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Microstructured electrodes for electrochemical energy storage

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy in Materials Science and Engineering

by

Leland Cramer Smith

2015
ABSTRACT OF THE DISSERTATION

Microstructured electrodes for electrochemical energy storage

by

Leland Cramer Smith

Doctor of Philosophy in Materials Science and Engineering

University of California, Los Angeles, 2015

Professor Bruce S. Dunn, Chair

Lithium-ion batteries and electric double-layer capacitors are two types of electrochemical energy storage devices that are characterized by high energy density and high power density, respectively. While these technologies have been successfully applied in applications such as personal electronics and electric vehicles, the potential for microscale energy storage devices remains unrealized. In this dissertation novel materials and processing methods are introduced for the fabrication of microscale lithium-ion batteries and electric double-layer capacitors. In the area of electric double-layer capacitors, carbon electrodes are fabricated by electrophoretic deposition and self-assembly and paired with a novel solid-state ionogel electrolyte. We successfully fabricate an on-chip electric double-layer capacitor that is just 0.14 mm$^2$ in electrode area, which is about 40 times smaller than any device so far reported in the literature. Microscale lithium-ion battery electrodes are prepared by micro-molding techniques. The composition of the anode and cathode are tuned to maximize mechanical durability, electronic and ionic conductivity. SU-8 photoresist is presented as a novel electrolyte material for conformally patterning 3D anode arrays. Both 2D and 3D lithium-ion batteries using SU-8 are presented. Initial results suggest that a working 3D microbattery based on SU-8 electrolyte is feasible. Finally, more fundamental research is presented on the
sol-gel encapsulation of lithium-polysulfide liquid catholytes. By carefully tuning the non-hydrolytic sol-gel reaction, water-reactive lithium-polysulfides are successfully encapsulated to form a polysulfide gel that retains its lithium storage activity. This polysulfide gel is used to fabricate a fully solid-state lithium-sulfur battery.
The dissertation of Leland Cramer Smith is approved.

Jane P. Chang

Chi On Chui

Bruce S. Dunn, Committee Chair

University of California, Los Angeles

2015
To my future wife Kate,

my sisters Caitlin and Eleanor

and my parents Mary and Laurence
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The Dunn Lab members reflect this same personality. Everyone in the group has always been enormously supportive and friendly. Especially in graduate school, where spirits can rise and fall as unpredictably as experimental results, it is great to have a group that can make you laugh and with whom you can commiserate. I will specifically thank a few people below. To those I do not mention, please know that this is only for the sake of brevity. I hope that we can all continue to work together – in one way or another – for the rest of our careers.

The electric double-layer capacitor work was initially a collaboration between Dr. Daniel Membreno and myself. Chapter 3 borrows some elements from the published work:


In the later work on electric double-layer capacitors Johnathan Lau synthesized the ionogel electrolytes and helped to characterize the devices. Dr. Greg Leung from the Chui Group in the Electrical Engineering Department conceived of device designs, prepared patterned gold-on-silicon electrodes and helped make our on-chip devices a reality. Chapter 4 presents some data that is common to the submitted work:

The 3D lithium-ion microbattery work involving carbon slurries (Chapter 5) was inspired by the work of Dr. Nicolas Cirigliano. I thank him especially for so generously sharing his previous data and literature searchers with me, which helped me to hit the ground running. The silicon micromolds used to make the carbon arrays were prepared by Dr. Janet Hur who was also immensely helpful in other aspects of the 3D battery project. Dr. Hur prepared the SU-8 coated silicon pillar arrays presented in Chapter 7.

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Chapter 1. Introduction and Objectives

Much of the technological progress achieved over the past decades can be understood as a process of miniaturization. Moore’s law describes the miniaturization of transistors and is one of the great success stories of materials science and engineering. In 1965 Gordon Moore observed that manufacturers had been doubling the density of transistors per area on integrated circuits every two years. He predicted that this trend would continue.¹ This prediction has played out with astounding accuracy for half a century, resulting in enormous improvements in both the processing speed and prevalence of integrated circuits. Consider that when ENIAC, the world’s first electronic computer, was built at the University of Pennsylvania in 1943 it contained just 17,468 transistors, yet weighed 30 tons and consumed 150 kW of power.² Compare this to the apple A8 processor used in the latest iPhones, which contains 2 billion transistors in an area of just 89 mm² and consumes power on the order of 10 mW.³

The benefits of miniaturization have been realized for electronic components besides computer processors. Antennas, actuators and cameras have all benefited from increased performance at smaller sizes with less power consumption.⁴,⁵,⁶ The continued miniaturization of electronic components opens up exciting opportunities in areas such as wireless communications, remote sensing and medical devices. A particularly exciting area is the continued miniaturization of satellites (Fig. 1.1A). The cost of sending a satellite into orbit is about $10,000 per pound, which makes clear the enormous benefits of increasing the functionality of smaller satellites.⁷ Just as small satellites can be used to measure the climate and biosphere of earth, unmanned aerial vehicles (Fig. 1.1B) are increasingly being used in wildlife ecology and precision agriculture.⁸,⁹ The cost and accessibility of these instruments will improve if they can maintain their performance in a smaller package.
Another popular design paradigm is the “internet of things”: the idea that wireless internet connectivity will be imparted to heterogeneous technology platforms. This can enable new data collection and control algorithms across diverse sets of technologies. This could have interesting applications, for example, in the area of electric power demand response. Devices such as water heaters, refrigerators and air-conditioners could have the built-in ability to communicate with each other to efficiently respond to fluctuating demand and supply of electricity. This can help to make the electricity grid more responsive, flexible and enable increasing penetration of renewable energy. For this vision to be realized, companies are developing small wireless connectivity nodes that can operate without external power (Fig. 1.1C). Smaller and cheaper nodes will require smaller components, especially small batteries that can supply energy reliably for long lifetimes.

Figure 1.1 – Potential applications for improved microscale batteries include: (A) small satellites (B) drones and small robots (C) small ubiquitous sensors for internet-of-things applications.

These sorts of miniaturized electrical technologies are intended to be inexpensive and reliable and give the same performance as their larger predecessors. Unfortunately while transistors, antennas etc. have all been successfully miniaturized, energy storage technologies remain stubbornly large. The Ragone plot in Fig. 1.2 summarizes the performance of commercially available lithium-ion batteries (LIB) and reveals how smaller battery designs
generally suffer lower volumetric energy densities. The different rechargeable (secondary) LIB belong to three general device formats. Cylindrical and prismatic cells are the type that we are familiar with in personal electronics such as cell phones, laptops and cameras. These formats were so successful in personal electronics that they have been adapted to power the latest generation of electric vehicles.\textsuperscript{11,12}

![Ragone plot showing the volumetric energy, volumetric power and volume of three formats of lithium-ion battery: cylindrical, button, and thin-film cells](image)

Figure 1.2 - Ragone plot showing the volumetric energy, volumetric power and volume of three formats of lithium-ion battery: cylindrical\textsuperscript{13,14}, button\textsuperscript{15,16} and thin-film cells\textsuperscript{17,18}

Button cells and thin-film cells are both much smaller in terms of total volume compared to prismatic and cylindrical cells, but they cannot match the high power and energy performance achieved by the larger formats. It is important to emphasize that the compositional differences between the materials used in these different cells are minor. Button and thin-film cells use metal oxide or metal sulfide cathodes and lithium metal as an anode. In general the charge storage mechanism is the same. Fundamentally the cylindrical and prismatic formats perform better because they pack a large amount of active material (high energy) into the cell while
concomitantly maintaining a large surface area between electrodes, which supports operation at high power. The smaller button and thin-film cells have a 2D interface between the electrode which results in an inherent tradeoff between energy and power. Thicker electrodes (button-cells) pack in more energy but it is only accessible at lower power. Thin-film electrodes have higher power but do not store much energy.

For some applications, the device footprint area is at a premium and thus areal power and energy density are the most important metric for evaluation energy storage devices. Still, from a research perspective volumetric energy density is a useful metric because: 1. it is related to the mass of the device through density which can be estimated fairly accurately 2. volumetric energy and power density gives a clearer idea about the geometric efficiency of a certain design, and its ability to effectively pack in active material.

In the field of electric double-layer capacitors (EDLC), microscale devices have yet to be realized commercially. For commercial applications, cylindrical and prismatic are the formats of choice for large applications, but researches are still discovering the best means to build supercapacitors on the microscale. It is even easier to foresee microscale applications for EDLC because there are already many applications for microscale dielectric capacitors. As will be discussed in Section 2.4, EDLC offer a large performance advantage over dielectric capacitors. Ultimately EDLC and LIB can work well in tandem because EDLC support higher power and long cycle life while batteries have more bulk energy storage. An EDLC/LIB hybrid could be an ideal power system for microscale electrical devices in the near future.

The work presented in the following chapters is unified around the common theme of new designs and fabrication techniques for microscale LIB and EDLC. Together my
collaborators and I have successfully pushed the limits by developing 0.014 mm$^3$ EDLC and 5 mm$^3$ LIB that offer state of the art performance. We focused especially on the unbreakable link between material processing and device performance. Chapter 2 introduces the technical and scientific details of microstructured LIB and EDLC. Chapters 3 and 4 present work on the development of microscale solid-state EDLC featuring a novel solid electrolyte made by sol-gel encapsulation of an ionic liquid. The remaining chapters (5-8) all relate to microscale LIB. Chapters 5 and 6 discuss composite graphite anodes and ionically conductive cathodes, respectively. Chapter 7 features our work preparing working 2D and 3D LIB using Si as an anode and SU-8 photoresist as a conformal electrolyte. A more fundamental study on the encapsulation of lithium-polysulfide solutions by sol-gel chemistry is presented in Chapter 8. This polysulfide gel material is a potential cathode material for microscale LIB. Finally Chapter 9 will discuss the conclusions and future work that should be pursued in this field. Chapter 10 describes the electrochemical methods that are common to all chapters of the dissertation.
1.1 References


Chapter 2. Background on Electrochemical Energy Storage

This dissertation is concerned with how to develop new materials systems and processing methods in order to form microscale energy storage technologies. Some materials synthesis is discussed including the ionogel (Chap. 2 and 3) and polysulfide gel (Chap. 8). However, many of the active materials used in our LIB and EDLC were commercially available. The focus of this dissertation is on novel processing methods and electrode designs for microscale devices. Processing and structure are the key considerations for translating the energy storage properties of materials into a full device.

2.1 Structure-Property Relationship for Energy Storage Devices

One important construct for understanding the field of Materials Science is the structure-property-processing relationship. This is represented schematically by the pyramid in Fig. 2.1. Some important properties of energy storage materials are electronic and ionic conductivity, surface area, electrochemical stability and, in the case of LIB, lithium storage capacity. Energy storage devices are evaluated by related criteria such as total cell impedance, cycling rate, cycle life and capacity. However, good material properties do not guarantee a good energy storage device. For example the morphology, mixing ratios and chemical interactions between device components can make the correlation between material and device properties somewhat ambiguous.
Figure 2.1 – A pyramid describing the important relationships in the field of materials science. Properties, structure, processing and performance are all codependent for electrochemical energy storage devices.

Only through careful consideration of processing can we hope to build good devices from good materials. Processing parameters such as thermal budget, solubility and mechanical durability introduce an entirely new set of variables that must be considered. When adapting energy storage technologies to the microscale, it is necessary to rethink the entire structure and processing of the energy storage device. Materials that fulfilled seemingly mundane roles in larger devices may take on entirely new importance when adapted to the microscale.

2.2 General Design of an Energy Storage Device

Generally speaking, electrochemical energy storage devices consist of two electrodes separated by an electrolyte (Fig. 2.2). Electrons move between the electrodes via metallic current collectors connected to an external circuit. This circuit either supplies the energy needed to move the ions up their thermodynamic gradient (charge) or collects energy as the ions move down their thermodynamic gradient (discharge). Ions move between the electrodes inside the device by passing through an electrolyte. In this region of the device there is also a separator, which
prevents the physical contact of the electrodes, which would provide a direct internal path for electrons, i.e. a short.

In the case of EDLC, the electrodes are made of the same material, typically some form of high-surface area sp$^2$ carbon. Energy storage in EDLC occurs at the surface of the electrode. Thus EDLC operate over the full voltage range of electrochemical stability of the electrolyte, typically around 2.7 V for EDLC using acetonitrile electrolytes.$^1$

In LIB the two electrodes are chemically different and this results in a chemical potential within the battery. Lithium ions are stored within the bulk of the electrodes and the chemical potential of the battery changes depending on how much lithium is stored in each electrode (state of charge). The voltage range of LIB is determined by the chemical potential that exists between the two electrodes at different states of charge. Typical LIB (graphite anode and LiCoO$_2$ cathode) charge to around 4.2 V and discharge to 2.5 V.$^2$ Of course electrolytes must be used that are stable at such high voltages.

For both devices it is important to understand the distinction between electronic and ionic conduction. Both EDLC and LIB store and release energy by separating the flow of ions and electrons. The electrolyte/separator must block the flow of electrons in order to force them to travel through the external circuit. The current collectors must be electronically conducting to supply electrons to the two electrodes. The current collectors must also be ionically blocking to prevent corrosion, loss of active ions and low coloumbic efficiency. The electrodes meanwhile should ideally be mixed conductors: highly conducting to both electrons and ions in order to facilitate fast charge transfer and a homogenous electrochemical potential throughout the electrode.
Figure 2.2: A cross-section of typical energy storage devices shows the relationship between ionic and electronic conduction in the electrolyte, electrodes and current collectors.

The diagram shown in Fig. 2.2 is simplified, especially since the layers are shown as equal size. The thickness of each layer will in fact be quite different. The current collector should be as thin as possible as this material is not “active” in the charge storage mechanism. They are typically around 20 µm thick. The electrolyte/separator must be thick enough to provide adequate electronic resistivity to prevent the internal flow of electrons. At the same time the electrolyte/separator thickness should be minimized to increase ionic conductance. Table 2.1 shows some general conductivity values for organic liquid and inorganic solid electrolytes. The solid electrolytes have a wide range of ionic conductivities, with the prototypical LiSICON materials having values around $10^{-6}$ S/cm. Solid electrolytes do not require a separator for obvious reasons, but their lower ionic conductivities mean they have found limited application in commercial LIB (typically only for thin-film LIB). A solid electrolyte must have a ratio of ionic conductivity to electronic conductivity that is very high ($\geq 10^6$) so that electrolyte thickness can be decreased without problematically high electronic conduction.
Table 2.1 – Typical Conductivity Values for Liquid and Solid Electrolytes

<table>
<thead>
<tr>
<th>Electrolyte type</th>
<th>Ionic conductivity (S/cm)</th>
<th>Electronic conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic liquid</td>
<td>5 – 10</td>
<td>$10^{-10}$</td>
</tr>
<tr>
<td>Inorganic solid</td>
<td>$10^{-3} – 10^{-10}$</td>
<td>$10^{-20}$</td>
</tr>
</tbody>
</table>

To improve ionic and electronic conduction the two electrodes are pressed together, so the separator/electrolyte layer must also have adequate mechanical strength and chemical stability to hold up over thousands of cycles. The thickness of the electrode layers will generally vary in the range of 50 to 300 µm for cylindrical cells. Higher power cells have thinner layers while higher energy, lower power cells have thicker electrode layers. This tradeoff is due to the fact that it takes a longer time for ions to diffuse through thicker electrodes.

2.3 Energy Storage Device Formats

While a complete discussion of various large battery formats is outside the scope of this dissertation, it is worth discussing the cylindrical cell, which is the most successful format for both large EDLC and LIB (Fig. 2.3). The success of this design is due mainly to its manufacturability, scalability, ability to pack lots of active material into a tight volume, and ease of packaging.
Figure 2.3 – The cylindrical format (A) consists of alternating layers of electrolyte, electrode and current collector rolled up and packaged in liquid electrolyte. Both commercial supercapacitors (B) and lithium-ion batteries (C) are constructed in cylindrical cells.

The electrode layers are coated onto current collecting metal foil by techniques such as slot die, reverse roll coating or doctor blading. The electrode layer typically consists of three components: 96% active material, 2% binder and 2% electronically conductive additive such as carbon black. It is essential that all of these materials have adequate electrochemical stability across the operational voltage range of the device. The addition of binder and conductive additive is necessary to give the electrode sufficient mechanical and electronic properties so that the active material can be fully utilized. However, the amount of additives cannot be arbitrarily increased as this can have deleterious effects on electrode performance. For example, the binders typically used such as carboxymethyl cellulose (CMC) and polyvinylidene fluoride (PVDF) are electronic insulators and will increase the resistivity of the electrode.

From an experimental standpoint, the addition of multiple components to the electrode makes it more difficult to isolate the electrochemistry of the active material. Whenever possible the use of pure, binder free electrodes simplifies the experimental evaluation of new materials
and can also lead to better performance. Binders are a good example of a seemingly innocuous material found in large cylindrical cells whose role becomes increasingly consequential for microscale devices. A major theme of this dissertation is the preparation of binder-free electrodes.

Another interesting material system in the cylindrical battery is the separator. These are generally highly cross-linked polymers such as polypropylene, polyethylene and their co-polymers. They have good mechanical strength and low electronic conductivity. Separators are made by a variety of techniques involving melting, dissolving and/or extruding the polymer. The resulting nanoporous structure allows liquid electrolyte to percolate and conduct ions while preventing contact between electronically conductive materials in the opposing electrodes (Fig. 2.4). In one of the final steps of cylindrical cell manufacture (before packaging) the layered structure shown in Fig. 2.2a is tightly wound to maintain good electrical contact and minimized empty space. Without the separator, the cylindrical format would not be possible.

Figure 2.4 – Commercial porous polymer separators used in lithium-ion batteries: (A) Celgard, (B) Asahi, (C) Entek, (D) Tonen.6
The purpose of this brief discussion of the cylindrical cell is to understand the basic types of materials that exist in the case of mass-manufactured EDLC and LIB with planar (2D) interfaces. These technologies have reached a high level of maturity. While the morphology and material choices for 3D batteries may vary significantly from those used in cylindrical cells, the basic structure of inert and electrically conducting current collectors, mixed-conductivity electrodes and ionically conducting electrolyte must be maintained.

2.4 Electric Double-Layer Capacitors

There are many commonalities in terms of the materials and the methods used to build EDLC and LIB. The cylindrical EDLC and LIB cells in Fig. 2.3 are nearly indistinguishable to the layman. However, the charge storage mechanism in EDLC is entirely different than that in LIB. EDLC store energy in electrostatic layers at the interface of charged electrodes and liquid electrolytes. In an ideal capacitor no chemical reactions occur, and the potential on the device \(V\) is linearly proportional to the amount of charge \(Q\) that is applied to the electrodes through an external circuit. The proportionality constant \(C\) is the capacitance.

\[
V = \frac{Q}{C}
\]  

An understanding of EDLC begins with dielectric capacitors, in which planar metal electrodes are separated by a thin layer of insulating material (dielectric). If a voltage is applied across the two electrodes, charge will build up on the electrodes proportional to the applied field. The maximum voltage that can be applied is limited to the field strength which causes the dielectric to break down and electrons to flow. The subtle rearrangement of electrons in the dielectric will tend to counteract the applied voltage. As a result an even greater charge must be accumulated on the electrodes to reach the applied voltage. The ability of the dielectric to
establish this internal field is measured as the dielectric constant ($\varepsilon_r$) which is a multiple of the permittivity of free space ($\varepsilon_0$). For electrodes with area $A$, separated by distance $d$:

$$\mathcal{C} = A \varepsilon_0 \varepsilon_r / d$$

(2.2)

Thus the capacitance can be increased by increasing $A$, increasing $\varepsilon_r$ or decreasing $d$. The distance $d$ can only be decreased so much before the dielectric material becomes unstable. For example SiO$_2$ is commonly used as dielectric with 1.5 nm (~10 Si-O bond lengths) being the thinnest dielectric layers utilized. Below this thickness, electron tunneling current becomes too high.\(^7\) Furthermore there can be uniformity or pinhole problems when attempting to process such thin films over large areas.

The dielectric constant varies over several orders of magnitude and indeed there has been much excitement about high-k dielectrics, such as HfO$_2$, for applications in capacitors. However, there remain significant problems both in the fundamental science and engineering of high-k dielectrics. High-k materials are found to suffer from compositional defects such as oxygen vacancies and interstitials that affect the performance and lifetime of such devices.\(^8\) Despite much interest, high-k dielectrics have not yet achieved commercial success for capacitor applications.

With a 1.5 nm SiO$_2$ dielectric and smooth electrodes, dielectric capacitance is limited to about 20 fF/\(\mu\text{m}^2\). Given the difficulty of making thinner and higher-k dielectrics, researchers have focused on finding ways to prepare nanostructured dielectric capacitors, that is to increase the actual $A$ vs. the apparent $A$.\(^9\) Among the highest reported areal capacitances were obtained for rolled-up nanomembranes (2.0 pF/\(\mu\text{m}^2\)) and single nanowires (1.4 pF/\(\mu\text{m}^2\)).\(^10,11\) However, it is unlikely that such approaches will be scalable for practical on-chip use.
Given the apparent limits of dielectric capacitors, EDLC are an enticing alternative for microscale capacitive energy storage. EDLC are a well-known technology and large, cylindrical EDLC have been commercially available for decades. Compared to dielectric capacitors, EDLC have two key differences: 1. The insulating dielectric material is replaced with a liquid electrolyte that contains mobile ions. 2. The planar metal electrodes are replaced with high surface area, electrically conducting sp² carbon materials such as activated carbon, carbon black, graphene, carbon nanotubes (CNT) etc.

![Figure 2.5](image)

Figure 2.5 – (A) Mechanism of charge storage in electric double-layer capacitor. (B) Structure of the electric double-layer at the surface a negatively charged electrode. Adapted from Ref. 12.

When a voltage is applied across the carbon electrodes, the ions in the immediate vicinity of each electrode act to balance the charge on electrodes. Positively charged ions migrate closer to the negative electrode and negative charges migrate towards the positive electrode. This rearrangement only occurs in the first few nanometers of the electrode interface. Compared to the random arrangement of the positive and negative ions in the bulk of the electrolyte, in the vicinity of the electrode there is an ordered “double layer” of opposite charges (Fig. 2.5B). Each
ion at the surface of the electrode is extremely close to the electrode, separated by only the solvation distance which is on the order of angstroms. In this sense each ion acts as a tiny dielectric capacitor. When summed over the entire surface of each carbon electrode the two electrode/electrolyte interfaces essentially act as two capacitors in series, with a sum capacitance ($C_{dl}$):

$$C_{dl} = A \varepsilon \varepsilon_r / 2d$$ (2.3)

The carbon materials used in EDLC electrodes drastically increase the actual surface area of the electrode. For an electrode having a 0.1 mg/cm$^2$ loading of carbon material with 1000 m$^2$/g surface area, the actual surface area ($A$) exceeds the apparent area by a factor of 1000. Also $d$ is now only a few angstroms, compared to a nanometer or more for the dielectric capacitor. The dielectric constant for liquid electrolytes is comparable to that of SiO$_2$. For example $\varepsilon_r$ of SiO$_2$ and butyl methylimidazolium tetrafluoroborate (BMIM BF$_4$) are 3.9 and 12.2 respectively. The combined effect of these improvements (increase in $A$ and decrease in $d$) allows EDLC to have areal capacitances that are several orders of magnitude higher than planar dielectric capacitors.

Because EDLC store charge only at the surface of the electrode, they cannot store as much charge per mass of electrode as batteries, which store charge in the bulk of the electrode. However, double-layer formation is a surface process that does not require solid-state diffusion and chemical reactions. So, EDLC have much higher power and longer cycle life than batteries.
Because the large advantage in charge storage, supercapacitors have opened up new applications for capacitive energy storage in areas such as regenerative braking for large vehicles and elevators. EDLC are best-suited for applications where high power operation and cycle life are more important than specific energy (Fig. 2.6).

The success of large, cylindrical cell EDLC creates optimism about the potential for EDLC to surpass the limited capacitance of microscale dielectric capacitors. This possibility presents a slew of new questions to researchers: How can microscale EDLC electrodes be formed in a way that is scalable? What is the best way to process and package the liquid electrolytes required by EDLC? Because larger EDLC have been mostly applied to low frequency <10 Hz applications, how well can EDLC perform in some higher frequency applications where dielectric capacitors are currently used such as sensor integration or on-chip decoupling?
The efforts reported so far in the literature show a very diverse range of microscale electrode fabrication techniques (Table 2.2). The use of vacuum vs. atmospheric temperature, vapor vs. liquid deposition processes, scalability and thermal budget are some important metrics that are not included in Table 2.2, but will certainly affect which deposition methods succeed. The cylindrical format cell is not easily prepared on the microscale, so researchers in this field generally adapt a coplanar electrode configuration (Fig. 2.7).
Figure 2.7 – Examples of carbon electrodes from Table 2.2 prepared from (A) CVD-grown CNT, (B) laser-scribed graphene, (C) lost-mold Si etching and (D) pyrolysis of photoresist.\textsuperscript{18,20,16,21}

For very thick coplanar electrodes (Fig. 2.7 B and C), the adjacent electrodes are essentially parallel to one another. This is nearly the same geometry as the cylindrical cell in Fig. 2.2. But for thin coplanar electrodes (Fig. 2.7 B and D) the path lengths between different portions of the electrode clearly varies. While charge transport between parallel electrodes can be described by a single RC time constant, different regions of the coplanar electrodes can be expected to have different RC time constants due to the varying distances between electrodes (Fig. 2.7). This geometric consideration is expected to affect the frequency-dependent performance of the devices and will be explored in Chapter 4.
Figure 2.8 – Equivalent circuit representations of charge transfer between (A) coplanar and (B) adjacent electrodes. The coplanar electrodes have varying resistance and therefore time constant due to the varying distance between the electrodes.

Research so far has characterized frequency-dependent behavior of on-chip capacitors using electrochemical impedance spectroscopy (EIS, Chapter 10). One way to make a quantitative distinction between frequency ranges where the capacitor is active and inactive is using the phase angle measured by EIS. For capacitive behavior the measured voltage should lag the applied voltage by 90°, so high phase angles are associated with capacitive charge storage. Lower phase angles are associated with resistive behavior: the current is in-phase with the applied voltage so the device is not effectively storing charge. Many researchers will quote the relaxation time constant (Table 2.2) which is the inverse of the frequency at which the device phase angle = 45°, the transition from high to low phase angle.\textsuperscript{23} Intuitively, one would expect that smaller distances between adjacent electrodes would result in better high frequency performance. This trend is generally evident in the literature. However, there are other important
factors such as the composition and especially the electronic conductivity of the electrode itself. Chapter 4 will show how the geometry of the electrodes is an important determiner of the frequency-dependent performance of an EDLC.

2.5 Lithium-Ion Batteries

LIB have the highest energy density of all commercialized secondary batteries (160 Wh/kg). Unlike EDLC, LIB have a different material at each electrode. Lithium is the lightest alkali metal and Li ions can insert into a variety of materials. Good LIB electrode materials have high ionic and electronic conductivity and can insert Li ions reversibly. Lithium metal (Li\(^0\)) easily release ions (Li\(^+\)) because each lithium atom wants to lose an electron to attain the helium electron structure. For a hypothetical system of lithium metal and some insertion material (e.g. transition metal oxides and sulfides), the Gibbs free energy of the system can be lowered if the lithium atoms are transferred to the insertion material. There the lithium can donate some electron density to the host lattice (Fig. 2A).

LIB harness this chemical potential difference by separating the movement of lithium ions and electrons. While the ions move within the cell, electrons must travel through the external circuit where they can be used to do work (discharge). On charging an external voltage is applied such that the chemical potential of lithium in the host is raised and the lithium ions (and electrons) leave the host. (Fig. 2.8B) The energy \(E\) stored by a LIB is equal to the total charge transferred during charge/discharge \(Q\) times the voltage difference between the two electrodes \(V\):

\[
E = Q \times V
\]  

(2.3)
The Gibbs free energy reduction achieved by lithium intercalation varies depending on the nature of the host structure. This is manifest in the potentials measured in an electrochemical cell. For example, graphite intercalates lithium at a potential of between 0.6 and 0.1 V vs. Li/Li$^+$, while metal oxides such as LiCoO$_2$ insert Li ions in the range of 3.0 to 4.5 V.$^{24}$ Thus LIB can be constructed using graphite anodes and metal oxide cathodes that operate at voltages between about 3 and 4 V, depending on state of charge. Graphite anodes give superior safety and cycleability compared to lithium metal, with a small sacrifice in potential.

Figure 2.9 – Charge storage in an LIB occurs by the (A) insertion of Li ions into host materials at (B) different chemical potentials. Electrons flow through the external circuit to maintain charge balance.$^{24}$

Today’s highly successful LIB are based on graphite anodes coupled with metal oxide insertion materials as positive electrodes (cathode). However, these cathode materials have relatively low capacities for lithium insertion, frequently <150 mAh/g, so researchers have begun to explore other potential cathodes.$^{26}$ One promising material is sulfur with a theoretical capacity for reaction with lithium of 1675 mAh/g.$^2$ The challenges of designing sulfur cathodes will be
addressed in Chapter 8, along with a novel polysulfide gel material prepared via non-hydrolytic sol-gel chemistry.

The functional differences between LIB and EDLC can be understood on the basis of the materials chemistry occurring within the devices. Because solid-state diffusion is slower than liquid diffusion and LIB store charge in the bulk of solid materials, LIB charge and discharge much slower than EDLC. Repetitive insertion and de-insertion of lithium ions into the host materials lead to breakdown of the electrode materials, so LIB typically only function for 1000–2000 cycles. Because EDLC only store charge at the surface of the electrode materials, they can charge and discharge faster and survive many more cycles (100,000 or more), but they store only about 1/10 the energy per mass compared to LIB. EDLC can easily handle power spikes while LIB have superior capacity, so these two energy storage technologies can complement each other when used in tandem.

The cylindrical LIB cells that are so common today have a 2D electrode/electrolyte/electrode interface (Fig. 2.3), but the surface area : volume ratio of the electrode can be increased by decreasing the electrode thickness and increasing the number of windings. Thus higher power cells can be made, albeit with a penalty in energy density due to the increased current collector and separator material needed for more windings.

In thin-film and button cell LIB, each electrode is essentially a rectangular prism: the volume and surface area of the electrode cannot be varied independently. Thicker electrodes can store more charge than thinner electrode, but the long ion diffusion path in thicker electrodes limits how quickly the charge can be stored. This is clear in Fig. 1.2 where small batteries considerably underperform their larger counterparts. For small LIB the choice is effectively
between thin-film batteries, which have good volumetric power but low volumetric energy density and button cells, which have thicker electrodes, more energy, but less power (Fig. 2.9). Today there is no microscale LIB format that can deliver the high energy and power density of the cylindrical cell.

The goal for advanced microscale batteries is to develop non-planar (3D) electrodes with large surface area : volume ratios. As is the case for microscale EDLC, there is a great deal of variety in the approaches used by various researchers in the field of 3D LIB. Just two examples of these diverse approaches are shown in Fig. 2.10. On the left, Pikul et al. used electrodeposition to deposit two different lithium insertion materials on porous metal substrates. Sun et al. used 3D-printed inks containing active lithium insertion materials. Despite the dramatic difference in approach, there is a similarity in the two attempts in that they both feature relatively large inactive volumes that are filled with liquid electrolyte and do not contribute to the capacity of the microbattery. The batteries prepared by Pikul et al. and Sun et al. achieve around 0.05 mWh/mm\(^3\) and 0.065 mWh/mm\(^3\) which from Fig. 1.2 are around 25% of the energy density of currently available button cell LIB and 10x smaller than LIB cylindrical cells.
Figure 2.11 – Two recent reports of 3D lithium-ion batteries from the literature. (A) electrodes electrodeposited on a porous scaffold\textsuperscript{29} and (B) electrodes are 3D printed.\textsuperscript{28}

These two studies exemplify the dynamic relationship between the processing and properties of microscale LIB. For Pikul et al., the use of electrodeposition necessitates thin films of active material and limits the amount of active material that can be loaded. For Sun et al., 3D printing required the fine-tuning of the electrode slurries via the addition of ethylene glycol, glycerol, and cellulose-based viscosifiers to get the proper rheological properties.

It is notable that neither of the studies, which represent the state of the art in microscale LIB, made use of a conformal electrolyte/seperator. The fabrication of conformal, stable, uniform and defect-free solid electrolyte materials with adequate ionic conductivity remains a major material challenge for realization of a 3D lithium-ion microbattery (LIMB) with high energy and power density.

This dissertation addresses the need for conformal electrolytes in two ways. In Chapter 5, scalable and durable carbon microelectrodes will be presented for use as test structures for conformal electrolyte coating. Chapter 6 will address the electrolyte materials head-on and
present data concerning the use of a common epoxy-based photoresist (SU-8) as an electrolyte in LIMB.

2.6 Conclusions

EDLC and LIB store energy by entirely different mechanisms. EDLC store energy in adsorbed layers of ions at the surface of charged electrodes while LIB intercalate lithium ions directly into the atomic structure of host materials. However, the design of commercial EDLC and LIB is remarkably similar. Both types of devices are predominately manufactured in the cylindrical format with alternating layers of current collector, separator, and electrode built in a 2D sheets, rolled up and flooded with liquid electrolyte. The research community is actively pursuing microscale designs of both EDLC and LIB using a wide variety of methods. Microscale EDLC generally use coplanar electrodes deposited by liquid or vapor phase methods. Designs for microscale energy storage devices should be scalable, avoid relying on electronically insulating binder materials and minimize the volume of the device occupied by electrolyte.
2.7 References


In order to develop microscale solid-state EDLC we needed to address significant challenges both in terms of materials and device fabrication. We developed the required materials using large (~1cm²) prototypes. This chapter is focused on the development of carbon nanotube electrodes that are stable in electrolyte over a large voltage range. These electrodes enabled the development of a solid-state electrolyte prepared through the sol-gel encapsulation of an ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate. With these materials we were able to fabricate solid-state EDLC that operated at voltages up to 3.75 V.

It is difficult to imagine a means of fabricating hundreds or thousands of microscale capacitors on-chip using a liquid electrolyte. Leakage and evaporation issues would require elaborate packing techniques that may not be reliable. Still, EDLC necessarily require mobile cations and anions in order to function. Therefore we sought to address a major materials problem by developing a quasi-solid electrolyte that could function in an EDLC and maintain the macroscopic properties of a solid.

An EDLC electrolyte cannot be fully evaluated without some test electrodes. So we developed binder-free carbon electrodes in order to maximize electrical conductivity and also limit the number of chemical species (such as binders or additives) that could potentially complicate the study of our novel solid electrolyte. We also aimed to use electrode processing methods that were scalable, inexpensive and occurred at ambient temperature and pressure. Electrophoretic deposition (EPD) met these requirements and was used to develop high-purity carbon nanotube (CNT) electrodes.
Chronologically speaking, the development of electrodes made by EPD occurred in parallel with the development of our solid-state “ionogel” electrolyte. Extensive discussion of ionogel development can be found in Daniel Membreno’s thesis. Aside from a brief description of the ionogel, this chapter will focus on research pertaining to CNT electrodes prepared by EPD.

3.1 Introduction

The ionogel was prepared from mixtures of silica sol and ionic liquids. The goal here is to form an inert SiO$_2$ network that does not participate electrochemically, but imparts the ionic liquid with all the properties of a solid. Ionic liquids are an excellent choice for a pseudo-solid electrolyte because they have essentially zero vapor pressure. The sol-gel chemistry of the ionogel must be precisely controlled to achieve complete conversion of the sol-gel precursors to SiO$_2$. An incomplete sol-gel reaction could manifest obvious problems like a non-solid gel or more subtle issues that can only be probed electrochemically. Inert CNT electrodes offer the perfect opportunity to test the performance of the ionogel and compare it to the properties of the ionic liquid and ionogel.

CNT were chosen as an electrode material due to their good electrical conductivity and high surface area and EPD was chosen for its ability to produce uniform, binder free electrodes from liquid (aqueous and non-aqueous) dispersions of carbon. A key parameter for evaluating materials for EDLC is their voltage stability. As seen in equation 3.1, the energy ($E$) stored by and EDLC is proportional its capacitance ($C$) times the square of its maximum voltage ($V$).

$$E = \frac{1}{2} C V^2 \quad (3.1)$$
EDLC operate based on electrostatic interactions; no mass should cross the electrode/electrolyte interface. At a certain potential, however, redox reactions will occur between the polarized electrodes and the electrolyte. The highest voltage at which these reactions do not occur is the maximum voltage stability. Ionic liquids possess a high voltage stability, in some cases beyond 5V. The maximum voltage stability of an EDLC is limited by both the electrolyte and electrode. So, to get the full benefit of ionic liquids’ high voltage properties, highly stable electrodes are needed.

One of the most electrochemically stable forms of carbon is glassy carbon. This material inspires our design of highly stable CNT. Glassy carbon is so stable that, along with platinum, it is the material of choice for measuring the maximum voltage stability of ionic liquids. It is evident in Fig. 3.1A that glassy carbon is composed of highly-oriented and uniform graphitic layers and even polyhedral shapes. Glassy carbon is not suitable for EDLC because of its low surface area, but it proves the point that defect free sp2 carbon can achieve high voltage stability in ionic liquids. Fig. 3.1B shows the morphology of the CNT mats that we prepared by EPD from aqueous suspensions of CNT. Figure 3.1C shows ketjen black, another form of nanoscale carbon that will be used in Chapter 4.
Figure 3.1 – (A) The Highly uniform graphitic structure of glassy carbon. (B) CNT mat prepared by EPD from aqueous solutions. (C) Ketjen black consists of nanoscale carbon particles composed of ~20 nm primary particles.

In order to be deposited by EPD a material must have charge-bearing functional groups. This charge is necessary both to form a stable suspension and to move in response to an applied electric field. The velocity of the movement (electrophoresis) of a charged particle in solution is described by the Hückel equation:

\[ V = \frac{2 \varepsilon_o \varepsilon_r \zeta}{3 \eta} \]  

(3.2)

Electrophoresis velocity \( V \) is proportional to the electric field strength \( E \), dielectric permittivity of the EPD solvent \( \varepsilon_o \varepsilon_r \), the zeta potential \( \zeta \) and inversely proportional to the viscosity of the solvent \( \eta \). A common source of surface charge on carbon materials is oxygen-containing functional groups (Fig. 3.2).
Figure 3.2 – Examples of various oxygen-containing functional groups that exist on the surface of oxidize carbon nanotubes.

Pristine sp2 carbon, such as glassy carbon, does not have charged functional groups. So there is an interesting tradeoff that, in order to process our CNT electrodes by EPD, we must necessarily introduce defects that will decrease the electrochemical stability of our carbon electrodes. Like glassy carbon, pristine CNT are able to achieve the full voltage window of ionic liquids. The challenge is to prepare pristine CNT by EPD.

Figure 3.3 – (A) schematic of two-electrode electrophoretic deposition cell (B) process flow for the fabrication of 1 cm² CNT/ionogel EDLC
As will be shown in the following sections, the chemical functionality of the CNT was studied after all electrode processing steps and correlated to the electrochemical properties of the CNT electrodes. A generic outline of the processing steps is shown in Fig. 3.3. A schematic of an EPD cell is shown in Fig. 3.3A, while the full device processing including the ionogel electrolyte is in Fig. 3B. Ultimately, CNT were prepared that achieved the maximum voltage (4.2 V) in the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM BF₄). By using the optimized ionogel composition we were able to build CNT/ionogel capacitors that achieved a 3.75 V operating window. This is among the highest values reported in the literature for a sol-gel derived ionogel electrolyte.¹⁴

3.2 Experimental

3.2.1 Ionogel Synthesis

Ionogel was prepared according to the method reported by Membreno et al.⁵ BMIM BF₄ (Sigma) was stored in an argon-filled glovebox to prevent the uptake of moisture. About 1 ml of BMIM BF₄ was removed from the glovebox 30 minutes before the synthesis began. Sol was prepared containing a 2:2:5 volume ratio of tetramethoxysilane : vinyltriethoxysilane : formic acid. This sol was stirred in a 39°C oil bath for 19 minutes after which time BMIM BF₄ ionic liquid was added in two different ratios resulting in a 42% or 72% total ionic liquid volume in the sol. The sol/ionic liquid mixture was stirred for 30 seconds at which point it was applied to the devices being manufactured. The ionogel was then applied to the devices by drop-casting. The ionogel was allowed to solidify for 1 hour and then loaded into ovens for 12 hours at 50°C, 1 day at 100°C and 1 day at 100°C in vacuum oven to remove by-products from the sol-gel reaction.
3.2.2 Chemical Functionalization of Carbon Nanotubes

Multiwalled CNTs (30–70 concentric tubes, 0.5–200 µm in length) were purchased from Sigma Aldrich. Before CNT could be dispersed in polar solvents such as water or n-methyl pyrrolidinone (NMP) for EPD, they first needed a surface charge. This was introduced using HNO₃ which is a widely used technique in the literature.¹⁰ Two HNO₃ oxidation treatments were compared. One was a stirring the CNT in 12.6 M HNO₃ at 60°C for 72 hours and the other was refluxing in 2.6 M HNO₃ for 44 hours.

The concentration of CNT in the HNO₃ was 1.6 mg/ml. After HNO₃ treatment the CNT that remained dispersed in HNO₃ solution were collected, any CNT that adhered to the wall of the flask were discarded. To remove any adsorbed chemicals the CNT were dispersed in 500 ml of deionized water and vacuum filtered over 2.5 µm Whatman filter paper three times. Finally the CNT were dried in a 100°C oven for 24 hours.

3.2.3 Spectroscopic Characterization of Carbon Nanotubes

FTIR pellets were prepared using 1.5 mg of CNT in 80 mg of KBr (Sigma Aldrich), milled using an agate mortar and pestle to yield a light grey powder. Pellets were made by pressing the powder for 5 minutes under 900 psi. FTIR spectra were measured with the chamber flooded with argon (JASCO 670plus).

X-ray photoelectron spectroscopy (XPS) was performed on the Kratos DLD-ultra in the UCLA Chemistry Department. Samples were prepared by pressing CNT powder into conductive carbon tape. XPS spectra were averaged over 5 scans using a 20 eV pass energy, 15 kV accelerating voltage and 10 mA current. Raman spectra were collected using a Renishaw inVia Raman microscope using the 514 nm laser.
3.2.4 Electrophoretic Deposition of Carbon Nanotubes

CNT were dispersed in either water or NMP depending on their oxidative treatment (See 3.3.1). Before use, 304 stainless steel substrates were cleaned by sonicating in a 1:1 mixture of acetone and ethanol for 10 minutes. Two EPD cells were used. Initial experiments with 12.7 M CNT dispersed in water were conducted using a vertical arrangement of parallel electrodes with a 1 cm spacing such that the direction of electrophoresis was perpendicular to gravity. Later a custom built EPD apparatus (Fig. 3.4) was used where the electrodes were arranged horizontally such that electrophoresis occurred parallel to gravity. The electrode spacing on this apparatus was adjustable through the use of o-rings of various thicknesses. Electrode spacings as small as 100 µm were used to maximize the field strength between the electrodes (Eqn. 3.2). After EPD, the CNT on stainless steel were treated in a tube furnace (Applied Test Systems 3210) controlled by an Omega CN8240 controller under 5% H₂ / 95% N₂ for 2 hours at 200°C to remove the adsorbed oxygen created by electrolysis during CNT deposition. The surface roughness and thickness of the CNT electrode deposits were assessed qualitatively using scanning electron microscopy (Nova 230 SEM). The mass of CNTs deposited by EPD was measured using a microbalance.
Later, Daniel Membreno developed a modified procedure to produce CNT electrodes for prototype sandwich devices. For this procedure 1 mg of 12.6 M HNO$_3$ CNT was dispersed in 15 mL of deionized water. The vertical stainless steel electrodes were spaced 1 cm apart with an applied voltage of 14.5 VDC with 3 VAC at 0.3 MHz for 20 min. The use of AC voltage was based on reports of using dielectrophoresis to deposit aligned CNT.$^7,^8$ This modified AC EPD has also been shown to suppress bubble formation.$^9$ The deposition electrode assembly was designed such that the electrodes could be removed from the solution before turning off the deposition voltage to minimize the loss of CNT. The same post-deposition heat treatment was performed as described in the previous paragraph.
3.2.5 Fabrication of Sandwich Devices

Two CNT electrodes on stainless steel (1 cm x 1 cm CNT deposit) were used to fabricate one device. EDLC with parallel plate geometry were made by combining the CNT electrodes with the ionogel. EPD was used to deposit 190 µg of CNTs evenly onto the 1 cm² electrodes. 120 µm Teflon shims were used around the edges of the electrode to set the thickness of the ionogel layer. Devices were formed by drop casting 20 µL of ionogel onto the bottom CNT electrode after 19 min of hydrolysis. 20 µL is an excess of ionogel to ensure that the volume between the electrodes is filled. The top electrode was placed CNT side inward to complete the device fabrication. The device was then dried in ambient conditions for 1 hour prior to heat treatment as described in the ionogel procedure.

3.2.6 Electrochemical Characterization

CNT on stainless steel electrodes were by CV (Princeton VMP3) using BMIM BF₄ electrolyte a stainless steel counter and Pt foil as a pseudo-reference. These measurements were taken in an argon-filled glovebox with <1 ppm water and oxygen. CNT/ionogel devices were measured by CV and GV.

3.3 Results and Discussion

3.3.1 Morphology of Carbon Nanotube deposits

In order to achieve significant areal capacitance for our electrodes we aimed to have high areal CNT mass loadings (>100 µg/cm²). To avoid shorts in our prototype devices we also needed to try to make smooth deposits. Smoother deposits would in turn enable smaller electrode separation which would lower the ionic resistance of our electrolyte. Based on Eqn. 3.2 it was
hypothesized that the deposit mass and smoothness could both be increased with higher applied field strength \((E)\). In order to achieve high mass loadings and uniform deposits it was important to understand the stability and quality of the CNT dispersions. More stable dispersions are less likely to flocculate and should give fewer large CNT aggregates in the deposit.

Qualitative evaluation of CNT dispersion quality was undertaken by placing CNT in various amounts in a given solvent, sonicating for 1 hour and then observing the dispersion with the naked eye. Poor dispersions would immediately show settling and flocculation, especially around the liquid meniscus at the top of the vial. The 12.6 M CNT were found to be stable for 24 hours at a concentration of 0.5 mg/ml in deionized water. Using these aqueous dispersions and 1 cm electrode spacing, CNT were deposited on stainless steel at a field strength of 1 V/cm for 20 min. The resulting deposits had a mass around 50 \(\mu\)g/cm\(^2\). An example of one such electrode is shown in the SEM images in Fig. 3.5.

Figure 3.5 – SEM images of CNT electrodes prepared from aqueous suspension at a field strength of 1 V/cm
In order to increase the mass and smoothness of the CNT deposit it is desired to increase the velocity of electrophoresis according to the Hückle equation (Eqn. 3.2). This can be accomplished by increasing the potential applied across the electrodes. However, water-based dispersions are limited to around 1.3 V due to the electrolysis of water. Attempts were made to disperse the 12.6 M CNT into alternate solvents with higher voltage windows such as ethanol, dimethyl formamide (DMF) and n-methyl pyrrolidinone (NMP) but none of these dispersions displayed adequate stability to warrant attempts at EPD. From the literature it is understood that concentrated HNO$_3$ can aggressively degrade CNT structure and introduce an abundance of oxygenated functional groups. In order to tune the solubility of the CNT a less aggressive oxidation procedure was pursued.

The 2.6 M refluxing is a method previously employed to introduce a moderate amount of oxygen functional groups onto the CNT surface. The CNT prepared in 2.6 M HNO$_3$ showed markedly different dispersing tendencies compared to the 12.6 M HNO$_3$ CNT. While they did not disperse in water they dispersed readily in NMP in concentrations up to 5 mg/ml. By using organic solvents, much larger deposition voltages could be used because the problem of water electrolysis was mostly avoided (except for trace water in the NMP).

Deposition voltages of 15 V were used to deposit the CNT/NMP dispersions. Using the horizontal EPD set-up described in Section 3.2.4 the distance between the electrodes was set at 0.8 and 0.1 mm to give field strengths of 19 and 150 V/mm. The deposits prepared using these conditions are shown in Fig. 3.6. The 19 V/mm field strength (Fig. 3.5 A and C) was applied for 26 minutes to obtain a deposit with a mass of 274 µg/cm$^2$. The 150 V/mm field strength (Fig. 3.5 B and D) was applied for 3 minutes and 180 µg/cm$^2$ CNT were deposited. Both depositions used
5mg/ml CNT dispersed in NMP. There is a clear dependence of the morphology on the deposition field strength; the 150 V/mm deposit is clearly much smoother.

Figure 3.6 – SEM images of CNT electrodes prepared from NMP suspensions at field strengths of (A, B) 19 V/mm and (C, D) 150 V/mm

3.3.2 Spectroscopy of Carbon Nanotubes

Because EPD creates CNT electrodes without any binders or additives, the electrochemistry of the CNT can be studied as a direct function of EPD processing parameters.
To increase the energy density of an EDLC the voltage window should be maximized according to Eqn. 3.1. We aimed to maximize the electrochemical stability of the CNT by changing the HNO$_3$ oxidation procedure and EPD field strength. Highly stable CNT electrodes also provided the experimental benefit of helping us to maximize the voltage stability of the ionogel electrolyte. For example, if CNT electrodes are prepared that achieve a 4V electrochemical stability window in BMIM BF$_4$ ionic liquid, but the ionogel device with the same electrodes only achieves 3 V, we can safely conclude that some component of the sol-gel reaction is diminishing the voltage stability of the ionogel.

Figure 3.7 – FTIR spectra for CNT during various stages of processing. Nitric acid functionalization introduces oxygen-containing functional groups.

FT-IR and XPS were used to understand what types of functional groups exist on the CNT at various stages of processing. The as-received sample shows a relative flat FTIR spectrum that is typical of sp2 bonded carbon.$^{11}$ FTIR spectra (Fig. 3.7) reveal all of the expected
groups in the 2.6 M and 12.6 M HNO₃ CNT samples: those associated with C-O, C=O and O-H bonds that are introduced by exposure to nitric acid.¹² There is no major difference between these two curves except that the signal for the 12.6 M CNT is slightly weaker. This could be due to the ability of stronger HNO₃ to break down the structure of CNT or could just be due to some variation in the preparation and measurement of the KBr pellets. The CNT measured after deposition from NMP at 150 V/mm show an absence of functional groups, which suggests that high deposition field may be able to strip functional groups off of the CNT. This is a preliminary finding that could warrant further study.

While useful, the FTIR data does little to elucidate what specific chemical species (Fig. 3.2) are present on the oxidized CNT. A more quantitative picture can be obtained using XPS, which measures the bonding energy associated with atoms at the CNT surface. Because of differences in the orbital hybridization of C-O and C=O bonds, electrons in the C=O have more p-character and are less tightly held than the electrons in the C-O sigma bond. As a result the O 1s electrons in C=O bonds have slightly lower binding energy, around 531 eV vs 535 eV for C-O.¹² It is evident from the XPS data comparing the 2.6 M and 12.6 M CNT (Fig. 3.8) that the 12.6 M CNT have a preponderance of C=O double bonds compared to the CNT functionalized in 2.6 M HNO₃.
Figure 3.8 - XPS data showing the position of the O1s peak for CNT subject to different oxidative treatments in nitric acid.

Apart from the individual chemical groups on the functionalized CNT it is also important to consider the effect of functionalization on the higher-order structure of the CNT. It has been reported in the literature that aggressive HNO₃ oxidation can cause a breakdown in the long range order of CNT and create carbonaceous impurities.¹⁰ We sought to evaluate these structural changes using Raman spectroscopy (Fig. 3.9).
There are three main features of carbon evident in the Raman spectrum. The D peak at 1310 cm$^{-1}$ is due to disordered sp$^2$ carbon. The G peak at 1580 cm$^{-1}$ corresponds to graphitic domains and the D’ peak at 1620 cm$^{-1}$ arises due to surface defects or impurities.$^{13}$ The data shown in Fig. 3.8 are normalized to the D peak. Evidently the as-received CNT do have some defects based on the presence of the D’ peak. The existence of both the D and G peak in the as-received samples is inherent to CNT. The strain induced by bending the graphene layers to form a tube results in a material that is not perfectly graphitic. The as-received and 2.6 M functionalized CNT curves are nearly on top of each other, suggesting that the 2.6 M HNO$_3$ treatment does not significantly alter the CNT structure. The 12.6 M HNO$_3$ CNT deviate much more significantly from the as-received CNT. The 12.6 M CNT show a much higher background
noise level and a change in the ratio of the D and G peaks, suggesting that the disordered carbon in the CNT is preferentially oxidized by the HNO$_3$.

The spectroscopic studies presented in this section reveal generally that the 12.6 M HNO$_3$ treatment yields more dramatic changes to the CNT both in terms of higher order carbon oxygen bonding as well as changes to the long-range structure.

### 3.3.3 Electrochemistry of Carbon Nanotube Deposits

The previous section demonstrated that the morphology and chemical properties of CNT electrodes prepared by EPD is dependent on the processing conditions, especially the oxidative HNO$_3$ functionalization and the EPD field strength. The consequences of these electrode properties are evident in electrochemical studies of the CNT electrodes, which were mostly conducted by cyclic voltammetry (CV).

The simplest variable for the electrodes is the mass loading of CNT. In order to increase the areal capacitance of the electrode it is necessary to increase the mass loading. At the same time, thicker electrodes will have longer ion diffusion paths so thicker electrodes give diminishing returns in terms of areal capacitance. This trend is evident in our results for thin CNT electrodes prepared by aqueous EPD (Fig. 3.10). Increasing the mass loading from 10 to 40 $\mu$g/cm$^2$ increases the areal capacitance of the electrode, but the accompanying drop in CNT gravimetric capacitance indicates that less of the CNT surface area is effectively storing charge.
Figure 3.10 – The relationship between gravimetric and areal capacitance for CNT on stainless steel electrodes with low CNT mass loading. The areal capacitance of bare stainless steel is 0.02 mF/cm$^2$.

In addition to capacitance, voltage stability is the key parameter determining the energy stored by the electrode. Electrochemical stability was measured from cyclic voltammetry (CV) measurements at 100 mV/s. The maximum voltage is the potential at which the electrodes operate with at least 95% coulombic efficiency. Fig 3.11 shows the CV curves for three CNT electrodes that were prepared with a variety of processing parameters as described in Table 3.1.
Figure 3.11 – Comparison of electrochemical window for CNT prepared using varying process parameters: HNO₃ functionalization, CNT concentration and EPD field strength.

Table 3.1 – Summary of Electrodes in Fig. 3.11

<table>
<thead>
<tr>
<th>CNT functionalization</th>
<th>EPD solvent</th>
<th>CNT concentration</th>
<th>EPD field strength</th>
<th>Mass of CNT deposit</th>
<th>Voltage range by CV</th>
<th>Efficiency (at 100 mV/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.6 M HNO₃ 60°C</td>
<td>D.I. water</td>
<td>0.5 mg/ml</td>
<td>1.5 V/mm</td>
<td>50 µg/cm²</td>
<td>2.6 V</td>
<td>98.6 %</td>
</tr>
<tr>
<td>2.6 M HNO₃ reflux</td>
<td>NMP</td>
<td>5 mg/ml</td>
<td>5 V/mm</td>
<td>270 µg/cm²</td>
<td>3.1 V</td>
<td>99.5 %</td>
</tr>
<tr>
<td>2.6 M HNO₃ reflux</td>
<td>NMP</td>
<td>5 mg/ml</td>
<td>150 V/mm</td>
<td>440 µg/cm²</td>
<td>4.2 V</td>
<td>98.8 %</td>
</tr>
</tbody>
</table>

Some trends are clear from the electrochemical data. Comparing the different oxidative treatments it is clear that the 2.6 M HNO₃ CNT have higher electrochemical stability. This suggests that the more aggressive oxidation, characterized in Section 3.3.2 by an abundance of C=O groups and a breakdown in long-range CNT structure, results in CNT that are less stable to redox reactions at high potentials. This agrees with the starting design principle that highly ordered and defect free sp² carbon, resembling glassy carbon, should give better electrochemical stability.
A less expected result is the trend of electrochemical stability and deposition field strength. As shown previously in Fig. 3.7, the 2.6 M CNT deposited at 150 V/mm display almost a complete absence of the C-O and C=O peaks that are seen in both of the spectra for functionalized CNT. In the electrochemical tests, the 2.6 M CNT deposited at 150 V/mm show dramatically higher voltage window compared to the same CNT deposited from NMP at 5 V/mm (3.1 V vs 4.2 V). 4.2 V is the highest potential window measured for BMIM BF$_4$ ionic liquid with glassy carbon or platinum counter electrodes. Thus it appears that high deposition voltages can go beyond forming a CNT deposit and actually affect the chemistry of the CNT themselves. This is a very promising discovery considering that ionic liquids with voltage stability higher than 5 V have been reported.$^2$ If this same effect could be repeated for such ionic liquids, an electrode with just 50 F/g operating at 10 V would have a gravimetric energy density of 250 mWh/g. This is a very high value considering that LiCoO$_2$, a common cathode material for LIB, has an energy density of 480 mWh/g.

EPD proved to be a flexible, scalable and experimentally useful technique. We were able to easily deposit CNT electrodes over a wide range of mass loadings and CNT chemistries. Mass loadings from around 10 $\mu$g/cm$^2$ to as high as 0.8 mg/cm$^2$ were prepared, yielding an areal capacitance measured in the three-electrode cell as high as 5.8 mF/cm$^2$. The gravimetric capacity of this electrode was only 7.5 F/g, indicating that the electric double layer was not forming over the entire mass of the electrode. It is likely that ionic liquid could not penetrate the entire thickness of the electrode. The CNT used in this study are composed of 30 to 70 concentric tubes. The gravimetric capacity could be improved by starting with fewer-walled CNT that have a higher ratio of surface area to mass.
3.3.4 Performance of Carbon Nanotube/Ionogel Devices

While many full devices were prepared, the best voltage window was achieved using the 72% ionic liquid ionogel and CNT prepared from 12.6 M HNO$_3$ using AC-EPD as described in Section 3.2.5. These electrodes (190 µg/cm$^2$) were prepared by Daniel Membreno and achieved 98% coulombic efficiency at 3.75 V and 46 F/g when measured by CV in neat BMIM BF$_4$. The full ionogel device (Fig. 3.12) operated at 88% coloumbic efficiency at 3.75 volts. This is the highest voltage reported in the literature for an ionogel EDLC. Still it shows that the sol-gel processing of the ionogel does limit the electrochemical by about 0.4 V. The full device achieved 1.8 mf/cm$^2$ at 0.5 mA/cm$^2$, which corresponds to only about 20 F/g. This suggests that sol-gel polymerization might be blocking some of the active area of the CNT electrodes, or that the BMIM BF$_4$ in the gel is not fully wetting the CNT. The energy density could be improved by using fewer-walled CNT and better engineering the CNT/ionogel interface.

Figure 3.12 – Cycling data for full CNT/ionogel device. (A) CV at 100 mV/s (B) Summary of GV data shows drop in areal capacitance with current density.
3.4 Conclusions

The two crucial parameters determining the performance of a supercapacitor electrode are the specific capacitance of the material and the maximum voltage stability. The specific capacitance of CNT electrodes made by EPD was found to vary from as high as 120 F/g for ~10 µg/cm² electrodes down to only 7.5 F/g for electrodes with 0.8 mg/cm². The voltage stability of CNT electrodes measured in ionic liquid was strongly dependent on the presence of oxygen-containing functional groups on the surface of CNT. By tuning the nitric acid functionalization procedure and EPD processing parameters, electrodes were prepared that achieved the full 4.2 V window in BMIM BF₄ ionic liquid. Fully solid-state CNT/ionogel EDLC were made that gave 1.8 mF/cm² with a voltage window of 3.75 V.
3.5 References


Chapter 4. Microscale Planar Electric Double-Layer Capacitors

4.1 Introduction

Having developed the electrode and electrolyte materials for solid EDLC on the 1 cm$^2$ scale (Chapter 3), our efforts turned to adapting our processing methods to build EDLC on the microscale. The ionogel synthesis presented in Chapter 3 was used without modification. The major effort was to develop microscale EDLC electrodes patterned on silicon wafers (on-chip).

Patterned gold electrodes on silicon wafers, prepared by Greg Leung, replaced the planar stainless steel substrates used in Chapter 3. Fig. 4.1 shows a general schematic for the on-chip gold electrodes with ionogel electrolyte. As discussed in Chapter 2 this geometry is a major departure from the parallel electrode geometry used for the larger devices in Chapter 3. This new geometry presented novel challenges both in the processing and performance of the resulting devices.

Figure 4.1 – Geometrical description of the coplanar EDLC design presented in Chapter 4. Top view (left) and side view (right)
To minimize the electrolyte resistance between the coplanar electrodes, it is necessary to minimize the distance between them. This presents an immediate processing challenge; whatever electrode deposition technique is used must be able to deposit separate electrodes with high resolution. Initially EPD of CNT was pursued as a method for forming microscale electrodes, but both the length of our CNT (up to 200 µm) and the low precision of EPD quickly proved insurmountable. EPD consistently resulted in shorts between coplanar electrodes, even for electrodes spaced as far as 100 µm.

This problem was alleviated by changing both the carbon material and deposition method. The long CNT were replaced with ketjen black (KB) particles (Fig. 3.1) that are ~ 100 nm aggregates of 20 nm primary particles. EPD was replaced with a self-assembly method termed evaporation-induced self-assembly (EISA). By tuning the hydrophobic/hydrophilic surface chemistry of the patterned gold-on-silicon (GoS) electrodes, dispersions of KB were able to selectively wet and evaporate on the gold electrodes, resulting in relatively uniform carbon electrodes with spacing as small as 10 µm.

4.1.2 Evaporation-Induced Self-Assembly

Tuning surface chemistry to repel certain liquids is a well-explored area of research in fields such as protective coatings and semiconductor processing. However, there are limited reports of such schemes being used in the literature for self-assembly in general or microscale energy storage devices in particular. The driving force for self-assembly is based on the chemical interactions of various molecular moieties.

A simple example of such interactions is the de-mixing of water and oil. In water, highly polar O-H bonds leave the H atom with very little electron density making it energetically
attractive to the nucleophilic lone pair electrons on adjacent oxygen atoms. The non-polar C-H bonds on the oil molecules do not allow these favorable interactions. The energetic penalty for neighboring C-H and O-H groups is so great that oil and water molecules will self-segregate into separate phases.

Similar arguments apply for solid-liquid interactions. For example, a drop of water sitting on paraffin wax will bead up because, again, the O-H groups prefer to be near themselves. A simple and widely used method of evaluating the surface energy of a material is to measure the contact angle that a liquid drop makes with that surface. This technique is called goniometry and its theoretical basis is Young’s law (Fig 4.2A). For equivalent solid-gas and liquid-gas interfacial energies, an increase in the solid-liquid surface energy will cause a drop of that liquid to meet the surface with a higher contact angle.

\[
\cos \theta = \left( \gamma_{SG} - \gamma_{SL} \right) / \gamma_{LG}
\]

Figure 4.2 – (A) Young’s law describes how the contact angle (\(\theta_c\)) of a liquid drop on a surface relates to the interfacial surface energy (\(\gamma\)). (B) Scheme for the reaction between a hydroxylated silicon surface and FAS molecules.
Fluoroalkyl materials, such as polytetrafluorethylene, are well known to be both oleophilic and hydrophilic due to the extreme electronegativity of fluorine, which mitigates London dispersion forces between adjacent molecules. Fluoroalkysilanes (FAS) are a class of chemicals with a reactive Si group (typically trichlorosilane) attached to a fluoroalkyl chain. FAS can be incorporated into sol-gel reaction or reacted with hydroxylated Si surfaces according to the scheme in Fig. 4.2b, resulting in a surface that repels both polar and non-polar liquids.

Gold does not have reactive hydroxyl groups on its surface and is therefore inert to FAS chemistry. We were thus able to develop a scheme for the selective functionalization of our Si wafers with patterned gold electrodes. Typically the native oxide on a Si wafer (Fig. 4.3A) is quite hydrophilic such that polar solvents will selectively wet the native oxide rather than gold. After reacting the Si with FAS (Fig. 4.3B) the Si attained a contact angle ($\theta_c$) larger than 100°.

Dimethylsulfoxide (DMSO) proved to be a suitable solvent for preparing dispersions of KB. When KB/DMSO was applied to the FAS-treated patterned gold electrodes these surface interactions preferentially direct the KB/DMSO onto the gold portions of the wafer (Fig. 4.4). As the DMSO evaporates, the KB is left behind on the gold regions.
Figure 4.4 – The higher surface energy of the FAS-coated silicon surface causes polar solvents to preferentially wet the gold.

Before preparing KB electrode we studied simple bare gold electrodes with ionogel electrolyte. The area of the electrodes and the gap were both varied over the dimensions shown in Fig. 4.1. Solid ionogel electrolyte was applied over the top of the electrodes either by spin-coating or doctor blading. These experiments allowed us to elucidate the connection between electrode dimensions and the frequency response of our EDLC. Finally we used EISA to prepare on-chip KB EDLC with total electrode area of 0.14 mm$^2$ and a separation of only 10 µm.

4.1.3 Frequency-Dependent Capacitance Measurement

For measuring the electrochemical properties and low-frequency performance of the materials and devices presented in this chapter, we can rely on CV and GV techniques (Chapter 10). However, the evaluation of high frequency capacitance presents a greater challenge in terms of measurement and interpretation of data. The formation of a double layer is dependent on ions in the electrolyte having sufficient time to react to the applied field and adsorb onto the charged electrode. In the limit of low frequencies there is sufficient time for the double layer to form and in the limit of high frequencies the ions cannot respond to the applied electric field across the electrodes and there is no double-layer.
If EDLC are to supplant dielectric capacitors for on-chip applications they must not only overcome processing challenges in terms of size and scalability, but also meet the necessary performance metrics. Many on-chip applications require operation at frequencies well above the 10 or 20 Hz that are the typical upper limit of tests conducted by CV and GV. The new challenge presented in this chapter is evaluating different materials and device geometries for microscale supercapacitors at kHz frequencies.

Our approach to this measurement problem was to use another commonly used electrochemical technique, electrochemical impedance spectroscopy (EIS), which is represented as a real and imaginary impedance ($Z'$ and $Z''$) measured as a functions of frequency ($w$):

$$Z(w) = Z'(w) + iZ''(w)$$ (4.1)

EIS was used extensively in this work to compare different EDLC quantitatively and develop design rules for microscale EDLC with coplanar electrodes.

Equivalent circuits are used to convert real and imaginary impedance into capacitance. Hypothetical circuits containing elements such as resistors capacitors, inductors and constant phase elements can be used to build a mathematical model with frequency-dependent impedance. Circuits of arbitrary complexity can be used, and sometimes very complicated circuits are used to model EDLC, such as transmission line models. For our purposes we do not want complex models, rather we want a single frequency-dependent capacitance, $C(w)$. 
With simple RC circuit models it is possible to calculate a single frequency-dependent capacitance and resistance value at each frequency. This is not a fit, but rather a direct calculation according to the equations in Fig. 4.5. The question is whether the RC series or parallel arrangement more accurately represents the behavior of an EDLC. Parallel resistance is associated with leakage: the passage of current through the EDLC without storing any charge. Series resistance correlates with the movement of ions that are forming the double layer. Intuitively then the series arrangement appears to be more physically relevant. This sentiment is echoed by Taberna et al., who recommend using the RC series equivalent circuit for frequency-dependent capacitance measurements.\(^7\) Real EDLC have both finite series and parallel resistances, but still the RC series model is sufficient for making objective comparisons between EDLC. More elaborate test circuits would be required to prove whether an EDLC is truly suitable for a given application.

---

Figure 4.5 – Comparison between the series and parallel RC circuits used for interpretation of EIS data.
An alternative method for converting impedance data to capacitance is also suggested by Taberna et al and appears occasionally in the literature. This method involves the manipulation shown below:

\[
C'(\omega) = \frac{-Z''(\omega)}{\omega |Z(\omega)|^2} \quad (4.1)
\]

\[
C''(\omega) = \frac{-Z'\omega}{\omega |Z(\omega)|^2} \quad (4.2)
\]

Using this transformation it is possible to convert the real and imaginary impedance data (\(Z'\) and \(Z''\)) into real and imaginary capacitance (\(C'\) and \(C''\)). The real capacitance is taken as the effective capacitance of the device while the imaginary capacitance is related to lossy processes such as ion vibration that does not result in charge storage in the double layer. Typically \(C'\) exhibits a steady decay with increasing frequency, while \(C''\) peaks at the turn-off frequency of the EDLC, roughly the same point where the impedance phase angle = 45°.

**4.2 Experimental**

**4.2.1 Preparation of Patterned Gold Electrodes on Silicon**

Gold electrodes were prepared on silicon wafers (GoS) using photolithographic methods by Greg Leung. The starting substrate was 4” p-Si (100) wafers with 1 µm thick thermally grown SiO₂. Thin films of Cr/Au (20 nm/100 nm) were evaporated at room temperature onto the substrates and patterned into electrodes. For the supercapacitors with hard mask wells, 1 µm Si₃N₄ was deposited by plasma enhanced chemical vapor deposition followed by photolithography and dry etching of the nitride to define the wells.
4.2.2 Fluoroalkylsilane Functionalization of Patterned Gold Electrodes

The particular FAS molecule used in this work was (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane (Gelest, Morrisville PA). Vapor-phase FAS functionalization was performed in a reaction flask (Ace Glass) equipped with an o-ring sealed joint. The head of the flask had two threaded ports connected to tubing with “Ace-Safe” thread-to-tube connections. One port was branched through two PTFE needle valves (Omega) to a 25 ml vial and to room air for purging. The 25 ml vial was topped with a rubber septum so that the vial could be evacuated before introducing FAS via a syringe. The other port on the flask was connected by tubing to a liquid nitrogen trap, a pressure gauge (Omega), a ball valve (Swagelok) and finally a Welch 8905 vacuum pump in series. The ball valve allows the entire system to be isolated from the vacuum. This system achieved a base pressure of 40 mtorr.

Prior to FAS deposition, the patterned gold-on-silicon wafers were cleaned by sonicating for 10 minutes in a 1:1 mixture of isopropanol and acetone. The patterned wafers were then cleaned in Harrick PDC oxygen plasma cleaner for 8 minutes on high power. The plasma chamber was purged three times with oxygen and then kept steady at 900 mTorr of oxygen while the plasma was on. After plasma cleaning, the samples were immediately transferred to the reaction flask.

After loading the cleaned samples the deposition chamber was evacuated for 10 minutes. The patterned wafers were exposed to three FAS-deposition cycles. Each cycle consisted of: 1. 30 seconds of exposure to FAS vapor with the ball valve open (vacuum on), 2. 2.5 minutes of exposure to FAS with the ball valve closed, 3. 6 minutes with the FAS valve and ball valve both closed, 4. 10 minutes of pump down with the ball valve open. After three cycles the reaction
flask was purged three times with room air. The patterned wafers were then removed from the reaction flask and placed in a 60°C oven overnight.

### 4.2.3 Evaporation-Induced Self-Assembly of Ketjen Black

Before use the GoS pieces were sonicated for 20 minutes in acetone/IPA to remove any loose agglomerates. Carbon nanoparticle dispersions were prepared by dispersing KB (Printex XE-2B) with a primary particle size of 35 nm in DMSO at a concentration of 0.05 mg/ml. The DMSO was filtered before use using a 0.2 µm Whatman filter to prevent any dust or impurities from ending up in the dispersion. This dispersion was sonicated for two hours prior to use.

The functionalized wafer was cut into pieces, approximately 1 cm², which contained sixteen electrode pairs. The wafer pieces were prepared for EISA by masking off a single electrode with wrapped pieces of PTFE tape (Fig. 4.6). Only 2 mm² of wafer area was exposed with the electrodes approximately centered in this area.

![PTFE tape](image)

Figure 4.6 – Individual 1 cm² wafer pieces are masked with Teflon tape before self-assembly of ketjen black. A single pair of gold electrodes is exposed. The exposed area of the FAS-silicon surface is approximately 4 mm².
To self-assemble the carbon electrodes, 40 µl of the KB dispersion was placed on the exposed portion of the silicon wafer. Next a piece of celgard porous membrane was used to wipe away excess KB dispersion so that a smooth film of dispersion was seen to stretch uniformly across the exposed wafer. The electrode was placed on a 120°C hot plate so that the DMSO evaporated within 2 minutes. As the DMSO evaporated the film of KB dispersion would suddenly lose contact with one edge of the PTFE tape and shrink, always maintaining contact with the gold electrode until the drop finally disappeared. This process of dropping, wiping and drying the KB dispersion was repeated about 10 times after which the dispersion was sonicated again for 5 minutes while the KB coverage on the electrodes was evaluated using an optical microscope.

4.2.4 Preparation of Devices

Ionogel was prepared by Jonathan Lau as described previously in Section 3.2.2. Ionogel was applied to devices by both spin-coating and drop-casting. Spin-coated ionogel was deposited using an initial 1500 rpm (500 rpm/s ramp) spin for 1 minute, followed by either 3000 or 6000 rpm (1000 rpm/s ramp) for one minute. A Dektak 6 surface profilometer was used to measure the thickness of the spin-coated ionogel. The thickness of the 3000 and 6000 rpm spin-coats were 3 µm and 1 µm, respectively.

Ionogel was also applied to the KB electrodes by drop-casting. Ionogel was dropped between two pieces of Mylar tape and then spread with a razor blade, defining the thickness at 100 µm. After drop-casting the KB/ionogel device was allowed to dry at room temperature for 24 hours, dehydrated in a 100°C vacuum oven for two hours and then immediately coated with a layer of paraffin wax to prevent the ingress of water.
4.2.5 Electrochemical Measurements

Cyclic voltammetry was performed using a Biologic VMP3 potentiostat. EIS was performed using two setups. The ionogel devices were tested using a Solartron 1287 potentiostat and 1252a function generator with a 10 mV amplitude, 0 V bias and range of 0.1 to 100 kHz. EIS of the ketjen black electrodes with liquid BMIM BF\textsubscript{4} electrolyte (50 µL drop size) was measured under a probe station using an HP 4284A LCR meter with 10 mV ac amplitude and 0 V bias from 20 Hz to 1 MHz. The measured impedance values were represented by the series RC circuit model containing frequency-dependent capacitance and resistance.

Temperature-dependent capacitance of the solid-state EDLC was measured with the Solartron leads running into a laboratory refrigerator/freezer. The device was placed in the refrigerator/freezer and thermocouple leads were taped to the back of the chip carrier to monitor the temperature. Device performance at temperatures as low as -3.9°C was measured using this set-up.

4.3 Results and Discussion

4.3.1 Bare Gold/Ionogel Electric Double-Layer Capacitors

Before working with carbon electrodes, we sought to elucidate the effects of geometrical variables using a simple geometry of planar gold electrodes and spin-coated ionogel. The geometries of the bare electrodes tested in this manner are displayed in Table 4.1. Accompanying this information is a figure showing an example of one such electrode with 3 µm spin-coated ionogel.
Each of the four electrodes listed in Table 4.1 was coated with 1 and 3 µm ionogel layers. Frequency-dependent capacitance and resistance curves (calculated using the RC series approximation) are shown in Fig. 4.7 and Fig. 4.8. Accompanying these curves are two black lines labeled “floor” which represent the capacitance and resistance measured on the Solartron for an open circuit.

Several trends are evident in the data. First, thicker gels (e.g., 3 µm vs. 1 µm) have lower series resistance and greater capacitance at high frequencies. The reason for less resistance is the greater cross sectional area for diffusive flux of ions through the electrolyte in response to the ac signal; this is consistent with the concept of lower sheet resistance (equal to resistivity divided by film thickness) in thin solid films. Second, shorter electrode gaps also yield less series resistance and higher capacitance because the ion path between electrodes is shorter. At higher operating frequencies, the electrolyte resistance will limit the response of the electric double-layer (EDL) to the ac signal, which will result in lower effective capacitance of the EDLC as the frequency increases. By reducing the total electrolyte resistance, either through the use of thicker ionogel films or shorter electrode gaps, we expect that the effective bandwidth of the EDLC will increase (i.e., we retain more of the peak double-layer capacitance at higher frequencies).
In the capacitance data of Fig. 4.7 at frequencies greater than 10 Hz the trends are evident: devices with thicker gels and smaller gaps give higher capacitance. The capacitance of these devices also drops below the 150 pF internal limit of the Solartron measurement system at higher frequencies more slowly compared to the samples with thinner gel and wider gaps. The one outlier from these trends is the B33 3 µm sample, which may have a geometrical or compositional defect in the ionogel coating. It can be seen in Fig. 4.8 that for frequencies higher than about 2 kHz the expected resistance trends are also evident: wider gap spacing and thinner ionogel layers give higher series resistance. The noise around 60 Hz is due to interference from nearby electronic equipment.

For frequencies below 2 kHz, where the electrolyte resistance is no longer expected to limit the EDL response, there is no clear trend in the resistance data. Surprisingly, the thinner gels appear to give higher capacitance below 1 Hz. The expected trend was that the electrodes with smaller spacing, which have larger total electrode area (Table 4.1) would have higher total capacitance. It appears that other issues, such as inhomogeneous ionogel thickness or interfacial chemical reactions may be determining the low-frequency performance.
Figure 4.7 – Capacitance data for B30-type electrodes with 1 and 3 \( \mu \text{m} \) ionogel layers. Thicker ionogel layers and smaller electrode gaps give better high-frequency capacitance.

Figure 4.8 – Series resistance data for B30-type electrodes with 1 and 3 \( \mu \text{m} \) ionogel layers. Thicker ionogel layers and smaller electrode gaps give lower series resistance.
These results generally confirmed our expectation that for coplanar electrodes to achieve good high frequency performance they need to have small electrode spacings. This requirement presents significant processing challenges in depositing carbon electrodes from liquid dispersions. If any wayward carbon particles bridge the gap between electrodes they will create a short which will prevent the EDLC from storing any charge. Smaller gaps make it more likely that a short will form during electrode deposition.

4.3.2 Fluoroalkylsilane Functionalization of Patterned Gold Electrodes

Our FAS functionalization scheme was based on the work of Jung et al. who used a cyclical deposition of H₂O vapor and FAS to achieve a water contact angle of 118°. Higher water contact angles indicate a greater degree of purity and uniformity of the FAS single layer. The theoretical maximum contact angle for a smooth surface is 120°. However the reaction chamber used by Jung et al. was significantly more sophisticated than the vessel described in Section 4.2.3 and used for this work. Specifically, Jung et al. utilized a chamber with a base pressure about 10x lower than ours and also used heated chambers to precisely control the vapor pressure of the reactants and the rate of reaction.

Using our home-built setup it was attempted to replicate Jung et al. procedure. Initially, water was included as a reactant separate from FAS, but the results showed immediately that this procedure was producing much more than a single monolayer of FAS material (Fig. 4.9). Using water as a reactant also resulted in FAS material ending up on the surface of the gold; gold pieces subject to the FAS/water functionalization had contact angles above 95°.
Ultrathin layers of FAS material are an absolute necessity for EISA, otherwise the FAS material could extend onto the gold electrodes and prevent the KB/DMSO dispersion from settling there. After arriving at the water-free FAS deposition procedure (Section 4.2.2) we were consistently able to achieve water contact angles on our FAS surface of 105°, which was sufficiently high for our purposes.

More important than the absolute magnitude of the contact angle of our liquid on the FAS layer is the difference in contact angle ($\Delta \Theta_c$) between our deposition solvent on the FAS and gold surfaces. Water is not a good solvent for dispersing KB. Fortunately, DMSO disperses KB well and also gives a large $\Delta \Theta_c$. Table 4.2 summarizes the contact angle results for water and DMSO on FAS-treated GoS samples that had been through the FAS treatment procedure.
Table 4.2 – Contact Angles for Various Surfaces

<table>
<thead>
<tr>
<th></th>
<th>Water</th>
<th>DMSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>8°</td>
<td>X</td>
</tr>
<tr>
<td>FAS/SiO₂</td>
<td>105°</td>
<td>78°</td>
</tr>
<tr>
<td>Au</td>
<td>65°</td>
<td>22°</td>
</tr>
</tbody>
</table>

4.3.3 Self-Assembly of Ketjen Black on Patterned Gold Electrodes

The EISA technique applied in Section 4.2.3 is an entirely novel procedure that gave quite encouraging results. Fig. 4.10 shows the evolution of KB coverage on the gold electrodes after 0, 20 and 40 cycles of EISA. The KB dries quite uniformly giving good carbon coverage without any shorts. The supposed mechanism is that as the KB/DMSO droplet dries and becomes smaller it clings to the gold electrodes based on surface energy interactions. Eventually, the droplet cleaves along the gap between electrodes, rapidly pulling apart and preventing any carbon from coming to rest between the electrodes. This result was achieved on 2/2 attempts for this electrode geometry, indicating that the results in Fig. 4.10 are not a mere fluke. For these experiments the gold lines (right side) were exposed and received significant carbon coverage. A further development would be to more precisely define the electrode area by incorporating a masking layer on top of the gold electrodes.
Figure 4.10 – Images of GoS electrodes after (A) 0, (B) 20 and (C) 40 cycles of self-assembly.

SEM images (Fig. 4.11) reveal that the KB forms deposit of various thicknesses across the gold electrode. Individual KB particles with sizes on the order of 100 nm are visible. There does not appear to be carbon coverage thicker than 5 to 10 KB particles, indicating that electrode thickness is on the order of 1 µm. Also evident in the SEM is the slight roughness of the gold electrode.
The KB particles give a significant increase in the electrode surface area and capacitance. Fig 4.12 shows the capacitance of KB electrodes measured with a 50 µl drop of neat BMIM BF₄. The KB improves the capacitance by about 5x. Because this measurement was performed in liquid electrolyte, it was not possible to precisely control the area of the electrode exposed. The entirety of the electrode area shown in Fig. 4.10 was covered with BMIM BF₄.
Figure 4.12 – Capacitance data for electrodes with and without ketjen black, measured in neat BMIM BF₄ electrolyte.

4.3.4 Performance of Ketjen Black/Ionogel Solid-State Microscale Devices

Having proved the benefit of the KB electrodes, we then fabricated a solid state KB EDLC using 42% ionic liquid ionogel. The gel was applied by drop casting and doctor blading to a height of 100 µm. In Fig. 4.13 the extent of ionogel coverage is limited to the dark grey/purple region, while the lighter green is bare FAS treated silicon. The total electrode area coated by the electrolyte was 0.14 mm², which to our knowledge is smaller than any on-chip capacitor reported in the literature (Table 2.2). We expect that the farthest regions of the electrode do not contribute much to the capacitance at higher frequencies. Further refinements in device processing would be needed to confirm this.
Figure 4.13 – Optical micrograph of fully solid-state ionogel device with ketjen black electrodes. The edge of the ionogel coating is visible in the top and bottom of the image.

The DC capacitance of the device was confirmed by CV (Fig. 4.14). The device was scanned at 100 mV/s to a voltage of 1.0 V. The measured capacitance was 333 nF with a 78% coulombic efficiency. Scans were not conducted to higher voltages due to fears of electrochemical reaction between BMIM BF$_4$ and the Cr adhesion layer. The two curves were measured on consecutive days, indicating that the device performance is stable. The coulombic losses are related to the increased slope at high voltages and could be due to the electrolysis of some water in the ionogel and/or a corrosion reaction between the Au/Cr electrodes and the ionogel. BMIM BF$_4$ is known to be corrosive to some metals.$^{10}$
Figure 4.14 – CV measurements of the ketjen black/ionogel device measured at 100 mV/s sweep rate to 1 V. The measurement was repeated on consecutive days.

Based on the voltage range and scan rate, the CV measurement has a frequency of 0.05 Hz. The capacitance value (333 / 260 nF on charge/discharge) appears to be in good agreement with the capacitance measured by impedance (Fig. 4.15). The device maintains a capacitance of 1 pF/µm² out to 10 Hz, at which point the capacitance begins to drop off.

Figure 4.15 – Comparison of capacitance data obtained by CV and EIS for KB/ionogel device
A unique advantage of ionic liquids is their wide temperature window. For instance, BMIM BF₄ has a melting temperature of -71°C and a flash point of 288°C.¹¹,¹² EDLC based on BMIM BF₄ have the potential to perform over a temperature range of more than 200°C. The main consequence of changing the temperature is to change the viscosity of the ionic liquid. Higher temperatures (T) will tend to decrease the viscosity and increase the conductivity (σ) by an exponential relation:

\[
\sigma = \sigma_0 \exp \left\{ \frac{-B}{(T-T_0)} \right\}
\]

Here B is a fitting parameter. The pre-exponential factor (σ₀) is the conductivity at some reference temperature (T₀) which may be a glass transition temperature.¹³

When the KB/ionogel EDLC is cooled we observe the expected behavior. From the RC series approximation it is clear that the initial capacitance plateau drops off sooner as the temperature decreases. The resistance of the ionogel increases by about a factor of three when the temperature is decreased from 21.0 to -3.9°C.
Figure 4.16 – Temperature-dependent capacitance data for KB/ionogel device. From 10 to \(10^4\) Hz, capacitance decreases by about 5x when temperature decreases from 21.0 to -3.9°C.

Figure 4.17 – Temperature-dependent series resistance data for KB/ionogel device. Up to \(10^4\) Hz, series resistance increases with decreasing temperature.

The same data is plotted as a phase angle vs. frequency diagram in Fig. 4.18. As the temperature decreases from 21.0, 11.1, to -3.9°C the turn-on frequency (phase angle = 45°)
decreases from 8.66, 5.69 to 2.74 Hz. Experiments of this type could be used to measure the temperature-dependence of the ionogel conductivity, but because of the coplanar device geometry used here it is not possible to extract those values.

The shape of the EDLC phase angle curve in Fig. 4.18 is approximately U-shaped. At low frequencies the EDLC is effectively storing charge, so the phase angle approaches 90°. At very high frequencies the device shuts off and behaves like an open circuit with small (150 pF) capacitance. The colder the device, the lower the frequency at which it effectively shuts off.

![Phase angle vs Frequency](image)

Figure 4.18- Comparison of phase angle data for coplanar KB/ionogel device and prototype with adjacent stainless steel electrodes.

At intermediate frequencies one would expect a monotonous decrease in phase angle. This can be seen for a cm² prototype with parallel stainless steel electrodes (SS) and ionogel electrolyte. The SS sample shows a much higher turn on frequency, which is the inverse of the
device’s time constant ($\tau$). The time constant is inversely proportional to the product of the device’s resistance ($R$) times its capacitance ($C$).\(^8\)

$$\tau = \frac{1}{RC}$$

There are several reasons why $\tau$ is smaller for the stainless steel (SS) 2D capacitor than it is for the on-chip EDLC. The SS capacitor has a small, uniform electrode spacing of 40 µm. It has larger electrodes, lowering total $R$. Also, the bare SS electrodes have lower areal capacitance than carbon electrodes, lowering $C$.

Instead of the steady decline in phase angle, the on-chip microscale EDLC shows an increase at frequencies between 10 and 1000 Hz. We speculate that this increase is peculiar to the coplanar electrode configuration. The initial drop in phase angle is likely due to the portions of the electrode that are several hundred microns apart (Fig. 4.13) while the second increase is related to the regions of the electrode separated by only ten microns or so. If this is true it means that, using the same materials and gap spacing (10 µm) smaller electrodes could yield an on-chip EDLC with a turn-on frequency as high as $\sim$ 500 Hz. Further miniaturization and refinement in device processing would be needed to realize these gains.

4.3.5 Gold/Chromium Corrosion in Ionogel

One challenge throughout this project was controlling the interaction between the gold electrodes and BMIM BF$_4$, especially in the presence of water. Initial experiments used Ti as the adhesion layer for GoS, but after exposure to ionogel for two days at 100°C the Au/Ti was completely discolored purple grey. Corrosion progressed non-uniformly and seemed to begin at areas where the gold was defective or had been scratched, which suggested that the adhesion
layer was the weak point. Tetrafluoroborate imidazolium ionic liquids like BMIM BF$_4$ are known to break down and corrode metal interfaces. The replacement of BF$_4$ with other anions such as PF$_6$ appears to mitigate this effect.

After the failure of Ti adhesion layers, Cr was used instead. The durability of the Au/Cr was much better, but still not perfect. The images in Fig. 4.19 were taken one week after spin-coating on the ionogel. During this time the device was stored in air. There is clearly degradation and pitting of the Au/Cr. The contact pads (Fig. 4.19b) were masked with tape during spin-coating, yet they still show evidence of degradation.

![Figure 4.19](image)

Figure 4.19 – (A) Evidence of corrosion is seen on gold/ionogel device after being stored two weeks in air. (B) A close-up of the contact pad and aluminum wire

4.4 Conclusions

The ionogel electrolyte was integrated into solid-state on-chip EDLC with coplanar electrodes. Initial tests with bare gold electrodes revealed that frequency-dependent capacitance
is improved for electrodes with smaller spacing and thicker electrolyte layers. Ketjen black carbon particles were applied to gold electrodes using a self-assembly method based on hydrophilic/hydrophobic interactions. The silicon substrate was made hydrophobic ($\theta_c = 105^\circ$) by a vapor-phase deposition of a fluoralkylsilane molecule. Solid-state on-chip EDLC with area of 0.14 mm$^2$ and electrode separation of 10 µm were prepared and gave capacitance over 2 pF/µm$^2$ with a time constant of 0.12 seconds. This is the smallest on-chip solid EDLC reported in the literature.
4.5 References


Chapter 5. Pyrolyzed Carbon Composite Anodes for 3D Lithium-Ion Microbatteries

5.1 Introduction

Graphite has a theoretical lithium capacity of 370 mAh/g, which is more than double that of commercial LIB cathodes. This capacity is achieved with a small volume expansion of only 2%. The van der Waals gaps in graphite allow lithium ions to diffuse in two dimensions, so lithium ions can reversibly move in and out (insertion and de-insertion). Graphite intercalates lithium at a potential very close to the potential of lithium metal, which helps to maximize the voltage obtained in a lithium cell. These excellent physical properties coupled with the abundance and low cost of graphite, make graphitic carbon the anode material of choice for LIB.

In cylindrical LIB cells, the carbon anode is deposited in a slurry, which would typically contain 1-2% binder, 5% conductive additives and 95% graphite in a layer that is between 50 and 300 µm thick. Typical binders are polymers such as carboxymethylcellulose (CMC) and polyvinylidene fluoride (PVDF). The small amount of binder is used to hold the electrode together, but because electrodes in a cylindrical cell are thin and spread over very large areas, there is not a significant need for mechanical integrity beyond adherence to the current collecting substrate.

Chapter 5 will present work concerning the adaptation of carbon slurries for use as anodes in 3D lithium ion microbatteries (LIMB). The specific format of interest is a periodic array of cylindrical anodes, coated with conformal electrolytes and surrounded by cathode material (Fig. 5.1). This format has been previously studied in the Dunn Lab. The differences between the anode in cylindrical cell and the anode in Fig. 5.1 are dramatic. The anode pillars in the LIMB provide the initial structure for the 3Dbattery. They must not only have enough...
mechanical integrity to stand under their own weight, they also must be able to survive electrolyte and cathode processing. If the anode posts break at any point during processing, the resulting battery would likely be short-circuited. The conformal electrolyte and cathode are also areas of ongoing research in 3D batteries. More durable anode posts allow for a greater variety and number of processing steps in pursuit of a full 3D LIMB.

Figure 5.1 – General design for a 3D battery based on a regular array of cylindrical anode pillars

The value proposition for any microstructured 3D batteries is that the surface area/volume ratio of the electrode material can be increased. However, this necessarily requires the use of long, narrow or spindly electrodes. Prior work by Cirigliano et al. showed that microscale cylindrical post anodes can be fabricated through a Si molding technique. In order to give these pillars adequate mechanical integrity the amount of binder in the slurry was increased to 10%, much higher than the amount of binder used in anodes for cylindrical cells.
Figure 5.2 – Graphite anodes made using CMC binder (A) as-prepared and (B, C) after cycling.

One problem with increasing the binder content is that the CMC binder is electronically insulating. With increasing binder content the anode posts will suffer from increased resistance and voltage drop along the length of the posts, especially for high aspect ratios. Also, the individual CMC chains are not covalently bonded to one another or the graphite particles.

CMC is fully soluble in water and is likely to have some limited solubility in other organic solvents such as the carbonate solvents used in LIB. Even with 10% binder content, the CMC/graphite posts show in Fig. 5.2 do not have adequate mechanical integrity to survive submersion, extended cycling and removal in a flooded electrochemical test cell. After cycling in electrolyte composed of 1:1 EC:DMC electrolyte the posts are significantly weakened both at the base and along their length.
Figure 5.3 – Individual PAN chains of length $n$ polymerize and pyrolyzed to form amorphous carbon.$^5$

In order to remedy the limited electronic conductivity and poor mechanical integrity of the CMC-based carbon posts, we sought to replace the CMC binder with an amorphous carbon phase that is electronically conductive and covalently bonded. For this we chose polyacrylonitrile (PAN), which is the starting material for most carbon fibers. PAN is converted into carbon fibers by an initial treatment in air below 300°C which helps to cross-link the PAN chains followed by a pyrolysis step in inert atmosphere at temperatures up to 2500°C (Fig 5.3).$^4,5$ During the pyrolysis step, the PAN chains form C=C and C-N bonds, and shed small molecules such as acrylonitrile, acrylamide, hydrogen cyanide etc. As a result there is 40-60 % weight loss in the PAN phase.$^6$ The resulting material is both mechanically strong and electrically conductive with resistance values in the range of 0.01-0.001 ohm-cm$^7$ In addition to structural applications, PAN-derived materials have recently been applied in research as components in LIB anodes.
Ji et al. prepared PAN nanofibers by electrospinning followed by pyrolysis at 900°C (Fig. 5.4a) and tested this material as an anode for lithium storage. While they were able to store over 300 mAh/g of lithium using these nanofibers, they only did so by cycling between 2.5 and 0 vs. Li/Li⁺. This voltage range is too large to be used in a practical LIB.⁸

Pyrolyzed PAN is considered a “hard” carbon. In contrast to the ordered 2D ion-conducting planes that exist in “soft” carbon such as graphite, hard carbons have sp² bonded sheets that are disordered and tortuous.⁹ After heating to only 900°C very few graphitic domains should exist in the PAN-derived material. Higher temperatures (>2500°C) produce graphitic “soft” carbon from PAN, but this would in many ways defeat the purpose of using PAN-derived...
carbon as a durable component of graphite anodes. Graphite is notably weaker than hard carbons such as carbon fibers.

Recognizing this, other researchers have used pyrolyzed PAN as we used it, as a super-binder. PAN-derived hard carbon provides better mechanical strength and improved electrical conductivity compared to the binders that are typically used in cylindrical cell batteries. For example, Thakur et al. synthesized and pyrolyzed PAN/Si composites with between 10 and 40% weight PAN (Fig. 5.4c). The samples with intermediate PAN content demonstrated higher capacity and cycle life. The author proposed that this was because the PAN-derived carbon was electrically conductive and helped to restrict volume expansion in the silicon.10

5.2 Experimental

In order to produce carbon micropillars using mold filling it is essential to have a porous silicon mold, which were prepared from 0.5 mm thick Si wafers by Janet Hur. The production of the carbon micropillars was achieved in five steps: 1. Carbon slurry was prepared using mixtures of MCMB, flakey graphite, ketjen black and PAN using dimethylsulfoxide (DMSO) as the solvent. 2. Carbon slurry was filled into the mold using a combination of positive pressure and vacuum, which helped to remove any solvent and dry the posts. 3. The silicon mold filled with carbon slurry was heated in air and pyrolyzed in inert atmosphere in order to cross-link the PAN polymer chains together according to the scheme in Fig. 5.3. 4. The filled mold was affixed to a current collecting substrate using conductive paste (nickel or silver, Pelco). 5. XeF₂ etching was used to remove the Si array, leaving behind a free-standing carbon array.

This chapter will also present an alternative method of preparing single carbon rods of microscale dimensions using copper wires. This method is beneficial mainly for high throughput
testing. Silicon molds and conductive pastes are not necessary and one person can prepare five or more carbon rods in about two hours.

5.2.1 Composition of Carbon Slurries

This work follows from the work of Nick Cirigliano who used a slurry consisting of 80 wt% mesoporous carbon microbeads (MCMB, a spherical form a graphite), 8 wt% flakey graphite, 2 wt% ketjen black and 10 wt% CMC. For the PAN studies the ratios of the three carbon components were kept the same; CMC was simply replaced with PAN. Because of the mass loss in PAN during pyrolysis, it was assumed that approximately half the weight of the PAN would be lost after the heat treatments. Three compositions of PAN slurry were used with PAN concentrations of 5, 18 and 30 wt%. For all three compositions the balance of the solid content was a 40 : 4 : 1 mass ratio of MCMB : flakey graphite : ketjen black. The 30% PAN loadings resulted in more severe weight loss and bending of the posts while the 5% PAN samples had insufficient mechanical integrity. The 18% PAN composition was used for the majority of experiments.

The first step in preparing the carbon slurry was to mix 0.1 g/ml solution of PAN in DMSO. Separately the MCMB, flakey graphite and ketjen black were mixed with a mortar and pestle. 1 gram of this carbon mixture was added to 2.42 g of the PAN/DMSO solution to form the slurry. The slurry was sonicated for two hours and stirred overnight at 300 rpm. Before mold filling the slurries were vortex-mixed for one minute, sonicated for one hour and then vortex-mixed again for one minute immediately before use.
In addition to the 3D microstructured samples made by the mold filling process described below, 2D samples were prepared by dipping pieces of 304 stainless steel (Alfa Aesar, 200 mesh) into the slurry. These samples were then pressed between a sandwich of celgard separator, paper towel and glass slides. A 2 lb weight was placed on top of the slurries and they were left to dry overnight. The purpose of applying this pressure was to assure maximum density of the composite and to approximate the conditions that would occur during mold filling. The exact heating parameters used for the PAN and CMC slurries are shown in Table 5.1.

### 5.2.2 Mold Filling for Microscale Arrays

The mold filling method was adapted from the work of Nick Cirigliano. Several modifications and refinements were made. The mold filling chamber is 13 mm stainless steel filter holder (Pall Coporation, San Diego CA) as shown in Fig. 5.5. A polished ½” Ti washer with a 3 mm diameter hole was placed at the base of the filter holder (vacuum side). This provided a flat and hard surface. Above this was a piece of Whatman filter paper, which has sufficient mechanical integrity so that it will not break or tear when placed under vacuum. On top of this was a piece of porous polypropylene (Celgard) which could be easily peeled off of the dried carbon slurry. Above the Celgard was a holder for the mold that was cut from 0.8 mm thick PTFE sheet. The 0.5 mm thick Si mold fit neatly inside this holder.

### Table 5.1 – Comparison of CMC and PAN Slurry Processing

<table>
<thead>
<tr>
<th>slurry</th>
<th>MCMB (wt%)</th>
<th>binder (wt%)</th>
<th>solvent</th>
<th>heating schedule</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMC</td>
<td>80</td>
<td>10</td>
<td>water</td>
<td>Dry at 100°C</td>
</tr>
<tr>
<td>PAN</td>
<td>73</td>
<td>18</td>
<td>DMSO</td>
<td>Dry at 100°C, Heat 4 hrs at 280°C in air (52 min ramp), Heat 2 hrs at 800°C in argon (390 min ramp)</td>
</tr>
</tbody>
</table>
Figure 5.5 – A filter holder is used as the basis for a slurry-infiltration compartment.

The filter holder was arranged in the vertical direction so that gravity was pushing down in the same direction of filling. Pressure was applied using a modified 20 ml plastic syringe. On this syringe a hole was drilled through the plunger and the tube, and small stainless steel rod is inserted to hold the plunger in position. The maximum possible pressure that could be applied with this apparatus was about 10 atm based on the ratio of volumes before and after pumping and the ideal gas law. On the other end of the filter holder a Welch 2032 Dryfast ultra diaphragm pump operating at 2 Torr was used to apply vacuum and simultaneously remove DMSO solvent. Because DMSO has a high boiling point (189°C) the filter holder was wrapped in heating tape and heated to 100°C to help remove DMSO more quickly.

To fill the mold one drop (~ 50 µl) of slurry was applied to the square hole in the PTFE, then the Si mold was pushed into this drop such that it sank into the carbon slurry. An additional drop of slurry was then placed on top. The filter holder threads were wrapped with PTFE tape and closed firmly by hand. The syringe attached to the filter holder was then pumped 5 times over the course of 15 minutes. During these pumps the filter holder would not hold pressure for
more than a minute or two. After 15 minutes another drop of slurry was dropped in through the hole in the top of the syringe holder. After adding this drop the filter holder held pressure for 30 min or more. The heating tape was then switched on and the filter holder was pumped 6-8 times periodically over the next 6 hours. After the 6 hours of applying positive pressure, the filter holder would remain hooked up to vacuum for an additional 15 hours.

5.2.3 Preparation of Copper Wire Single Post Electrodes

To prepare single carbon posts, 5 cm long strands of 40 gauge copper wire (80 µm) were bent such that they could lay flat with about 2 mm of wire pointing vertically. The copper wire was then cleaned by submerging it in glacial acetic (Sigma Aldrich, St. Louis MO) acid for 2 minutes. After cleaning the copper wires were repeatedly dipped into 50 µl pools of carbon slurry. Both PAN and CMC slurries (Table 5.1) were used. Dipping the bent point of the copper wire 6 times in the slurries over 30 minutes yielded a coating of 5-20 µg on the end of the wire. After drying and heat treating (PAN slurry only), the wires were then mounted in a shallow plastic. Epothin epoxy (Buehler, Lake Bluff IL) was filled around the wire so that only the top 1-2 mm of carbon-coated wire was exposed.

5.2.4 Polyacrylonitrile Heating Schedule

After mold filling was complete, the filter holder was placed in a 50°C oven for at least 12 hours to remove any remaining DMSO. The filled mold was then cut out of the PTFE holder using a razor knife. The filled molds were heated in a box oven at 280°C for 4 hours using a 52 minute ramp time. High temperature heating was performed in a tube furnace under flowing argon. A 390 minute ramp to 800°C was followed by a 2 hour hold.
5.2.5 Mounting and Releasing Filled Mold

Heated samples were mounted onto stainless steel shim current collectors using silver paste (Pelco). Silver paste was applied in a small dab to the shim and then the filled mold was pressed into it. Pressure was applied first by hand for 5 minutes and then using a metal c-clamp with the mounted mold pressed between two glass slides. After 2 hours at room temperature the c-clamp was transferred into a 100°C oven for an additional 2 hours in order to fully cure the paste.

After the silver paste cured, the Si mold was removed by etching in XeF₂ gas using the custom built XeF₂ etcher in the UCLA Nanolab. The settings used were: 60 pulses with a 60 second hold at 2500 mTorr XeF₂ followed by a pump down to 50 mTorr.

5.2.6 Infrared Spectroscopy of Pyrolyzed Polyacrylonitrile Composite

FT-IR was used to confirm that the conversion of PAN to amorphous carbon occurred as expected. A 2D piece of the 18% PAN slurry was prepared in the manner described in Section 5.2.1. Pieces of this material were subject either one, two or three of the heat treatments listed in Table 5.1. Samples were prepared by grinding 1 mg of sample into 80 mg of KBr. This powder was pressed in a steel bolt press for one hour under vacuum before being measured using a Jasco 670 FTIR plus.

5.2.7 Electrical Conductivity Measurements

The conductivity of the filled posts was measured using a Hewlett Packard 4284A LCR meter. Contact was made to the sample using 2.5 µm tungsten probe tips controlled by micromanipulators. Two probes (low potential, low current) were applied to the silver paste.
current collector while the other two (high potential, high current) were gently placed on the top of several PAN/graphite posts

### 5.2.8 Electrochemical Measurements

Electrochemical tests on carbon microelectrodes were performed in an argon-filled glovebox with less than 10 ppm combined water and oxygen. Freshly polished lithium metal was used as reference and counter electrodes. The electrolyte was 1 M LiClO₄ in a 1 : 1 mixture of ethylene carbonate : dimethyl carbonate (EC : DMC). GV tests were performed at various currents with a voltage range of 0.02 to 0.6 V vs Li/Li⁺. CV measurements were performed over the range of 0.02 to 1.2 V at a 0.1 mV/s sweep rate.

### 5.3 Results and Discussion

#### 5.3.1 Processing of Polyacrylonitrile Composite Electrodes

Initial experiments were aimed at testing the basic value proposition for adding PAN into the carbon anodes. Specifically, can a small amount of PAN effectively prevent the disintegration of the entire slurry? Fig. 5.6 shows two pieces of tape cast slurry consisting of 90% KS4 graphite and 10% PAN. Piece A was only heated to 150°C. Piece B was heated to 350°C under N₂ in order to induce some cross-linking in the sample. After 12 hours soaking in DMF, piece A is completely disintegrated, while B is completely undissolved. This confirms the basic assumption that by cross-linking the PAN phase we can effectively lock in the carbons and prevent them from falling apart.
The amount of PAN in the slurry was shown to have a strong effect on the morphology of the resulting carbon posts. As shown in Fig. 5.7A the posts prepared from 5% PAN were fairly straight, but did not hold together after heating. The 30% PAN posts (Fig. 5.7B) displayed significant shrinking and deformation likely due to the loss of 15% of the post mass during heating. The 18% PAN composition (Fig. 5.7C) displayed a nice balance of properties with relatively straight posts and adequate mechanical integrity.
FTIR was used to track the chemical changes occurring in an 18% PAN sample during heating. The sensitivity of FTIR was decreased somewhat by the presence of 73% MCMB in the electrode. Graphitic carbons like MCMB have a broad flat absorbance across the IR spectrum. Furthermore, the pyrolyzed carbon samples were significantly harder to grind using a mortar and pestle. The result is that the FTIR pellet for the pyrolyzed carbon contains larger particles which lead to scattering. This is evident from the sloping background observed in Fig. 5.8. Despite these issues, it is possible to observe the chemical changes occurring in the PAN graphite composite.

![FTIR results for PAN/MCMB composite after various stages of heating](image)

**Figure 5.8** – FTIR results for PAN/MCMB composite after various stages of heating

For the PAN composite sample that was heated to 100°C (drying) the spectrum shows peaks that are characteristic of CH₂ stretching and nitrile C=−N (2940 cm⁻¹ and 2240 cm⁻¹). The spectrum also displays the characteristic fingerprint peaks of acrylonitrile around 1500 cm⁻¹. After heating to 280°C in air there are only two apparent peaks, C-N/C-C conjugated at 1580 cm⁻¹.
1 and CO-H at 1390 cm\(^{-1}\). These peaks support the hypothesis that heating in air partially oxidizes and cross-links the PAN chains. After heating to 800\(^{\circ}\)C the CO-H peak disappears and only the conjugated C-N/C-C peak remains.

5.3.2 Electrical and Electrochemical Properties of Polyacrylonitrile Composite

An expected benefit of replacing CMC binder with PAN-derived carbon was improved electronic conductivity. This was confirmed by measuring the electronic conductivity of the posts using a 4-point probe technique. The measured conductivity values show that the PAN micropillars have a volumetric resistivity that is intermediate between previously reported CMC posts and literature values for PAN-derived carbon fibers.\(^3,^7\)

Table 5.2 – Results of Four-Point Probe Measurements on Carbon Posts

<table>
<thead>
<tr>
<th>Resistance @ 10 Hz</th>
<th>Phase angle (rad)</th>
<th>Vol. resistivity ((\Omega)-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>85</td>
<td>0.002</td>
<td>0.12</td>
</tr>
<tr>
<td>11</td>
<td>0.0014</td>
<td>0.02</td>
</tr>
<tr>
<td>7.3</td>
<td>-0.00001</td>
<td>0.01</td>
</tr>
<tr>
<td>CMC posts*</td>
<td></td>
<td>0.20</td>
</tr>
<tr>
<td>Conductivity of carbon fiber*</td>
<td></td>
<td>0.001-0.01</td>
</tr>
</tbody>
</table>

The electrochemical cycling performance of the PAN composite material was confirmed using CV and GV for both 3D and 2D samples. The CVs (Fig. 5.9A) reveal the expected shape for lithium insertion into graphite and a gravimetric capacity around 260 mAh/g (normalized to MCMB). In GV testing (Fig. 5.9B) the 3D micropillar gives higher areal capacity, achieving areal capacity around 1 mAh/cm\(^2\). The capacity fade for the 3D sample is about 10\% over 17 cycles and the 2D sample does not fade at all.
5.3.3 Mechanical Properties of Polyacrylonitrile Composites

The prime advantage of the PAN composite electrode is not the electrochemistry but rather the mechanical strength. There is currently an enormous range of processing approaches being explored for the development of 3D microbatteries. The more mechanically stable the 3D anode is, the greater the range of possible processing methods that can be applied to that electrode in pursuit of a working full 3D battery.

A stark example of the durability of the PAN composite is seen in Fig. 5.10 where the PAN posts are able to maintain their structure after extensive electrochemical cycling and even flooding with SU-8 photoresist. By comparison the CMC posts are completely obliterated during the SU-8 filling process (Fig. 5.10D). This is a prime example of the interplay between processing and properties. In this case mechanical properties of the electrode influence possible processing techniques for the conformal electrolyte. It is easy to imagine other electrolyte processing techniques that would be impossible using the CMC posts. For example anything...
involving aqueous solutions, like self-assembly or electropolymerization, would be impossible with water-soluble CMC binder.

Figure 5.10 – (A) As-prepared PAN array (B) Same array after testing (C) CMC array after SU8 patterning (D) PAN array after SU-8 patterning

5.3.4 Single Post Electrodes

In order to simplify the system and more easily study the effects of various conformal electrolyte strategies, it is helpful to simplify the micropillar electrodes from a 17x17 array down to a single pillar. This also eliminates the effect of possible line-of-sight issues in the coating process that might make it more difficult to coat micropillar arrays.

As shown in Fig. 5.11 single posts were prepared first by replacing the 17x17 pore silicon molds with single-pore molds. The electrochemical results however showed anomalously high
capacitance and a CV shape that deviates from the expected shape for lithium intercalation in graphite (Fig. 5.9A).

Coating the single post with 5nm of lithium aluminosilicate solid electrolyte (LASO) reduces the peaks. However, even with the LASO coating the CV shape is still not representative of graphite and Coulombic efficiency is still only 73%. This suggests that we are getting stray capacity from Li reaction with the conductive silver paste which consists of silver flakes in a silicate matrix. Both silver and silica are known to have non-zero capacities for lithium reaction.\textsuperscript{14,15} In fact many metals have some capacity for lithium reaction, meaning the strategy of attaching a single post to a large substrate using conductive metal pastes may be unworkable.

Figure 5.11 – Single PAN posts mounted on 9 mm\(^2\) of silver paint shows anomalously high capacity.
For this reason we sought to develop an alternate single post that would have the same carbon composition and capacity and approximate the dimensions of a single post in our micropillar array. The resulting method is the dipping procedure described in Section 5.2.3. Using this procedure, single posts composed of PAN slurry (Fig. 5.12 A, B) and CMC slurry (Fig. 5.12C) were prepared.

Figure 5.12 – (A, B) Copper wire PAN single post before and after pyrolysis. (C) CMC single post embedded in epoxy

The electrochemical properties of the Cu-wire single posts (CWSP) are certainly an improvement those of the substrate-mounted single posts. However, from the CV (Fig. 5.13A) it is clear that there is some impurity in the PAN CWSP giving rise to an irregular peak shape. This may result from partial oxidation of the carbon. The tube furnace is not perfect and there is inevitably some oxygen around during the pyrolysis step. Because the active mass on these single posts is only 10 µg a small amount of oxygen can significantly oxidize the carbon.
The capacity data measured by GV reveal that the PAN CWSP performs comparably to the CMC CWSP. The PAN (Fig. 5.13C) electrode gives 140 mAh/g (total electrode mass) with a coulombic efficiency of 87%, while the CMC electrode (Fig. 5.13D) has a capacity of 122 mAh/g at 90% coulombic efficiency. This is not outstanding capacity, but it is sufficient to test conformal electrolyte strategies in a single post format.

5.4 Conclusions

A new graphite slurry composition containing polyacrylonitrile was prepared for application as a micromolded anode in 3D batteries. Upon heating to 280°C and 800°C, the polyacrylonitrile cross-links forming an amorphous carbon phase that stabilizes the other
components of the slurry. PAN-derived carbon showed improved electrical resistivity (0.05 ohm-cm), which is about four times lower than CMC based anodes. Also, the PAN posts showed superior survivability for testing in liquid electrolyte and coating with photoresist. This was all achieved without sacrificing electrochemical properties. The micro-molded PAN composite gave 260 mAh/g on the basis of MCMB active material and delivered 1 mAh/cm$^2$ at a C/5 rate over 17 cycles. Also, a simplified method for fabricating single microscale posts based on copper wires was presented. These were prepared from both CMC and PAN slurries and achieved $> 120$ mAh/g.
5.5 References


Chapter 6. Vacuum-Infiltrated Composite Cathodes for 3D Lithium-Ion Batteries

6.1 Introduction

In addition to an anode material described in Chapter 5, a working 3D LIMB based on the micropillar array design (Fig. 5.1) also requires a conformal electrolyte and cathode material. For the cathode, again our goal is not to invent totally new materials, but to find novel material combinations and processing methods to build a LIMB with high power and energy density. In order to achieve good gravimetric capacity from our micro-molded cathode, it was necessary to introduce an ionically conductive gel additive that was formulated from a mixture of lithium salt, polyethylene glycol and tetruglyme.

LIB cathode materials are dominated by transition metal oxides. Originally LiCoO$_2$ was used in the first commercialized LIB, but recent years have seen the emergence of binary and ternary transition metal oxides, which give incremental improvements in safety, cost, cycle life and capacity compared to LiCoO$_2$.\(^1\) One ternary oxide is LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ (NCA). Pure LiNiO$_2$ has a rhombohedral structure with trigonal symmetry (space group: R-3m) comprising of two interpenetrating closepacked FCC sub-lattices: one consists of oxygen anions, and the other consists of Li and Ni cations on alternating (111) planes.\(^2\) This structure is shown in Fig. 6.1. Unlike LiCoO$_2$, LiNiO$_2$ is not suitable as a lithium insertion material because upon cycling the Ni atoms become disordered and migrate to the lithium layers. Eventually the material collapses to form the spinel phase, which does not reversibly store lithium.\(^3\) The substitution of Ni by Co can stabilize the structure and inhibit the phase transition. The addition of small amounts Al improves the high temperature stability of the material.\(^4\) This allows NCA to cycle stably, achieving a lithium capacity around 145 mAh/g.\(^5\)
Figure 6.1 – Comparison of the crystal structures of (A) LiNiO$_2$ and (B) LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$.

Adapted from Ref. 3

In cylindrical format LIB, the cathode material is deposited as slurry on a current collector such as aluminum foil by doctor blading, slot-die or reverse roll-coating. A typical cathode slurry composition for cylindrical cells is 97% active material, 2% carbon (e.g. acetylene black, for electronic conductivity) and 1% binder.$^6$ The slurry is deposited to form an electrode that is 50 – 300 µm thick depending on cell design. As the cathode slurry is dried the evaporation of the solvent and incomplete packing of electrode particles results in some porosity. This porosity allows liquid electrolyte to penetrate the cathode and improve ionic conductivity. Ionic conduction in liquid electrolytes is several orders of magnitude higher than it is in solid transition metal oxides, so long range ion diffusion in the electrode is facilitated almost entirely by this liquid electrolyte.$^7$
The micropillar 3D battery design (Fig. 5.1) requires a cathode processing method other than slot or roll-coating. To fill around the posts, without trapping bubbles, we use a sequential vacuum infiltration method where the slurry is applied around the posts and then vacuum is applied both to remove air bubbles between the posts and also to speed drying. The solvent used to prepare the slurry should be fast drying and also sufficiently dissolve all of the components of the slurry.

The design of a successful LIMB presents different material requirements. The 100 µm diameter posts presented in the previous section have a center-to-center distance of neighboring posts of 175 µm and the posts are up to 500 µm tall, resulting in fairly thick regions of cathode between anode pillars. This presents a long ion diffusion path for accessing the entire capacity of the cathode, so electronic and ionic conductivity must be maximized.

LIB electrodes typically feature electronically conductive additives, typically carbon micro or nanoparticles that facilitate electron transfer through the bulk of the electrode. An ionically conductive additive should have negligible vapor pressure so that it does not evaporate during the life of the battery. It should also be solid, or at least highly viscous so that it does not leak. These material requirements are met by at least three classes of materials: ionic liquids, ceramic solid electrolytes and polymer electrolytes. Ionic liquids have been explored for LIB, but electrochemical stability remains a problem. In particular the cations can undergo reduction at the anode. Ceramic solid electrolytes have lower ionic conductivity and require high temperature processing to achieve phase purity.

Polymer electrolytes have demonstrated good electrochemical stability and are processed from solutions at room temperature. Polyethylene oxide (PEO) is a commonly polymer and has
shown room temperature ionic conductivity in the range of $10^{-8}$ S/cm at room temperature.\textsuperscript{10} Another promising gel polymer system is a 1:1 molar mixture of lithium bis trifluoromethanesulfonate salt (LiTFSI, Fig. 6.2C) tetraglyme. This system has shown ionic conductivity of $1.1 \times 10^{-3}$ S/cm and stability up to 5V (platinum working electrode, lithium counter).\textsuperscript{11,12} In addition to having good ionic conductivity and electrochemical stability the LiTFSI : tetraglyme mixture has good temperature stability. Tetraglyme (TG, Fig. 6.2B) has a high boiling point (275°C) and a low vapor pressure (< 0.01 mmHg at 20°C).\textsuperscript{13}

![Chemical structures](image)

Figure 6.2 – The chemical structures of the three components used in the conduction gel electrolyte: (A) polyethylene oxide (B) tetraglyme and (C) LiTFSI

For this work we chose to explore a variation on the 1:1 LiTFSI : TG mixture by replacing half of the TG with polyethylene glycol (PEG, Fig. 6.2A) for a molar composition of LiTFSI : TG : PEG of 2 : 1 : 1. The PEG (MW = 1450) offers higher viscosity and, because it is a solid at room temperature (MP = 44°C), essentially zero vapor pressure. This material was essential to achieving good capacity from our micro-molded cathode.
6.2 Experimental

6.2.1 Preparation of Cathode Slurries

Two cathode slurry compositions were prepared. Slurry without ionically conductive additive (slurry A) was prepared with a mass composition of 75% NCA (5.0 µm particles, NEI Corp), 20% KS6 graphite and 5% PVDF. The other slurry, with ionically conductive additive (slurry B) consisted of 75% NCA, 18.3% KS6 graphite, 1.7% PVDF, 2.8% LiTFSI, 1.1% TG, 1.1% PEO (MW=1450).

Slurries were prepared by first mixing LiTFSI, tetraglyme, PEO and PVDF in acetonitrile overnight, then adding the appropriate amounts of graphite and NCA with additional acetonitrile. Two concentrations of total electrode materials in acetonitrile, 30 mg/ml and 300 mg/ml, were compared in vacuum infiltration experiments.

6.2.2 Vacuum Infiltration

The silicon post arrays used in this section were prepared by Janet Hur. For vacuum infiltration slurry was applied drop-wise over a 17 x 17 array of 100 µm diameter x 350 µm tall silicon posts. The macroscopic dimensions of the silicon array are 3 mm x 3 mm x 0.5 mm. Drops of slurry were applied using a pulled plastic pipette in drops that were between 50 to 100 µl each. Vacuum was applied using the house vacuum line connected by a hose to polyethylene funnel. The array being filled was placed on a smooth piece of polyethylene that formed a good seal with the inverted funnel. For the 30 mg/ml slurry 25 drops of slurry were applied, each one followed by about 2 minutes of vacuum, until the tops of the silicon rods were no longer visible under the optical microscope. For the 300 mg/ml slurry, this was achieved after only 4 drops were applied.
6.2.3 Evaluation of Micro-Molded Cathodes

After vacuum infiltration, the molds were either measured electrochemically or mechanically polished to observe the cathode. Those samples that were polished were first potted in Epothin epoxy (Buehler) and cured for 24 hours. Afterwards they were cut using a low-speed diamond saw and polished to expose various cross-sections of the infiltrated cathode.

For electrochemical characterization the samples were mounted (cathode side down) on stainless steel shim using nickel paste (Pelco). The silicon array was etched away using the XeF$_2$ etcher in the UCLA nanolab. The sample was exposed to 60 cycles with 60 seconds of XeF$_2$ exposure at 2500 mTorr followed by a pump-down to 50 mTorr. Microstructured cathodes prepared by slurries A and B were tested using CV (0.05 mV/s), GV (220, 550 and 1100 uA/cm$^2$) in electrochemical half-cells (Li counter, Li reference, 1 M EC : DMC electrolyte). The voltage limits used for both CV and GV were 3.0 to 4.3 V vs Li.

6.2.4 Measurement of the Ionic Conductivity of Gel Electrolyte

The conductivity of the gel electrolyte with molar composition of LiTFSI : TG : PEG of 2 : 1 : 1 was measured by EIS in a two-electrode configuration. The electrodes were polished tungsten metal rods 6.4 mm in diameter. They were fitted into a polypropylene (PP) sleeve of the same diameter and separated by PP spacer 2.9 mm tall. The resulting cavity (4.2 mm inner diameter, 2.9 mm tall, 91 µl total volume) was filled with the gel electrolyte. A small slit in the side of the sleeve allowed for air to be pushed out of the cavity as the rods were pushed together so that the cavity was completely filled with the gel. EIS scans were performed with a 10 mV signal over the frequency range of 100 kHz to 100 mHz.
6.3 Results and Discussion

6.3.1 Vacuum Infiltration

Molded cathodes were first prepared from the type A slurry using concentrations of 30 and 300 mg/ml. These experiments were conducted to determine if the vacuum infiltration procedure described above was adequate to produce a well-filled mold without voids. After filling, the epoxy-imbedded cathodes were cut using a low-speed diamond saw and then polished to give cross-sectional views at 1 mm increments across the 3 mm sample.

Figure 6.3 – (A) Si array filled using 300 mg/ml cathode slurry (B) Si array filled using 30 mg/ml cathode slurry (C) cathode array after etching away Si

The 300 mg/ml slurry (Fig. 6.3A) was clearly too concentrated as it dried around the posts before the slurry had the opportunity to infiltrate around the base of the posts. By contrast 30 mg/ml slurry (Fig. 6.3B) effectively filled in a uniform cathode after 25 cycles of dropping and applying vacuum. After XeF₂ etching the silicon array was removed using XeF₂ exposing a uniform array of pores forming a 3D microstructured cathode.
6.3.2 Electrochemical Testing

The microstructured cathode prepared from slurry A was tested using both CV and GV. CV was performed both before and after GV in order to evaluate any changes to the cathode (Fig. 6.4B). Initial CV performance was very poor giving just 5.9 mAh/g of NCA active material. The GV cycling behavior was also poor. In terms of capacity vs current density, we would expect capacity to decrease with increasing current density because higher current densities result in larger overpotentials and thus the voltage limits are met after a shorter time. However, for the slurry A cathode this trend is obscured by a trend of increasing capacity with cycling (Fig. 6.4A). The most straightforward explanation for this behavior is that with increasing cycle number and more time spent soaking in the liquid electrolyte, that electrolyte is slowly working its way into the bulk of the electrode structure and improving the ionic conductivity. This is supported by the drastic increase in the capacity measured by CV before and after cycling. After cycling CV measurements gave an improved gravimetric capacity (48.0 mAh/g) albeit still far below theoretical.
Figure 6.4 – Electrochemistry of cathode slurry with 5% PVDF binder and no conductive additive. (A) GV data shows a trend of increasing capacity with cycle number (B) CV curves of the same cathode before and after GV cycling.

The hypothesis that the cathode A performance is limited by ionic conductivity is supported by the performance of cathode B which has 5 wt% of LiTFSI:TG:PEO as an ionically conductive additive. The conductivity of the gel additive was calculated from the EIS data. The data showed a vertical line beginning as a point on the real impedance axis. The value of the horizontal intercept was attributed to the ionic resistance of the gel.

A simple comparison of the first GV cycles of electrode A and B reveals the benefit of the gel electrolyte. Electrode B achieves 129 mAh/g which is about three times higher than electrode A and much closer to the theoretical value of NCA, at a current density of 0.55 mA/cm² (Fig. 6.5A). At that current density the cycling was fairly stable with >95% coulombic efficiency. At 1.1 mA/cm² the initial capacity was lower and capacity faded much faster (50% over 20 cycles), indicating that the full capacity of the cathode was not accessible at that high current (Fig. 6.5B).
Figure 6.5 - (A) comparison of first cycle GV performance for cathode A (gel electrolyte) and cathode B (5% LiTFSI:TG:PEO). (B) capacity and coulombic efficiency data for extended cycling of cathode B.

The electrochemical changes to the electrode were evaluated using EIS and CV before and after GV cycling. In the CV there is only a subtle change in the cathode performance with gravimetric capacity dropping from 132 to 117 mAh/g after GV cycling (Fig. 6.6A). The peaks in the CV are flatter and shifted to higher potentials, which could indicate an increasing internal resistance in the cell. The EIS results before and after cycling (Fig. 6.6B) are nearly identical, suggesting that changes to the electrode during cycling are minimal.
Figure 6.6 - (A) Cyclic voltammetry of cathode B before and after GV cycling shows capacity fading. (B) EIS data is relatively unchanged before and after cycling.

It is possible that with only 1.7% PVDF in the slurry, the cathode B began to swell and break apart after being immersed in electrolyte in the half cell for over two weeks. There is some evidence of this in 3D microscope images taken before and after cycling. The image taken after cycling (Fig. 6.7B) shows some cracks in the electrode that were not evident before cycling (Fig. 6.7A). This cracking could account for increased resistance in the electrode and the capacity fade seen in the cycling data.
6.4 Conclusions

Micro-molded cathodes with a structure inverse to that of the micropillar array (Chapter 5) were prepared by vacuum-infiltrating slurry around an array of silicon posts and etching away the silicon. To form a cathode without any macroscopic voids the concentration of solids in the slurry had to be limited to 30 mg/ml. In order to achieve near theoretical capacity for the \( \text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2 \) cathode material it was necessary to include 5% gel electrolyte in the cathode. This gel consisted of a 2:1:1 molar mixture of lithium bis trifluoromethanesulfonate : polyethylene oxide : tetraglyme. By including this gel the capacity of the cathode material increased from 40 to 129 mAh/g. The areal capacity of the cathode was 3.7 mAh/cm\(^2\) and cycling was relatively stable at 0.22 mA/cm\(^2\) over 38 cycles. This cathode material and infiltration technique appear suitable for building a full battery with capacity up to 5 mAh/cm\(^2\).
6.5 References


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Chapter 7. Conformal Electrolyte and Full Battery Fabrication

7.1 Introduction

The electrolyte and separator in LIB perform the critical functions of conducting lithium ions between the anode and cathode while of preventing the flow of electrons. Therefore the electrolyte and separator should have high ionic conductivity and high electronic resistivity. The separator must have strong enough mechanical properties to prevent the formation of defects during battery manufacture, good chemical stability to remain insoluble in liquid electrolyte, and the electrochemical stability to resist oxidation at the cathode and reduction at the anode. Typical separators used in cylindrical LIB are nanoporous polymers that are wet with liquid electrolyte.¹

![Figure 7.1](image)

Figure 7.1 – (A) Process flow for the fabrication of a 3D battery using SU-8 photoresist (B)

During the exposure step, UV light is used to control the polymerization of SU-8.

In order to implement the micropillar array battery design (Fig. 5.1), the solid electrolyte must be able to conformally coat the anode pillars. Such a material would allow for 3D battery processing along the lines of the flowchart in Fig. 7.1A.

Similar to the electrolyte and separator in cylindrical cells, polymer solid electrolytes also feature a polymer structure filled with liquid electrolyte. Typical polymers are polyethylene oxide, poly(methyl methacrylate) and various block copolymers.² In this case the polymer is not
porous per se, rather the liquid electrolyte wets and swells the polymer chains, allowing for sufficient space and flexibility for the ions to move.

This chapter will present out work on using SU-8 photoresist (PR) as a conformal polymer electrolyte. The key advantage of SU-8 is that it has already been rigorously engineered to form high aspect-ratio polymerized structures with resolution down to 1 µm. Because our micropillar arrays are uniformly ordered, it is possible to conformally coat SU-8 around them using photolithography (Fig. 7.1B).

PR generally fall into two categories, positive and negative, depending on how the PR interacts with UV light. Exposure to UV light causes some portion of the PR to change its solubility in certain solvents. After UV exposure the unwanted photoresist is dissolved using a solvent called a developer.

Positive PR consist of two components: a polymer resin which is water soluble and a photosensitizer that is water insoluble. When the photosensitizer is exposed to UV light it degrades. The region that does not have photosensitizer is then soluble in aqueous developer. There is no extensive covalent cross-linking in positive PR. Both the polymer and photosensitizer are soluble in organic solvents such as acetone and acetonitrile. Therefore positive PR do not have adequate chemical stability for use as conformal electrolytes in 3D LIMB.

The negative PR SU-8 also consists of two solid components. The bulk of the PR is an epoxy resin with 8 reactive epoxide groups per monomer (Fig. 7.2A). The other component is a photosensitizer, also called a photoacid generator (PAG), which yields a proton under exposure to UV light. The PAG in SU-8 is taken from the family of triarylium-sulfonium salts.
The selective polymerization of SU-8 occurs in two steps. First the SU-8 is exposed to UV light using the desired photo pattern. After UV exposure the SU-8 is heated to 100°C. In regions that were exposed to UV light, the proton from the PAG acts as a catalyst causing the polymerization of neighboring epoxide groups on the polymer (Fig. 7.2B). Because the exposed region of the PR is now covalently cross-linked, it is not soluble in any solvent. SU-8 is also well known to have good mechanical and chemical stability making it a promising candidate for a conformal electrolyte. SU8 is unique because its monomer is quite large, around 2 nm based on bond length calculations (Fig. 7.2A). This is advantageous as the polymerized material is likely to have sufficient flexibility and porosity to soak up liquid electrolyte needed for ionic conductivity.

![Figure 7.2](image)

Figure 7.2 – (A) Chemical structure and approximate size of an SU-8 monomer. (B) Mechanism for polymerization of adjacent SU-8 monomers in the presence of an acid catalyst (HA)

A series of experiments was conducted on SU-8 in order to test the chemical changes to the SU-8 on exposure to UV light and the conductivity of SU-8 after soaking in electrolyte. Planar SU-8 was then applied as the solid electrolyte in a simple 2D LIB battery. Finally, a prototype 3D LIMB with photo patterned SU-8 electrolyte was prepared.
The electrode used for both of these batteries is highly doped silicon (0.001 to 0.005 ohm-cm B-doped). Silicon is an advantageous material for use as an anode in 3D LIMB for several reasons. It is easily processed to form a micropillar array using well-established techniques such as deep-reactive ion etching. The resulting posts are highly uniform and smooth which is essential for photolithographic patterning of SU-8. The Si posts are also strong enough to survive SU-8 patterning and cathode filling.

Si has long been sought as high-capacity (>3000 mAh/g) anode material for LIB. However, lithiation of Si to this degree results in dramatic volume expansion and a crystalline to amorphous phase change.\textsuperscript{6} Compared to the layered structure of graphite, crystalline silicon has a diamond cubic lattice that does no easily transport lithium ions. The diffusivity values for lithium in both crystalline and amorphous Si is around $10^{-12}$ cm$^2$/s.\textsuperscript{7} Despite these challenges researchers have been able to engineer Si anodes to achieve capacities around 1000 mAh/g for hundreds or thousands of cycles.\textsuperscript{8}

In this work we sought to use silicon as a substitute anode material in place of graphite. The ease of processing, excellent uniformity and durability of silicon posts made them well suited for applications using a photoresist electrolyte. Our aim was only to get graphite-like capacity, around 300 mAh/g, from the silicon posts. In this way we hope to avoid destructive volume changes to the silicon posts.

\textbf{7.2 Experimental}

\textbf{7.2.1 Characterization of SU-8 Photoresist by Infrared Spectroscopy}

SU-8 was spin-coated onto NaCl plates (Edmund Optics, 1” diameter, 2mm thick) in a yellow room to avoid any unwanted light exposure. The plates were stored in a vacuum
desiccator and dried on 160°C hot plate for 10 minutes before spin-coating. SU-8 3010 (Microchem) was applied to the plates by spin-coating at 3000 rpm for 30 seconds resulting in 10 µm coatings. After spin-coating the samples were heated on a 100°C hot plate for 7 minutes. The samples were exposed to UV light at 8 mW/cm² for varying times: 2, 10, 40 and 80 seconds. After exposure the samples were again placed on the 100°C hot plate for 7 minutes. The samples were covered in aluminum foil in the yellow room and transported to a dark room. FTIR (Jasco-670 plus) was performed using a 4 cm⁻¹ resolution and averaged over 100 scans. The background scan was performed on an uncoated NaCl plate that had accompanied the coated samples through all processing steps.

### 7.2.2 Ionic Conductivity of SU-8 Photoresist

SU-8 was spin-coated onto indium-tin oxide (ITO) substrates and exposed to UV light in the same manner described in section 7.2.1. After UV exposure and heating the samples were loaded into an argon-filled glovebox so that atmospheric moisture could not contribute to the ionic conductivity. The samples were soaked in an anhydrous 1:1 mixture of ethylene carbonate and dimethyl carbonate (EC : DMC) containing 1 M LiClO₄. EIS spectra were taken after 4, 8 and 24 hours of soaking using a VMP3 potentiostat (300 kHz to 0.1 Hz at 10 mV amplitude). EIS was measured using ITO as the working electrode. The counter electrode was a 0.5 cm² piece of stainless steel (SS) that was pressed into the SU-8 using a c-clamp.

### 7.2.3 2D Lithium-Ion Battery with SU-8 Electrolyte

In order to test the cycling of SU-8 electrolyte a 2D battery was fabricated. A 0.5 mm thick piece of high conductivity (0.001 – 0.0005 ohm-cm) Si wafer was used as the anode and 10 um of SU8 was applied on top by spin-coating. The SU8 was exposed to 10 mW/cm² of UV light.
for 20 seconds and then heated on a 100°C hot plate for 7 minutes. The Si piece with SU-8 was loaded into the argon-filled glovebox and soaked for 24 hours in a 1:1 mixture of EC:DMC containing 1M LiClO₄.

After soaking, the edges of Si wafer were masked with kapton tape, leaving an exposed area of 0.2 cm². About 1 mg of cathode slurry with ionically conducting gel (Section 6.2.1 slurry B) was applied on this area, giving a maximum capacity around 530 µAh/cm². A SS foil current collector was pressed into the cathode using a c-clamp. The 2D battery was cycled at three current densities: 37, 74 and 147 µA/cm². EIS of the cell was measured periodically using a VMP3 potentiostat (300 kHz to 0.1 Hz at 10 mV amplitude). A few drops of 1 M LiClO₄ in propylene carbonate (PC) was added every two days to ensure that the SU-8 electrolyte did not dry.

7.2.4 3D Lithium-Ion Battery with SU-8 Electrolyte

Approximately 10 µm of SU-8 was patterned onto a 15 x 15 array of 100 µm diameter Si posts by Janet Hur. The coated array was mounted onto an ITO current collector using nickel paste (Pelco). A cube of wax approximately 3 mm on a side was prepared. A piece 200 mesh SS gauze (Alfa Aesar) was heated on a hot plate an pressed gently into the wax. The mounted SU-8 coated array was placed in a 100°C oven and filled with small pieces of wax so that a meniscus of liquid wax was seen to rise ~0.5 mm above the top of the array. After removing the array from the oven the wax with the affixed SS gauze was placed on top of the array with the SS gauze down.

The Si/SU-8 array with SS gauze and wax was potted in epothin epoxy (Buehler) and left to cure overnight. The next day the excess epothin was cut away using a low-speed diamond saw. The
wax around the array was removed by soaking three times in 20 ml of n-heptane heated to 62°C. The array was filled with an unknown amount of cathode slurry (Section 6.2.1 slurry B) and tested using GV and EIS.

7.3 Results and Discussion

7.3.1 Chemistry and Ionic Conductivity of SU-8 Photoresist

From a processing perspective, the sensitivity of SU-8 conductivity to UV exposure is extremely important to understand. As seen in the diagram in Fig. 7.1B, the UV light is exposed on the top of the Si pillars. As UV light transmits through the SU-8 it will be absorbed by the PAG. Therefore, the top of the posts is likely to get a higher effective dose of UV radiation than the bottom.

Typical exposure parameter for the coating of Si posts is 8 mW/cm$^2$ for 60-80 seconds or around 500 mJ/cm$^2$. However this corresponds to a maximum exposure for the SU-8 at the top of the posts. It is important to know how the chemical structure and conductivity of the SU-8 change for exposures that are significantly less than this.

FT-IR is useful for tracking the degree of polymerization in the SU-8 epoxy. The bulk of the SU-8 monomer is very stable; the only groups that are expected to react are the epoxide rings on the edges of the monomer (Fig. 7.1A). Based on the reaction mechanism in Fig. 7.1B, these epoxide groups (910 cm$^{-1}$) are expected to react to form either ether (1070 cm$^{-1}$) linkages to neighboring monomers or become hydroxyl groups (3450 cm$^{-1}$), which are not covalently linked to neighboring monomers.
Of the three prominent infrared peaks, the epoxide peak has the smallest peak absorbance. Still, after UV exposure there is a noticeable decrease in the intensity of this peak. For the 80 second exposure the peak is almost completely lost in the background. Meanwhile there is a strong increase in the ether peak from 2 to 10 seconds of exposure. Further increasing exposure time (40, 80 sec) results in a more moderate increase in this peak, indicating that the number of new ether linkages formed is somewhat limited. Interestingly the hydroxyl peak continues to increase steadily for these exposure times. All together, this data suggests that with increasing exposure times relatively fewer ether linkages and more hydroxyl groups are formed. Perhaps the formation of the initial ether linkages restricts the movement of the SU-8 monomers, preventing them from getting close enough to form more links.

The conductivity data obtained by soaking the electrolyte and measuring EIS is consistent with this interpretation. The first key observation is that the SU-8 exposed for only 2 seconds
dissolved in the 1 M LiClO₄ in EC:DMC after 4 hours. This suggests that the limited cross-linking generated from 2 seconds of UV exposure was not sufficient to adequately cross-link the SU-8 monomers into an interconnected structure. The remaining samples (10, 40 and 80 sec) all displayed a reduction in total impedance with increasing soak time, however the rate of reduction was different (Fig. 7.4). The 10 sec exposed sample displays very similar EIS curves after 4, 8 and 24 hours of soaking. For the 40 and 80 sec UV exposures one day of soaking was required for the total impedance to drop, but the final impedance values are similar to those of the 10 sec exposed sample.

Figure 7.4 – Variation of total impedance vs. frequency for various UV exposure times (10, 40 and 80 sec) after various soaking times (4, 8 and 24 hours) in 1 M LiClO₄ in EC:DMC electrolyte

The most important impedance regime for ionic conductivity measurements is at high frequencies. Fig. 7.5 shows the Nyquist impedance representation for the 10, 40 and 80 sec exposed samples after 24 hours of soaking. All three show very similar semi-elliptical shapes that are characteristic of charge transfer. At lower frequencies the data sets become constant-phase lines that are indicative of long range ionic diffusion.
Figure 7.5 – Nyquist representation of EIS data for 10, 40 and 80 second UV-exposed samples after 24 hours soaking in 1 M LiClO$_4$ in EC:DMC electrolyte

The ionic conductivity of the soaked SU-8 was calculated from the data by segmenting the curved portion of the data from the linear portion at lower frequencies. These data points were fit to a semi-ellipse beginning at the point $(Z', Z'') = (0, 0)$ using the fitting parameters $a$ and $b$.

$$\left(\frac{Z' - a}{a}\right)^2 + \left(\frac{Z''}{b}\right)^2 = 1$$

The ionic conductivity of the soaked SU-8 is taken to be the second horizontal intercept of the EIS curve. The average value obtained in Fig. 7.6 is 34 kohm for the 10 μm thick layer with area $= 0.5 \text{ cm}^2$. This gives an average ionic conductivity value of $6 \times 10^{-8} \text{ S/cm}$.
Figure 7.6 – Semi-elliptical fit applied to high-frequency impedance data for 10, 40 and 80 sec UV-exposed samples after 24 hours of soaking in in 1 M LiClO_{4} in EC:DMC electrolyte

7.3.2 Full Battery Performance

There are other considerations besides ionic conductivity that affect how well a material will perform as an electrolyte in a LIB. For example is the SU-8 stable against the highly oxidizing and reducing potentials that exist at the cathode and anode in a LIB? Does the durability of the SU-8 change after extended cycling? Will pinholes form over time?

The 2D Si/SU-8/NCA battery (Section 7.2.3) was used to test whether SU-8 electrolyte could perform during extended cycling with lithium. In order to determine the expected voltage profile of the 2D battery, voltage profiles for Si anode and NCA cathode taken from half-cell experiments were subtracted from each other (Fig. 7.7). The voltage limits of the full battery in 2-electrode testing should be 4.1 V on charge and 2.6 V on discharge.
Figure 7.7 – Expected cell voltage for a silicon anode and NCA cathode. Cathode and anode data taken from GV half-cell experiments at 0.2 mA/cm$^2$: 1 M LiClO$_4$ in EC:DMC electrolyte, Li counter, Li reference.

A schematic of the 2D Si/SU-8/NCA battery is shown in Fig. 7.8A. The main shortcoming of this battery is that while the capacity of the 1 mg of NCA cathode is around 1 µAh, the Si wafer piece is so enormous that its theoretical capacity is many orders of magnitude higher. We expect that only the Si near the electrolyte will lithiate significantly, but still the bulk of the Si has the ability to act as a sink for lithium. Even a small irreversibility in the silicon lithiation could result in a major loss of capacity for this battery.
As shown in Fig. 7.8B the first charge on the 2D battery gives about 175 µAh/cm$^2$, which is about a third of the theoretical capacity of the lithium in the cathode. There is a large irreversible capacity loss during the first few cycles. After this initial capacity loss, however, the battery exhibits reversible cycling over many cycles and high coulombic efficiency.

Interestingly a closer look at the coulombic efficiency does suggest that the Si is acting as a sink for lithium ions. Fig. 7.9 shows how, especially when changing between current densities, there are cycles with coulombic efficiency > 100%. This indicates that some lithium that had been trapped in the silicon is being released due to the transient behavior between cycling rates. Even more remarkable is stability of the SU-8 electrolyte. No shorts develop and coulombic efficiency remains high after 70 cycles.
Figure 7.9 – Coulombic efficiency vs. cycle number for the 2D Si/SU-8/NCA battery

In addition to the capacity and coulombic efficiency data, it is useful to look at the shape of the charge and discharge curves. It is clear from Fig. 7.10 that the power performance of the 2D battery is limited. There is a steep drop in capacity for higher current densities. Also evident is the ohmic drop, or the part of the cell voltage that scales linearly with applied current. Each charge and discharge cycle was followed by a five second open circuit period during which the current was equal to zero. These data are the lone points at the end of each scan. During this time the measured voltage on the battery equilibrates towards its equilibrium voltage, i.e. the voltage that the battery would have had if the ohmic drop was zero.
Figure 7.10 – (A) Charge and (B) discharge curves for the 2D NCA/SU-8/Si battery at various current densities.

Based on the ionic resistivity value calculated from the impedance data (2 \times 10^7 \text{ ohm-cm}) it is straightforward to calculate what the ohmic drop should be for a given current density. This line is shown in the blue curve in Fig. 7.11. Compared to this are the ohmic drops measured at the end of the charge and discharge curves in Fig. 7.10 A and B. These points show a linear correlation to current density where the slope is the resistivity in Mohm-cm. Comparing the predicted ohmic drop to the measured values indicates that the ionic resistance of the SU-8 after cycling is about six times lower than the resistivity of the SU8 measured on ITO electrodes (Fig. 7.6).
Figure 7.11 – Ohmic drop vs. current density calculated from GV cycling data for the 2D NCA/SU-8/Si battery. Predicted ohmic drop curve is calculated from EIS data of SU8 on ITO \( (\rho = 2 \times 10^7 \text{ ohm-cm}) \).

This conductivity value is corroborated by the EIS data taken for the 2D battery after cycling. Based on the ionic resistivity calculated from the ohmic drop \( (\rho = 3 \times 10^6 \text{ ohm-cm}) \) the ionic resistance of the SU-8 in the 2D device should be about 15 kOhm. Before cycling the impedance is high and there is no clear semicircular shape. However, after extended cycling a semicircle is seen with a horizontal intercept in the range of 15 to 20 kOhm. This data agrees with the ohmic drop data and suggests that electrochemical lithiation produces an even bigger increase in ionic conductivity of the SU-8 compared to soaking in electrolyte.
Figure 7.12 – EIS data for the 2D NCA/SU-8/Si battery before, during and after cycling. The magnitude of the second real intercept is attributed to the resistance of the SU-8.

The prototype Si/SU-8/NCA 3D LIMB is shown in Fig. 7.13 after wax removal and before cathode filling. The stainless steel mesh is situated directly above the Si/SU-8 array allowing for good electronic conductivity to the cathode after filling. Unfortunately this device had defective Epothin epoxy, which caused the cell to leak. This prevented us from adequately pre-cycling the cell, made cathode filling extremely difficult and also caused the cathode to dry out very quickly.
Figure 7.13 – 3D test structure featuring SU8-coated electrodes and stainless steel mesh current collector. This cell was later filled with cathode slurry and liquid electrolyte, but defective epoxy caused the cell to leak and perform poorly.

Despite these issues we were able to take some meaningful electrochemical measurements on this device. For a perfect array of 350 µm tall 100 µm diameter Si posts coated with 10 µm SU-8 we would expect a total ionic resistance of around 10 kOhm (calculated from 3 * 10^6 ohm-cm ionic resistance). EIS of the 3D battery was measured while adding drops of 1 M LiClO₄ in PC and acetonitrile. Acetonitrile is a highly conductive solvent, but it evaporates very quickly. PC is more viscous with a lower vapor pressure. Using PC electrolyte (Fig. 7.14A) it was only possible to decrease the electrolyte resistance of this battery to around 130 kOhm, or about 10x higher than predicted. This is understandable considering that we were not able to soak and pre-lithiate due to the defective Epothin epoxy.
By adding acetonitrile to the cell (Fig. 7.14B) the impedance of the cell could be decreased to around the expected value of 10 kOhm. This is very encouraging, but unfortunately the impedance could not be kept at this value because acetonitrile evaporates so quickly. Unfortunately this device was stuck with stubbornly high impedance. Nevertheless, it was still possible to charge and discharge the battery, albeit at low current density (Fig. 7.15). As was the case for the 2D battery, the first lithiation had low coulombic efficiency. This was exacerbated by the slow leaking of electrolyte from the battery. Despite its many defects this 3D prototype proves that SU-8 can conformally coat a Si array and form a working 3D LIMB. Improved cell fabrication will allow for thorough pre-lithiation, lower impedance and better current density and cycle life.
Figure 7.15 – Single cycle GV data for the prototype 3D NCA/SU-8/Si battery. The poor Coulombic efficiency demonstrates the need to pre-cycle the cell before cathode filling.

7.4 Conclusions

SU-8 photoresist was adapted as a conformal electrolyte for 3D lithium-ion microbatteries. 2D SU-8 samples that had been soaked in liquid electrolyte for 24 hours showed an average ionic conductivity of $6 \times 10^{-8}$ S/cm. A 2D Si/SU-8/NCA battery was prepared that showed stable cycling and good Coulombic efficiency over 70 cycles. Ohmic-drop and impedance data of the 2D battery post-cycling shows the ionic conductivity of the SU-8 in the 2D battery was $3 \times 10^{-7}$ S/cm, which suggests the conductivity of SU-8 electrolyte may increase with cycling. Finally a prototype 3D NCA/SU-8/Si battery was prepared with a built-in cathode current collector. The rate capability of the device was limited because the cell leaked liquid electrolyte. Initial cycling showed approximately the expected voltage profile, albeit with <20% Coulombic efficiency.
7.5 References


Chapter 8. Lithium Polysulfide Gel Cathode Synthesized by Sol-Gel Chemistry

8.1 Introduction

The capacity of modern lithium-ion batteries is primarily limited by the capacity of transition metal oxide cathodes, which at $\leq 150$ mAh/g is less than half of the gravimetric capacity of graphite anodes.¹ Sulfur is a promising alternative cathode material, with a theoretical lithium capacity of 1675 mAh/g for complete reduction to Li$_2$S.² Unlike the topotactic lithium insertion reactions that occur in transition metal oxide cathodes, lithium reacts with sulfur through the formation of polysulfide species with different sulfur chain lengths (n) giving a general formula of Li$_2$S$_n$.

While promising, the Li-S system is beset by a number of problems. Sulfur is a poor electrical conductor and requires the addition of conductive additives. The lower order polysulfides (n < 3) are generally insoluble in the aprotic solvents (e.g. tetrahydrofuran, dioxolane) used in electrolytes for lithium-sulfur batteries (LSB), which can lead to irreversible capacity loss and low cycle life. Because the longer (n ≥ 3) polysulfide species are soluble in these solvents, they have a tendency to diffuse to the lithium electrode and react directly thereby circumventing the external circuit and acting as an internal short.³ This effect is often refered to as the shuttle mechanism.

Various groups have worked to improve the cycle life and efficiency of LSB either by trapping the sulfur species in the cathode, passivating the lithium anode surface, or both. A typical entrapment method is forming a composite cathode by coating sulfur particles with polymers such as polyethylene oxide and various forms of carbon including graphene.⁴
Researchers have also used oxides (silica and titania) as reservoirs to help trap the soluble polysulfides.\(^5\)

Passivation methods are used to inhibit the shuttle mechanism and improve the cycle life of LSB. Yang et al. used a fully liquid polysulfide cathode in a flow battery configuration, with LiNO\(_3\) as an additive used to passivate the lithium metal.\(^6,7\) Demi-Cakan et al. reacted sulfur powder directly on the surface of lithium metal, forming a passivating polysulfide layer in-situ.\(^8\) In another approach, Lin et al. synthesized lithium polysulfidophosphates, sulfur containing materials with high (10\(^{-4}\) to 10\(^{-6}\) S/cm) lithium-ion conductivity, as a fully solid-state sulfur cathode.\(^9\)

The present paper applies sol-gel chemistry to solutions of lithium-polysulfides and leads to a unique material, a polysulfide gel, which is electrochemically active. One unique feature of the sol-gel process is its ability to produce materials in which a continuous liquid phase is confined within an interconnected porous network composed of the sol-gel derived oxide. By tailoring the nanoscale morphology of the oxide, typically silica, the resulting gels are macroscopically rigid and yet exhibit properties which are characteristic of the liquid. Some of the first examples of this approach are the encapsulation of organic liquid electrolytes producing gels with conductivity \(~10^{-3}\) S/cm.\(^10,11\)

One of the most successful applications of sol-gel encapsulation is in combination with ionic liquids. Vioux et al. showed that sol-gel encapsulated ionic liquids (ionogels) couple the unique properties of ionic liquids, such as low-vapor pressure, ionic conductivity and high electrochemical stability, with the advantages of the solid phase.\(^12,13\) In recent years sol-gel
derived ionogels have been applied in lithium-ion batteries\textsuperscript{14,15} drug delivery\textsuperscript{16} and luminescence.\textsuperscript{17,18,13}

In this report we use non-hydrolytic sol-gel chemistry to encapsulate a solution of lithium polysulfides. The resulting material is solid gel that contains mobile lithium polysulfides. This material offers the potential for improved LSB, especially in helping to contain and package polysulfide catholytes. At the same time, this work demonstrates that through precise control of sol-gel chemistry a water-reactive liquid can be encapsulated and retain its ionic conductivity and redox activity.

For this synthesis, a water-free sol is required due to the reactivity of lithium polysulfides, which undergo vigorous reaction with water according to Eqn. 8.1:

\[ \text{Li}_2\text{S}_n + 2 \text{H}_2\text{O} \rightarrow 2 \text{LiOH} + \text{H}_2\text{S} + \text{S}_{n-1} \]  

(8.1)

In order to retain active lithium polysulfide species in the final gel it is extremely important to minimize the amount of water that is in the sol during gelation. To this end, we used a non-hydrolytic sol created by the reaction of silicon tetrachloride (SiCl\textsubscript{4}) and tertiary butanol (t-butanol). The nucleophilic substitution of t-butanol onto SiCl\textsubscript{4} (Fig. 8.1) constitutes the initial step in the formation of the sol. Electron-donor effects from the alkyl radical tend to direct the alcoholysis reaction in Fig. 8.1 towards formation of silanol and t-butyl chloride (pathway b).\textsuperscript{19} However in reactions between SiCl\textsubscript{4} and t-butanol, both hydrogen chloride gas and t-butyl chloride are produced.\textsuperscript{20} The reaction rate can be controlled by modifying the ratio of SiCl\textsubscript{4} : t-butanol and/or by adding a co-solvent. Prior work has shown that the gelation time can be controlled by adjusting the amount of t-butanol.\textsuperscript{21} For instance, Corriu et al. found that a 2:1 molar mixture of t-butanol and SiCl\textsubscript{4} gelled within three hours.\textsuperscript{22}
Figure 8.1: The alcoholysis reaction is the initial step in the non-hydrolytic sol-gel reaction between t-butanol and SiCl₄ and proceeds by two possible pathways. Pathway b produces hydroxyl groups which could later condense to form water.

While this reaction does not include water as a starting material or solvent, water can still be generated via the condensation of hydroxyl groups created by pathway b (Fig. 8.1). For this reason, we fine-tuned the gelation time of the sol in order to generate a stable sol and this sol was heated under vacuum to remove as much water as possible. The result is a two-step synthesis for producing a water-free sol. In the first step anhydrous SiCl₄, tetraglyme and t-butanol are reacted under flowing nitrogen (Fig. 8.2A). In the second step, the sol is heated under vacuum to remove any volatile reaction products, but without inducing gelation (Fig. 8.2B). Finally gelation is induced by mixing the sol with lithium polysulfide solutions.
Figure 8.2: Flow diagram of the PG synthesis. The two-step synthesis of water-free sol consists of (A) mixing anhydrous reactants under nitrogen followed by (B) heating the sol under vacuum. Finally the sol is mixed with Li$_2$S$_6$ catholyte (C) to form the PG.

8.2 Experimental

8.2.1 Materials

Lithium sulfide (Li$_2$S, 99.9%, Alfa Aesar), inhibitor-free anhydrous tetrahydrofuran (≥99.9%, Sigma-Aldrich) and anhydrous 1,3-dioxolane (99.8%, Sigma-Aldrich) were used as received. Sulfur (99.98%, Sigma-Aldrich), lithium triflate (LiSO$_3$CF$_3$, 99.995%, Sigma-Aldrich) and tetraethylene glycol dimethyl ether (tetraglyme, 99%, Sigma-Aldrich) were dried separately on a Schlenk line. After drying, tetraglyme was passed through a column of dry 4 Å molecular sieves in an argon-filled glovebox. Silicon tetrachloride (SiCl$_4$, 99.998%, Sigma-Aldrich) and anhydrous t-butanol (≥99.5%, Sigma-Aldrich) were used as received.

8.2.2 Catholyte Preparation

In order to prepare the gel, first a lithium polysulfide solution is prepared. Later this solution is mixed with the water-free sol to form the polysulfide gel. A lithium polysulfide solution with an average composition of Li$_2$S$_6$ was prepared in an argon-filled glovebox using a method adapted from Rauh.$^{23}$ Tetrahydrofuran (THF) was added to Li$_2$S and sulfur powders in a
molar ratio of 1:5::Li$_2$S:S and stirred for several hours. The powders reacted forming a blood-red solution. Tetraglyme (TG) was added and the resulting solution was stirred for one day at 55°C. The THF was then extracted from the solution by evaporating under vacuum at 85°C. Separately, electrolyte solution was prepared by adding LiSO$_3$CF$_3$ to dioxolane (DXL) and stirring for several hours. Once dissolved, the electrolyte solution was added to the Li$_2$S$_6$ solution. This combination of dissolved cathode material and electrolyte is referred to as a catholyte. Catholytes were made with two polysulfide concentrations: 0.5 M and 1.5 M Li$_2$S$_6$ in TG/DXL (30/70 by volume). These solutions contain 16.0 and 48.1 g/L of sulfur, for a maximum volumetric capacity of 26.8 and 80.6 Ah/L, respectively. Both catholytes contained 0.8 M LiSO$_3$CF$_3$ electrolyte.

**8.2.3 Non-hydrolytic sol synthesis**

To implement the sol processing scheme in Fig. 8.2, the initial sol composition must be stable against gelation. Otherwise, the processing could not proceed to the evacuation step (Fig. 8.2B) where water and other volatile products are removed from the sol. A series of sols were prepared in order to determine the gelation time for the SiCl$_4$ / t-butanol / TG system. The molar ratios of SiCl$_4$::TG::t-butanol were 1:0.43::X where 1.49 < X < 1.92. First, the t-butanol and TG were mixed together in a Schlenk flask in an argon-filled glovebox. The flask was fitted with a turnover septum stopper, removed from the glovebox and attached to high-purity nitrogen, which flowed through the flask and out through a bubbler containing 10 M aqueous potassium hydroxide. While stirring the t-butanol/TG mixture, SiCl$_4$ was added drop-wise over one minute and vapor was observed to condense on the walls of the flask (Fig. 8.2A). The sol containing 1.49 moles of t-butanol was found to be stable against spontaneous gelation for over a day. This sol composition was used to encapsulate the catholyte solution.
After 18 hours of mixing under flowing nitrogen the flask containing the sol (1.49 moles t-butanol) was attached to a vacuum line equipped with a liquid nitrogen trap. The pressure was decreased to 500 mtorr and the sol was heated to 95°C over three hours (Fig. 8.2B). The sol bubbled initially as volatiles were removed, but eventually the bubbles ceased and the sol began to reflux. The sol was kept under these conditions for an additional six hours. The flask was then purged three times with nitrogen and moved into an argon-filled glove box with water concentration of 0.5 ppm. Opening the vial inside the glovebox had no effect on the measured water levels in the glovebox. Over the course of two months in the glovebox, the sol remained fluid with no evidence of gelation.

8.2.4 Sol-gel encapsulation of polysulfides

Sol-gel encapsulated polysulfides were prepared by mixing volume ratios of sol and polysulfide solution. Polysulfide solution was added to the sol and stirred gently for 30 seconds to mix the components. The mixture was then loaded into electrochemical cells for testing and any remaining gel was saved for physical characterization.

8.2.5 Characterization of the polysulfide gels

We used both FTIR and Raman spectroscopy to identify the constituents of the polysulfide gel. After gelation and drying for two weeks, fragments of the polysulfide gel were crushed, mixed with potassium bromide (KBr) and pressed into pellets in an argon-filled glovebox. The pellets were removed in argon-filled jars and quickly transferred into an FTIR chamber flooded with argon for FTIR analysis (Jasco FT/IR 670plus). Additionally, sodium chloride (NaCl) plates were used to obtain FTIR spectra of the liquid components of the gel, including the sol, catholytes, and LiSO₃CF₃ electrolyte. Again, the components were placed
between the NaCl plates in the glovebox and transported to the FTIR chamber under argon. These spectra were used to help identify the peaks in the spectrum of the polysulfide gel. Lithium polysulfides were identified in the gel using Raman spectroscopy (Renishaw inVia Raman Microscope, 514 nm). Two samples were measured: a 1.5 M Li$_2$S$_6$ in THF solution and a 0.75 M gel, which were sealed in quartz cuvettes.

The microstructure of the sol-gel network was characterized by nitrogen gas adsorption analysis (Micromeritics ASAP 2010). In this case it was important to fully remove the polysulfide component without collapsing the silica network. These experiments were carried out with the 2:1 gel and involved immersing the gel sample in a series of solvents. The initial immersion in THF is used to dissolve the polysulfide phase. Subsequent immersions are designed for solvent exchange with a series of solvents (DXL → acetone → pentane → cyclohexane) with decreasing polarity. Solvent exchange has been shown to be a good means of producing aerogels while maintaining the oxide structure. The nonpolarity of cyclohexane allows it to evaporate without collapsing the porous silica network. After solvent removal, the porous gel network was loaded into the sample tube for analysis.

### 8.2.6 Electrochemical Characterization of Polysulfide Gel

Electrochemical measurements of the gels were carried out in 3-electrode cells that used a molybdenum working electrode, with a lithium counter electrode and lithium reference electrode (Fig. 8.3). The area of the electrodes was 0.9 cm$^2$ and the distance between the working and counter electrodes was fixed at 1 mm using a polyethylene (PE) spacer. The cell contained approximately 100 µl of 0.25 M Li$_2$S$_6$ gel. This gives a theoretical capacity of 7.48 mAh/cm$^2$ for the full reduction of sulfur to Li$_2$S. However, because Li$_2$S$_n$ species with n<3 are insoluble, the
sulfur should not be reduced beyond Li₂S₃ giving a theoretical capacity for reversible cycling of 2.48 mAh/cm².

Figure 8.3 - Schematic of three-electrode cell used for electrochemical testing of PG. The anode is lithium metal applied to a polished Ni rod. The cathode current collector is a polished Mo rod. The rods are pushed together in a polyethylene sleeve and separated by a 1 mm spacer. Before gelation PG is cast into the opening and an external Li reference electrode is applied.

These cells were evaluated using cyclic voltammetry (CV) between 0.5 and 4.0 V versus lithium at a sweep rate of 5 mV/s and galvanostatic cycling (GV) at current densities of 10, 50 and 100 µA/cm² with voltage limits of 1.8 and 2.8 V vs. Li. (Bio-logic SA VMP3 Multi-Channel Potentiostat). Electrochemical impedance spectroscopy (EIS) over the frequency range 10⁵ to 10⁻¹ Hz using a 10 mV signal was performed before and after gelation (Solarton 1252A Frequency Response Analyzer with Solartron SI 1287 Electrochemical Interface). Because gelation results in some shrinkage, the gel may detach from some portion of the electrodes resulting in anomalously high impedance. To overcome this problem, it is possible to re-establish contact by wetting the cell with 0.8 M LiSO₃CF₃ electrolyte.
8.3 Results and Discussion

The gelation times we observed for various ratios of SiCl$_4$ and t-butanol (Table 8.1) are roughly consistent with those reported by Corriu.$^{22}$ Gelation time increased as the molar ratio of t-butanol was decreased. The sol containing 1.49 moles of t-butanol remained liquid after over a day of observation.

Table 8.1 – Gelation Times for Sols of Varying Composition

<table>
<thead>
<tr>
<th>moles SiCl$_4$</th>
<th>moles TG</th>
<th>moles t-butanol</th>
<th>gelation time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.43</td>
<td>1.49</td>
<td>&gt; 1 day</td>
</tr>
<tr>
<td>1</td>
<td>0.43</td>
<td>1.74</td>
<td>1 hour</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.92</td>
<td>45 minutes</td>
</tr>
</tbody>
</table>

When polysulfide was added directly to the sol with 1.49 moles t-butanol, the mixture turned yellow and remained liquid for several months. The yellow color is attributed to sulfur that was produced via reaction with water in the sol according to Eqn. 1. Thus we introduced a drying step (Fig. 8.2B) where heat and vacuum were applied to the sol to remove any byproducts, especially water, which would have a deleterious effect on the battery. After nine hours of heat and medium vacuum we obtained a sol that, when combined with polysulfide, formed a blood-red gel without any evidence of sulfur precipitation.

The FTIR spectrum of the sol (Fig. 8.4) shows peaks for Si-O ($1100$ cm$^{-1}$) and O-H ($3300$ cm$^{-1}$).$^{25}$ In addition there are peaks at $1365$, $1392$ and $2967$ cm$^{-1}$ that are characteristic of C-H bonds on the butyl group. Because t-butyl chloride is quite volatile ($P_{\text{vap}} = 34.9$ kPa) it cannot remain in the sol after nine hours of heat and vacuum. This provides convincing evidence that the nucelophilic substitution of t-butanol on SiCl$_4$ (Fig. 8.1) proceeds by pathway a. The
presence of the O-H peak confirms that pathway b also occurs and suggests that some water will be produced during the gelation reaction, but evidently this is not enough water to produce a macroscopic color change in the polysulfide gel. After gelation the polysulfide gel retains its characteristic electrochemical properties.

![FTIR spectra](image)

Figure 8.4 – FTIR spectra of the sol after 9 hrs at 95°C and 500 mtorr. Both hydroxyl (3300 cm\(^{-1}\)) and t-butyl (2976, 1365, 1392 cm\(^{-1}\)) groups are present.

Gelation of the sol/polysulfide mixture is caused by the lithium polysulfides and not by any other component of the mixture. A 1:1 volume mixture of sol and 0.8 M LiSO\(_3\)CF\(_3\) electrolyte remained liquid after several months. Furthermore, 1:1 mixtures of sol and Li\(_2\)S\(_6\) solution that did not contain LiSO\(_3\)CF\(_3\) also gelled. As seen in Table 8.2, the gelation time was affected by the sol : catholyte volume ratio. The 1.5 M Li\(_2\)S\(_6\) catholyte was too viscous to
accurately pipette, so 0.5 M Li$_2$S$_6$ catholyte was used instead. For the 0.5 M Li$_2$S$_6$, decreasing the sol : catholyte volume ratio decreased the gelation time. One hour was an experimentally useful gelation time because it allowed us to perform EIS before the system gelled, so this system was studied extensively. Higher capacities should result from gels with a higher concentration of sulfur.

Table 8.2 - Gelation Behavior of Dehydrated Sol Mixed with Li$_2$S$_6$ Catholyte

<table>
<thead>
<tr>
<th>sol : catholyte (by volume)</th>
<th>concentration Li$_2$S$_6$ in catholyte (M)</th>
<th>gelation time</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 : 1</td>
<td>1.5</td>
<td>2 hours</td>
</tr>
<tr>
<td>1 : 1</td>
<td>0.5</td>
<td>1 hour</td>
</tr>
<tr>
<td>1 : 2</td>
<td>0.5</td>
<td>20 minutes</td>
</tr>
</tbody>
</table>

Solvent exchange of the gel confirmed that the polysulfide species are effectively confined in an interconnected nanoscale network. After solvent exchanging the gel, a pale pink monolith remained. Nitrogen gas adsorption results show that the gel has high surface area and fine pore size. The 2:1 gel had a BET surface area of 520 m$^2$/g, BJH pore volume of 0.254 cm$^3$/g and an average pore diameter of 1.96 nm. Considering that the as-prepared polysulfide had an average composition of Li$_2$S$_6$ and that the S-S bond length is 2.05 Å, the pores in the 2:1 gel are on the same size scale as the polysulfide chains.$^{26}$

The FTIR spectrum for the complete 1:1 polysulfide gel is shown in Fig. 8.5 The spectrum is similar to that of the as-prepared sol, with the addition of peaks associated with the SO$_3$CF$_3$ anion at 640, 1253 and 1302 cm$^{-1}$. These peaks were identified by measuring the FTIR spectra of all the individual components of the catholyte solution (Fig. 8.6). The FTIR peak
positions for the gel are summarized in Table 8.3. The only potential evidence in the FTIR data for polysulfide species in the gel is a small peak at 517 cm\(^{-1}\), but this is inconclusive. Based on the thorough spectroscopic study performed by Clark et al., we expect only this one weak absorbance for polysulfide species in the IR region.\(^{29}\)

Figure 8.5 – FTIR spectrum for the polysulfide gel prepared from 1:1 volume ratio of sol and 0.5 M Li\(_2\)S\(_6\), 0.8 M LiSO\(_3\)CF\(_3\) catholyte.
Figure 8.6 - The peak identities for the catholyte (Table 8.3) were determined by measuring the FTIR spectra of its various components. The number of components measured increases moving upward. In addition to 30:70 TG:dioxolane, the electrolyte contains 0.8 M LiSO$_3$CF$_3$. In addition to the electrolyte, the catholyte contains 0.5 M Li$_2$S$_6$. 
Table 8.3 – Identification of FTIR Peaks Observed for Polysulfide Gel

<table>
<thead>
<tr>
<th>Band</th>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Assignment</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>symmetric bend SO$_3$</td>
<td>640</td>
<td>LiTf</td>
<td>28</td>
</tr>
<tr>
<td>symmetric stretch CF$_3$</td>
<td>1228</td>
<td>LiTf</td>
<td>29</td>
</tr>
<tr>
<td>asymmetric stretch SO$_3$</td>
<td>1258, 1302</td>
<td>ion pairs (LiTf), LiTf$_2^-$, LiTf$_2^{2-}$</td>
<td>29</td>
</tr>
<tr>
<td>asymmetric stretch SiO</td>
<td>1100</td>
<td>SiO$_2$</td>
<td>26</td>
</tr>
<tr>
<td>bend C-H</td>
<td>1365, 1392</td>
<td>t-butyl</td>
<td></td>
</tr>
<tr>
<td>stretch C-H</td>
<td>2976</td>
<td>t-butyl</td>
<td></td>
</tr>
<tr>
<td>stretch O-H</td>
<td>3300</td>
<td>SiOH</td>
<td></td>
</tr>
</tbody>
</table>

Note: Tf = SO$_2$CF$_3$.

Raman spectroscopy was used to confirm the presence of lithium polysulfides in the gel. Polysulfide species have a triplet of strong Raman scattering signals between 350 and 550 cm$^{-1}$. Also the Raman spectrum is simplified because Si-O bonds are not Raman active. The Raman spectrum was further simplified by using a solution of Li$_2$S$_6$ without any LiSO$_3$CF$_3$ electrolyte. THF was used as the solvent to lower the viscosity of the polysulfide solution and increase the solubility of Li$_2$S$_6$. Fig. 8.7 shows the Raman spectra obtained from a solution 1.5 M Li$_2$S$_6$ in THF and a gel made by combining dehydrated sol with the 1.5 M Li$_2$S$_6$ solution in a 1:1 volume ratio. In both the solution and the gel we observe a triplet of peaks (393, 447 and 511 cm$^{-1}$) that is similar to that observed by Clark (384, 439 and 518 cm$^{-1}$) for solutions of Na$_2$S$_4$ in dimethylformamide. The peak position and shape are essentially unchanged after gelation, indicating that the polysulfide chains are largely unaffected by the encapsulation process.
Figure 8.7 – Raman spectra for a 1.5 M Li$_2$S solution and a 0.75 M Li$_2$S$_6$ gel, normalized to the peak near 393 cm$^{-1}$. A similar triplet of peaks is seen for both samples, indicating that the lithium polysulfide species are present in the PG.

The electrochemical properties of the polysulfide gel were evaluated using CV, EIS and GV. In an early work on lithium polysulfide electrochemistry, Yamin et al. reported a lithium metal/liquid polysulfide battery that displayed three distinct peaks in its CV while discharging and one peak during charging. The three discharge peaks are all associated with reduction of sulfur, i.e. breaking longer polysulfide chains into progressively shorter ones by adding lithium. In our cyclic voltammetry experiment (Fig. 8.8), at a sweep rate of 5 mV/s we observed only a single, broad reduction peak. The peak-to-peak separation for the polysulfide gel is about 3 V, compared to only 1 V for the liquid polysulfide solution. The polarization seen for the gel is likely a result of the restricted motion of polysulfide species as well as the lower concentration of
LiSO$_3$CF$_3$ electrolyte in the gel. CV at 5 mV/s is equivalent to one cycle in about 20 minutes. Evidently this sweep rate is too fast for the gel to respond.

Figure 8.8 - Cyclic voltammograms of: 1. A battery prepared from 1:1 volume mixture of dehydrated sol and catholyte (0.5 M Li2S6 and 0.8 M LiSO3CF3 in 30/70 TG/DXL) and 2. A battery prepared with polysulfide catholyte (8 mM Li2S6 and 0.8 M LiSO3CF3). Electrodes: Mo, working; Li, counter; Li, reference. The gel displays a similar shape, but with wider voltage separation between peaks.

The same electrochemical cell was used to monitor the impedance of the sol/catholyte mixture in-situ before and after gelation and cycling. The EIS results are summarized in Table 8.4. The shapes of the EIS curves in Fig. 8.9A are consistent with the Randle’s circuit. The first intercept of the real impedance axis is associated with electrolyte resistance. Before gelation the electrolyte resistance of the cell is about 100 Ω, but after gelation this value doubles. This could be due to dilution of the LiSO$_3$CF$_3$ from the catholyte by the addition of sol, which does not contain any salt. Our EIS spectra do not display the Warburg diffusion tails seen in other works.
with liquid polysulfide batteries\textsuperscript{31,32}. The time constant of charge-transfer is calculated from the inverse of the frequency where the imaginary impedance peaks (Fig. 8.9B).\textsuperscript{33} The time constant increases after gelation and cycling, though not dramatically. The increase could be due to the reaction of polysulfide species with the lithium electrode, creating insoluble polysulfides on the metal surface.

Figure 8.9: (A) Nyquist representation of EIS data taken for the PG before gelation, after gelation and after cycling. The inset shows the high-frequency intercept of the real impedance axis. (B) The peak in the imaginary impedance vs. frequency corresponds to the time constant of charge-transfer in the PG.
GV experiments were performed using upper and lower voltage limits of 2.8 and 1.8 V vs. Li with cycle times in the tens of hours. During GV experiments at 100 µA/cm² negligible (<1% of theoretical) capacities were obtained. Overpotentials caused the voltage limits to be reached very quickly, indicating the power of this cell is limited. Using a current density of 50 µA/cm² reasonable capacities were obtained (Fig. 8.10). At this current, charging capacity was equal to about 67% of the theoretical capacity. Discharge capacity was significantly lower, only about 28% of theoretical. The low coulombic efficiency suggests that the shuttle mechanism is occurring in this cell; longer chain polysulfides are reacting at the lithium electrode, effectively creating an internal short. Still, the capacities are fairly stable over four cycles. The GV cycling data is summarized in Table 8.5.

### Table 8.4 – Summary of EIS Data for Polysulfide Gel

<table>
<thead>
<tr>
<th>Polysulfide cathode (state)</th>
<th>OCP (V)</th>
<th>Solution Resistance, $R_s$ (Ω)</th>
<th>Charge-transfer resistance, $R_{ct}$ (Ω)</th>
<th>Time constant, $\tau$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before cycling (sol)</td>
<td>2.29</td>
<td>103</td>
<td>1570</td>
<td>32</td>
</tr>
<tr>
<td>Before cycling (gel)</td>
<td>2.24</td>
<td>200</td>
<td>1960</td>
<td>50</td>
</tr>
<tr>
<td>After cycling (gel)</td>
<td>2.36</td>
<td>200</td>
<td>1300</td>
<td>88</td>
</tr>
</tbody>
</table>
Figure 8.10: Galvanostatic discharge of battery prepared from 1:1 volume mixture of dehydrated sol and catholyte (0.5 M Li$_2$S$_6$ and 0.8 M LiSO$_3$CF$_3$ in 30/70 TG/DXL). Four discharge curves are shown at a current density of 50 µA/cm$^2$ and one at 10 µA/cm$^2$.

Having observed that LiSO$_3$CF$_3$ does not cause gelation, the power of the cells could be improved by increasing the concentration of LiSO$_3$CF$_3$ in the gel. Also, many contemporary studies on lithium sulfur batteries make use of high surface area carbons as a means of increasing the conductivity at the cathode. This could give significant power improvements over our flat molybdenum current collector.
Table 8.5 - Summary of Galvanostatic Cycling Data for Polysulfide Gel

<table>
<thead>
<tr>
<th>cycle number</th>
<th>current density (µA/cm²)</th>
<th>charge capacity (mAh/cm² // mAh/g)</th>
<th>discharge capacity (mAh/cm² // mAh/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - 5</td>
<td>100</td>
<td>0.032 // 14.5</td>
<td>0.055 // 25</td>
</tr>
<tr>
<td>6 - 9</td>
<td>50</td>
<td>1.65 // 750</td>
<td>0.69 // 314</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>1.19 // 541</td>
<td>1.00 // 454</td>
</tr>
</tbody>
</table>

8.4 Conclusion

The synthesis employed in this work produces a water-free sol that successfully encapsulates water-sensitive lithium polysulfide. Nitrogen adsorption demonstrates that the gel is porous and interconnected. Raman spectroscopy confirms that the polysulfides are largely unaffected by encapsulation. Electrochemical impedance spectroscopy reveals that there is only a minor change in the impedance properties of the gel before and after gelation. The gel undergoes cyclic voltammetry and galvanostatic cycling, displaying the peaks and plateaus associated with liquid polysulfides. The capacity obtained by GV is around 50% of theoretical, even with the shuttle mechanism contributing to poor coulombic efficiency. The ability to form a solid gel material by containing lithium polysulfides may contribute to improved designs for lithium-sulfur batteries.
8.5 References


Chapter 9. Summary and Future Work

While LIB and EDLC store charge by different mechanisms, both feature the same general device structure including current collectors and electrodes separated by an electrolyte. Pseudo-solid electrolytes where a liquid electrolyte is trapped within a porous solid structure were explored both as EDLC electrolytes (ionogel, Chapters 3 and 4) and for LIB (SU-8, Chapter 7). The encapsulation of a redox-active lithium polysulfide catholyte (Chapter 8) represents a novel application of sol-gel chemistry. A variety of methods were explored to form microstructured electrodes for EDLC, namely electrophoretic deposition (Chapter 3) and self-assembly (Chapter 4). Microstructured electrodes were prepared for LIB by micromolding (Chapters 5 and 6). As a result of these efforts novel microscale EDLC and LIB were prepared and characterized.

As demonstrated in this dissertation the processing of materials for electrochemical energy storage has a direct impact on their final performance. In Chapter 3 the use of binder-free carbon nanotube (CNT) electrodes allowed for the elucidation of the link between CNT chemistry and voltage window. In Chapter 4 electrode gap was shown to be a major factor in determining the frequency-dependent capacitance for on-chip electric double-layer capacitors. Through careful selection of materials and a novel deposition method devices with electrode gap as small as 10 µm were prepared. Future work should be devoted to refining this self-assembly method and incorporating masked wells to more precisely define the device dimensions. Ionic liquid compatibility with the gold/chromium electrodes appears to be a major barrier to higher voltage operation and long-term device stability and should be a top priority for further research.
In the battery work presented (Chapters 5-8) it is clear that suitable anode and cathode materials are now in hand to make working 3D lithium-ion microbatteries. The PAN composite from Chapter 5 increases the durability of the micropillar anode array and makes more elaborate processing possible. The cathode slurry presented in Chapter 6 gives performance that is consistent with the maximum performance of currently available cathodes. While higher-capacity cathodes are desirable, their discovery and synthesis is outside of the scope of this thesis. The principle direction of future work revolves around the development of conformal electrolytes. The results so far from SU-8 are very promising. Efforts should be made to fine-tune the SU-8 conductivity perhaps by changing the composition of the SU-8 itself to limit the extent of cross-linking. The most immediate future work is to improve the design and fabrication of full 3D batteries (Section 7.3.2) so that more stable performance can be tested. Pre-cycling of the SU-8 coated Si array will require more durable device packaging but should result in lower electrolyte resistance and stable cycling performance based on the results for the 2D Si/SU-8/NCA battery.
Chapter 10. Electrochemical Methods

Presented here is an outline of the electrochemical methods used throughout this dissertation. The figures and information are taken from “Electrochemical Methods: Fundamentals and Applications” by Allen J. Bard and Larry R. Faulkner. The specific chapters that are cited from this text are Chapter 1 (cell configuration), Chapter 6 (cyclic voltammetry), Chapter 8 (galvanostatic cycling) and Chapter 10 (electrochemical impedance spectroscopy).

10.1 Cell Configuration (Three-Electrode vs. Two-Electrode)

The Biologic VMP3 potentiostat that was used to conduct electrochemical measurements is a four-probe instrument. It has dedicated leads for working electrode (WE), counter electrode (CE), reference electrode (RE) and ground (G). Typically we do no connect the ground to our electrochemical cells and we are left with the choice of using the WE, CE and RE independently (three-electrode configuration) or connecting the CE and RE to form a single electrode (two-electrode configuration).
Figure 10.1 – Comparison of circuit diagrams for two-electrode and three-electrode configuration. (A) In a two-electrode cell the CE and RE are connected. (B) In a three-electrode cell the reference electrode is used to measure the WE voltage electrode with respect to a known redox couple.

Two-electrode configuration (10.1 A) is used to measure packaged devices that do not have a built-in reference. While the set-up is simpler, there is more ambiguity in the measurements. The cell voltage is subject to changes due to polarization and ohmic effects so it is more difficult to identify the meaning of, for example, peaks in a CV.

In three-electrode configuration (Fig. 10.1 B) the CE is used to supply current to the WE, while the voltage of the WE is measured with respect to the RE. Because the RE is not passing significant current it is essentially at equilibrium and voltage of the WE can be reliably identified with respect to the redox couple on the RE.
10.2 Cyclic Voltammetry

In a cyclic voltammetry experiment (CV) the potential of the WE is changed at a constant rate over a set potential range (Fig. 10.2 A) and the resulting current through the cell is measured (Fig. 10.2 B). For a redox-active electrode the resulting currents will peak at certain potentials, indicating the occurrence of a redox reaction. CV is most often conducted in a three-electrode configuration in order to study the capacity or kinetics of a given redox species. For an ideal capacitor, the CV curve should be box-shaped (i.e. no redox reactions) while battery electrodes will show sharp peaks at a given potential.

Figure 10.2 – In a cyclic voltammetry experiment (A) a change in applied voltage results in (B) a changing current response. Peaks in the current response are indicative of redox reactions.

10.3 Galvanostatic Cycling

The specific type of galvanostatic cycling (GV) used in this dissertation is chronopotentiometry. With this technique a set current is applied to the working electrode and the resulting potential is measured. Redox reactions are characterized by plateaus in the measured potential. Step-functions of positive and negative current can be applied to charge and discharge (cycle) the WE. For packaged devices, GV measured in a two-
electrode configuration most closely approximates the real-world used of electrochemical energy storage devices.

Figure 10.3 – In galvanostatic cycling (A) a constant applied current results in (B) a changing potential on the working electrode. Plateaus in the potential indicate a redox reaction occurs at that potential.

10.4 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is a technique that uses small-amplitude (< 100 mV) ac signals of varying frequency (ω) to probe the charge-transfer phenomenon in an electrochemical cell. For an applied potential sine wave (Fig. 10.4 B, curve e) there will be a response current sine wave (Fig. 10.4 B, curve i). This response is characterized by both phase and magnitude. The response signal may be out of phase with the applied signal by an amount, Φ:

\[ i = I \sin(\omega t + \Phi) \]  

(10.1)
The lag in the response current is captured by the phasor diagram in Fig. 10.4 A. For an applied potential represented by vector \( \vec{E} \) and a response current with vector \( \vec{I} \), the impedance vector \( (Z) \) connects them.

\[
\vec{E} = \vec{I} Z \tag{10.2}
\]

Because \( Z \) is a vector it is represented by both real \( (Z_{re}) \) and imaginary \( (Z_{im}) \) portions:

\[
Z(\omega) = Z_{re} - jZ_{im} \tag{10.3}
\]

\( Z_{re} \) is that part of \( Z \) which is in-phase with the applied potential signal and \( Z_{im} \) is the part that it is out-of-phase by \( \pi/2 \) radians.

Figure 10.4 – (A) diagram showing the phase difference between the applied potential vector \( (\vec{E}) \) and the current response vector \( (\vec{I}) \) for an electrochemical cell at a single frequency \( (\omega) \). (B) Same signal plotted as two sine waves with phase difference \( \Phi \).
10.5 References