrodes and then varying the potential linearly up and down for a set number of cycles while the current is measured. The rate at which the potential is varied is called the scan rate. By assuming that the capacitance is constant in time, equation (1) can be rearranged and differentiated with respect to time to yield

$$\frac{C}{\Delta t} = \frac{I}{\Delta U}$$

recognising that the change in charge per time is the current, \(\frac{dQ}{dt} = I\). The current and the scan rate can thus be used to determine the capacitance.

In our setup, we performed a two-point measurement which is less accurate but quicker than 3- or 4-point measurements. The working and counter electrodes were put in a beaker with the electrolyte 1M H\(_2\)SO\(_4\), and a measurement was made using a scan rate of 10 mV/s.

7.1.4 Electrochemical impedance spectroscopy (EIS)

Electrochemical Impedance Spectroscopy (EIS) provide information about electrochemical systems and are often used to characterize devices for energy storage such as batteries, fuel cells and capacitors. As with the cyclic voltammetry, the faster but less accurate two-point measurements were made instead of 3-point measurements. A working and counter electrode was connected to the potentiostat, and a FRA (frequency response analyser) measured the performance. In our experiment, the frequency was varied from 100 kHz to 0.1 Hz, and the applied voltage was 5 mV. The experimental setups (that are identical to those used for cyclic voltammetry) can be seen in figures 15, 16 and 17 in the appendix.

The output of the EIS measurements is a Bode plot of the phase shift and modulus of the impedance as a function of the frequency, and a Nyquist plot of the real and imaginary part of the impedance. To analyse this data, a model based on an equivalent circuit needed to be fitted to these plots. The simplest model was an RRC circuit as seen in figure 9(a). This includes a resistance in the wires and the capacitor and a resistor representing the resistance in the capacitor. The other model was a resistor, capacitor and a “constant phase shift” in series as seen in figure 9(b) - the addition and of the phase shift will not be discussed in this report, but it was added to improve the model.

![Equivalent circuit models used to analyse the EIS data.](image)

Figure 9: Equivalent circuit models used to analyse the EIS data.

7.2 Results and discussion

7.2.1 Resistivity

The resistivity was measured as described above, and the results are summarized in table 3, where ID is inner diameter and OD is outer diameter. All the polymers have been pyrolysed before testing the resistivity.
Table 3: Rough calculations of the resistivity of the various samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\rho$ [(\Omega\text{cm})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flat SU-8</td>
<td>500</td>
</tr>
<tr>
<td>Flat AZ</td>
<td>800</td>
</tr>
<tr>
<td>Flat PLLA</td>
<td>1000</td>
</tr>
<tr>
<td>SU-8 rings 1, ID: 356 (\mu m), OD: 462 (\mu m)</td>
<td>30</td>
</tr>
<tr>
<td>SU-8 rings 2, ID: 244 (\mu m), OD: 363 (\mu m)</td>
<td>70</td>
</tr>
<tr>
<td>SU-8 rings 3, ID: 164 (\mu m), OD: 291 (\mu m)</td>
<td>100</td>
</tr>
<tr>
<td>SU-8 rings 4, ID: 69 (\mu m), OD: 189 (\mu m)</td>
<td>140</td>
</tr>
<tr>
<td>SU-8 rings 5, ID: 31 (\mu m), OD: 136 (\mu m)</td>
<td>170</td>
</tr>
<tr>
<td>Chinese ink G-18</td>
<td>300</td>
</tr>
<tr>
<td>Chinese ink G-20</td>
<td>250</td>
</tr>
<tr>
<td>Chinese ink G-0</td>
<td>50</td>
</tr>
</tbody>
</table>

The backside of the silicon wafer was also measured to see if this would have any impact on the capacitance of electrodes based on these wafers, but the resistivity was found to be in the order of 10-20 M\(\Omega\)cm, so no current should go through the silicon as this is many orders of magnitudes larger than the resistivity of the pyrolysed AZ, SU-8 and PLLA.

It is seen that the smaller the diameters of the SU-8 rings, the larger the resistivity. As the smaller diameters will give a larger total surface area, a compromise between surface area and resistivity should be found to optimise the performance of the capacitors.

It was also noted that the Chinese ink had a rough side and a smoother side, and the rough sides had many times higher resistivities than the smooth sides (only the smooth sides have been given in table 3). This is something to consider in supercapacitor applications.

### 7.2.2 SEM images

The SEM images of the flat SU-8 and AZ samples showed no pores, indicating a very low specific surface area. However it is possible that the pyrolysis created nanopores too small to detect with the SEM.

The images of the aerogel revealed a very porous structure though as can be seen in the figures below, figure 10 shows the aerogel made from 100 % graphene oxide, while the aerogel in figure 11 is made from 50 % graphene oxide and 50 % carbon nanotubes (CNT).
Figure 10: SEM pictures of carbon aerogel made of 100% graphene oxide. **Left:** Overview image **Right:** Zoom of a smaller area which shows the sample has a high surface area.

Figure 11: SEM pictures of carbon aerogel made of 50% graphene oxide and added 50% carbon nanotubes. **Left:** Overview image **Right:** Zoom of a smaller area which shows the sample has a high surface area, notice the small carbon nanotubes.

Both samples show a very porous surface and the carbon nanotubes are visible in the zoom image in figure 11 as tiny structures as compared to the sheet-like structure in figure 10. The CNTs were added to increase conductivity.

**Measurement and calculations on surface area and shrinkage**

Here a sample calculation of the increase in surface area by patterning the structure is done. The parameters used are measured from SEM images of the samples with pillars of pyrolysed SU-8 on top of pyrolysed AZ resist. For the pillars created by the mask with an outer diameter of 380 μm the created pillars have a height of 106 μm and a diameter of 215 μm. The height of the pillars before and after pyrolysis have been measured by Stephan Keller using a Dektak profilometer. A unit cell (the square area that will later be occupied by a single pillar) has an area of \(450\mu m \times 450\mu m = 2.0 \times 10^5 \mu m^2\). The pillars after pyrolysis is seen to retain its pillar shape but with alterations, see Figure 12(b). The connection between the pillar and the base is rounded lowering the surface area per volume, as well as the top of the pillars are rounded inwards giving a higher surface area per volume. For simplicity the produced unit cell is approximated with a a
pillar, standing flat on the surface. The area of the unit cell is then given by: \[450\mu m \times 450\mu m + \pi 215\mu m \times 106\mu m = 2.0 \times 10^5 \mu m^2 + 0.7 \times 10^5 \mu m^2 = 2.7 \times 10^5 \mu m^2\]. Adding the pillars creates an increase in surface area by \[\frac{2.7 \times 10^5 \mu m^2}{2.0 \times 10^5 \mu m^2} = 135\%\].

![SEM images of unpyrolysed and pyrolysed SU-8 pillars on top of pyrolysed AZ resist.](image1.png)

(a) Pillars of unpyrolysed SU-8 on top of pyrolysed AZ resist. The pillars depicted have a diameter of 390 \(\mu m\) and a height of 243 \(\mu m\).

(b) Pillars of pyrolysed SU-8 on top of pyrolysed AZ resist. The pillars depicted have a diameter of 215 \(\mu m\) and a height of 106 \(\mu m\).

Figure 12: SEM images of unpyrolysed (a) and pyrolysed (b) SU-8 pillars on top of pyrolysed AZ resist. Notice the change in size and geometry.

As seen in Figures 12(a) and 12(b) the pillars shrink during pyrolysis. To investigate how much the volume of the pillars are calculated before and after pyrolysis. Again the produced structures are approximated by pillars.

Before pyrolysis:

\[
V = \pi r^2 h = \pi 195^2 \mu m^2 243\mu m = 2.9 \times 10^7 \mu m^3
\]

(7)

After pyrolysis:

\[
V = \pi r^2 h = \pi 107.5^2 \mu m^2 106\mu m = 0.4 \times 10^7 \mu m^3
\]

(8)

The pyrolysis then results in a volume decrease of around 725\%. Looking at shrinkage of the base layer, the thickness of the AZ resist layer before pyrolysis was 2.2 \(\mu m\) and after pyrolysis it is barely 200 nm thick. This is a decrease in the one direction by 1100\%.

7.2.3 Cyclic voltammetry

The cyclic voltammetry should have produced almost rectangular \(IV\)-graphs with well-defined areas, as is the case for ideal capacitors as seen in figure 13(a). However, this was not the case, as all of our graphs were more or less smeared out, and it was almost impossible to determine the area as seen in figure 13(b). Furthermore we experienced a lot of drift - the cycles weren’t aligned. It is possible that this could be improved by changing the parameters, but unfortunately we did not have time for this. It should be noted that the graph in figure 13(a) was made on a normal capacitor and with a scan rate of 1 V/s, 100 times higher than in our other experiments. A scan rate this high might have produced different results. This should also be clear from equation (6), as a higher scan rate should yield a higher current and thus a better defined area, as the capacitance is constant.
7.2.4 EIS

We also had several difficulties with the EIS measurements, as the models either didn’t fit our data or gave too big uncertainties on the values for them to be of any use. For example, the Bode and Nyquist plots for the 220µF capacitor can be seen in figures 14(a) and 14(b) respectively. As it can be seen, the RRC model fits the Bode plot well and gives a capacitance of 216.9±2.2µF, which is very close to the specified 220µF. However, the Nyquist plot shows a substantial discrepancy between the plot and the model, so something is definitely not right. The model with the constant phase shift fitted well to both plots, but then the values were way off.
We wanted to measure the capacitance of the SU-8 structured electrodes and compare them to the flat electrodes to see how the change in surface area affected the capacitance. However, the RRC model did not fit the data at all, and though the constant phase shift model fitted the data reasonably well as can be seen figures 18 and 19 in the appendix, the capacitance given was 86.12 $\pm$ 3.58 $\mu$F - with an uncertainty around a million times bigger than the actual value, these results are completely useless.

Another thing we wanted to measure was whether the entire volume of the carbon aerogel contributes to the capacitance or if it is only a surface effect. To test this, we used one big piece of the aerogel as the counter electrode and then two pieces of aerogel were tested as working electrodes - one quite round and chunky with a low surface-to-volume ratio, and the other very thin with a large surface-to-volume ratio. Oddly enough, the constant phase model both fitted the data well and gave off usable values as seen in figures 20, 21, 22 and 23 in the appendix. The results are listed in table 4.

As seen in the table, the experiment indicates that the inner volume does contribute to the capacitance, and not just the outer surface. This was also indicated already when we started the experiment, as we could see the electrolyte being sucked all the way up the aerogel even though we didn’t fully submerge it, as we wanted to avoid contact between the copper wires and the sulfuric acid. This indicates that the capillary forces in the pores are big enough to suck the electrolyte into the inner volume of the aerogel as well, so this should also contribute to the capacitance.

It would be expected that the normalised capacitances should be equal, as the electrodes are from the same material, and the entire bulk of the material apparently contributes to the capacitance. But the results show that the electrode with high surface-to-volume ratio actually has a lower normalised capacitance. This may be due to chemical reactions with the copper wires or that some of the aerogel might simply have broken off after we measured the mass. It may also indicate that even though the model seems to fit well, it doesn’t fully describe the system, and the results may therefore not be conclusive. In any case further experiments should be made in order to confirm this.

As the models we used did not fit our data very well, unfortunately we haven’t got any usable capacitance results for either the flat SU-8 and AZ electrodes, the structured SU-8 rings and pillars, the pyrolysed PLLA or the Chinese ink. Changes in the EIS parameter values may yield better
results, but unfortunately we did not have time to tweak the experimental setup in order to obtain these results.

8 Outlook

As our capacitance tests of the SU-8 and AZ structures did not work out as planned, this is definitely something to look further into. Our initial goal was to examine how much you could increase the capacitance by adding microfabricated structures to flat surfaces, and this is still an interesting question. If it is possible to create high capacitances, these thin supercapacitors may have uses in micro electro mechanical systems (MEMS) devices or other devices where tiny components are needed.

Our pyrolysis of PLLA did not go as well as hoped, but since this polymer is biodegradable and derived from renewable resources, this is definitely a material that should be investigated further, as this has the potential to create new, greener supercapacitors. The fabrication and pyrolysis need to be improved in order to get a uniform distribution of pyrolysed PLLA on the silicon wafer, and this is something that could be further tested. The capacitance of the pyrolysed PLLA should of course also be tested if PLLA is to be used in supercapacitors.

Chinese ink is another carbon-based electrode that should be looked further into, as this is a cheap and very flexible material that could have uses where the hard pyrolysed structures and the brittle aerogel will not be usable. The resistivity of some of the Chinese ink samples was relatively high, which will give a lower power output and slower charge/discharge times. This could possibly be improved by pyrolysing the ink and thereby carbonizing the PVA. It is uncertain whether pyrolysis of the Chinese ink would give a usable material or just carbon dust, but it could be interesting to find out.

From our tests on the carbon aerogel we learned that the entire bulk material (and not only the outer surface) contributes to the capacitance of the aerogel. This indicates that bulky porous carbon structures may be a good way to create supercapacitors in the future compared to making 3D structures on flat surfaces as we did with the photoresists. Because the aerogel has a very low density, it might be possible to create relatively big electrodes with big capacitances that are still very light, that can be used to collect brake energy in cars and busses. Because fuel efficiency decreases and carbon emission increases as the weight of the car goes up, lightness is a very important factor in creating an environmentally friendly car - and recycling as much brake energy as possible is another important factor.

It would be interesting to see how large carbon aerogel structures can be made and if there is a limit where the inner volume no longer contributes to the capacitance of the electrode. We also learned that it was quite hard making a good electrical contact to the aerogel, and it would be interesting to see if there is a better way to do it than using silver epoxy or simply sticking copper wires directly into the aerogel as was done in the experiments.

Another aspect to look further into is pseudocapacitance. The capacitance we have measured has been purely electric double layer capacitance (EDLC), as carbon doesn’t react with the electrolyte. However, the pseudocapacitance is usually higher than the EDLC per unit area, so it would be an obvious choice to try to create supercapacitors using pseudocapacitance. Metal oxides are usually used for this, and especially ruthenium would be a good choice of metal as RuO$_2$ has a high conductivity [4]. It is probably difficult to coat the carbon aerogel with ruthenium, but it should be possible to coat the 3D SU-8 structures with a thin layer of Ru using electron beam evaporation and thus see how this affects the capacitance. This would combine the stability, cheapness and easy fabrication of the carbon with the high pseudocapacitance of RuO$_2$ and could potentially be a good candidate for future supercapacitors.
Conclusion

In this project we have tried to fabricate different kinds of carbon samples. We have conducted numerous tests to gather data and analyse the material properties. We focused on capacitance readings to quantify which carbon compound was most suitable to serve as electrodes in supercapacitors. In our report, we measured the resistivity of the samples in order to get an idea of the possible power output of the capacitors. All samples tested showed reasonably low resistivity values (30-170 ohm cm). Hence, obeying ohm’s law, this translates to a high power output making it an ideal supercapacitor. Interpreting our results, several conclusions can be drawn about the individual samples. Through SEM and EIS experiments, we can conclude that pyrolysis of flat SU-8 and AZ did not fabricate a porous carbon structure. It is unlikely that it will make an ideal electrode for a supercapacitor, however it is pertinent to note that the fabrication technique is still an important concept that should be built upon. The use of other polymer precursors could have other results and the possibilities are immense. Pyrolysis of PLLA ended up with a non homogeneous product which seemed unsuitable for use as an electrode. If PLLA is to be pyrolysed for use as an electrode the pyrolysis process should be optimized for PLLA. MWCNT-ink-PVA showed promising results as a suitable electrode. Furthermore, its material flexibility provides many applications for use in small electronic devices. EIS experiment on it revealed that it was chemically unstable and even water soluble. We would suggest trying to pyrolyse the Chinese ink to remove possible remains of PVA or implementing a conductive, protection layer around the material before using it as an electrode to ensure the efficiency and stability of the supercapacitor. Lastly, carbon aerogels were qualitatively tested for capacitance to investigate if the entire structure adds to the capacitance or just the surface. The entire structure was found to contribute to the capacitance and further studies to upscale the production of carbon aerogels could be conducted.

Through the different experiments and subsequently the compilation of a nominal database, our report should help readers grasp a basic understanding of carbon materials as electrodes and their fabrication method. More research should definitely go into experimentation of pyrolysed polymers to form 3D carbon scaffolds and create supercapacitors.
A Appendix

A.1 Experimental setups

The setups used for cyclic voltammetry and EIS measurements are illustrated below. The different electrodes needed different electrical contacts and some were submerged in electrolyte and some had a piece of filter paper with electrolyte between the electrolytes.

Figure 15: The wires were connected to the pyrolysed polymers using a silver epoxy.

Figure 16: The Chinese ink was clamped between gold plate to create a good electric contact.
Figure 17: For tests on the aerogels as well as some of the other electrodes, the electrodes were submerged into the electrolyte.

A.2 EIS measurements

The Bode and Nyquist plots of various electrodes are presented with different models used to analyse the data.

The Bode and Nyquist plots for the SU-8 rings can be seen in the figures below.

Figure 18: The constant phase shift model fits reasonably well to the Bode plot of the data obtained from the SU-8 structured rings.
Figure 19: The model also fits the Nyquist plot. However, the output capacitance has an uncertainty of several MF, yielding the results useless.

Two aerogel electrodes were tested to determine whether the entire volume of the aerogel contributed to the capacitance or whether it was just the outer surface. The Bode and Nyquist plots are shown below. The equivalent circuit model fitted is the constant phase shift model.

Figure 20: Bode plot of the electrode with small surface-to-volume ratio.
Figure 21: Nyquist plot of the electrode with small surface-to-volume area

Figure 22: Bode plot of the electrode with high surface-to-volume ratio.
Figure 23: Nyquist plot of the electrode with high surface-to-volume area
References

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