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Three-dimensional Batteries using a
Liquid Cathode

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

by

Peter Moneir Malati

2013
Abstract of the Dissertation

Three-dimensional Batteries using a
Liquid Cathode

by

Peter Moneir Malati

Doctor of Philosophy in Materials Science and Engineering
University of California, Los Angeles, 2013
Professor Bruce S. Dunn, Chair

Three-dimensional (3D) battery architectures have emerged as a new direction for powering microelectromechanical systems and other miniature autonomous devices. Although to date there are few examples of fully functioning 3D batteries, these power sources have the potential to achieve high power density and high energy density in a small footprint. Current batteries are composed of solid state systems. In our system, the cathode and electrolyte are combined to form a liquid cathode (or catholyte). This catholyte is based on the lithium-sulfur system, which has a high theoretical gravimetric capacity of 1672 mAh/g_{Sulfur}.

This dissertation focuses on creating a rechargeable 3D lithium battery using a liquid cathode. The first part of the dissertation describes the liquid cathode, which is a lithium polysulfide
(Li$_2$S$_n$). The second part of the covers the formation of the 3D lithium-containing anode and its integration into the battery. Two new routes to achieve 3D lithium anodes have been developed. One approach involves the electrodeposition of lithium onto a 3D nickel current-collector array. The second method involves the electrodeposition of lithium directly onto the current collector through a polymer mold. 3D batteries fabricated using Li$_2$S$_6$ liquid cathodes exhibit power densities of 1.1 mW·cm$^{-2}$ at current densities as high as 0.5 mA·cm$^{-2}$.

Also included in this dissertation is a unique lithium polysulfide gel cathode which has been synthesized using sol-gel processing. Using a non-hydrolytic sol-gel route, a polysulfide-gel cathode has been integrated into a 2D battery. Similar to the liquid cathode, the polysulfide-gel battery requires no separator, i.e., is does not short with the lithium anode. The combination of high surface area (519 m$^2$·g$^{-1}$) and pore diameter (2.0 nm) of the silica matrix allows lithium polysulfide to diffuse to and from the current collectors. Cyclic voltammetry shows the electrochemical activity within the same potential window as that of the liquid cathode. First generation polysulfide-gel batteries exhibit areal capacities of 1 mA·h·cm$^{-2}$ at a current density of 10 μA·cm$^{-2}$. 
The dissertation by Peter Moneir Malati is approved.

__________________________________
Thomas Mason

__________________________________
Yang Yang

__________________________________
Bruce Dunn, Committee Chair

University of California, Los Angeles

2013
To the love of my life

My beautiful wife

Phoebe Yoakim Malati!
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Chapter 1 - Objectives and Introduction

As batteries become miniaturized, their energy densities become limited due to the small surface area of the two-dimensional surface of their electrodes. With the increasing demand for smaller batteries, as is occurring with battery powered microelectromechanical systems (MEMS), it is evident that the need for high energy density and power density batteries in small sizes will continue to grow. Current thin-film lithium ion (Li-ion) batteries are unable to fulfill the energy and power needed to power MEMS, not necessarily due to the materials, but rather, to space confinement. Much effort has been focused on finding new materials for Li-ion batteries. However, battery architectures are equally, if not more, important than the materials. It has been proposed that by using three-dimensional (3D) electrodes, high power densities can be attained without sacrificing energy density.\(^1\)

The principal objective of the research described in this dissertation is to develop a rechargeable 3D battery to provide power for small-scale devices. In particular, this dissertation addresses the development of two major components of the 3D battery. The first component that is presented is the cathode, which is a liquid consisting of lithium polysulfide. Aside from the fact that it has a theoretical energy density of approximately 1,532 mA·h·g\(^{-1}\) (i.e., as Li\(_2\)S\(_{12}\)), lithium polysulfide is a promising cathode material because it is ionically conducting and electrically insulating. This is extremely important because it means that it can be used in direct contact with the anode without electrically shorting. In other words, this cathode requires no separator. In most other cases, the battery must incorporate a separator between the cathode and anode to prevent electrical shorting between the two electrodes. In a 3D battery, forming this separator is very difficult, as any pinhole resulting from incomplete coverage will result in an electrical short. By
using lithium polysulfide as the cathode, however, there is no need for a separator in the 3D battery. One of the key research goals in this research is to synthesize a lithium polysulfide cathode that can yield a reversible capacity greater than 5 mA·h·cm$^{-2}$.

The second component that is addressed is the 3D anode. Currently, most 3D anodes consist of a lithium host material (usually a highly graphitized carbon powder) and a polymer binder. The capacities of these anodes are limited to the capacity of lithium insertion into carbon, which is 372 mA·h·g$^{-1}$. Our efforts at developing 3D anodes are focused on two different approaches. The first approach is to electrodeposit lithium onto a 3D nickel current collector array. The second approach is to electrodeposit a 3D lithium array. Both of these approaches insure that the anode structure will provide adequate capacity for the liquid cathode in the 3D battery.
Chapter 2 - Background

2.1 Lithium Battery Chemistries

2.1.1 Lithium versus Lithium ion Batteries

Lithium systems are appealing for use in batteries because lithium is the most electropositive element, generating a large potential difference when paired with a positive electrode material. In addition to being the lightest electrical conductor, lithium is a low density electrode material. As a result, lithium batteries have larger gravimetric and volumetric energy densities than other battery systems. Figure 2.1 compares common rechargeable battery systems such as lead-acid, nickel-cadmium (Ni-Cd), nickel-metal hydride (Ni-MH), lithium ion, plastic lithium ion (PLiON), and lithium metal batteries. The increase in gravimetric energy density (horizontal axis) in lithium battery systems can be close to an order of magnitude larger than that of lead-acid systems, while volumetric energy density (vertical axis) can be as high as eight times greater. This means that lithium batteries can store more energy in smaller volumes with less mass.

Lithium batteries are electrochemical cells which convert chemical energy to electrical energy through chemical reactions. They consist of three major components; the anode, cathode, and electrolyte. All of the battery’s energy is stored in the anode and cathode. In a charged battery, the anode is the negative electrode, i.e. lithium. However, to be precise we define the anode as the electrode which undergoes oxidation. Similarly, the cathode, which is usually a high-potential lithium host material, is the electrode which undergoes reduction upon discharging. The electrolyte is a lithium salt solution whose purpose is to transport lithium ions between the anode and cathode; it does not store energy. When a load is applied to a lithium battery, electrons exit the battery from the anode (i.e. lithium), travel through the load via an external circuit, and then re-enter the battery
at the cathode. Within the battery, on discharge, lithium is oxidized to lithium cations, which travel from the anode towards the cathode while the load is applied. During charging, this process is reversed and lithium cations are reduced at the lithium anode.

![Figure 2.1](image_url) Comparison of different battery technologies in terms of volumetric (vertical axis) and gravimetric (horizontal axis) energy density.²

Lithium ion batteries are an alternative to lithium metal batteries. They produce electrical energy through an intercalation mechanism, rather than through chemical reactions.³ This mechanism is illustrated in Figure 2.2.² Instead of using lithium metal, lithium ion batteries use lithium host materials for both the anode and cathode. During discharge, lithium ions exit the lower-potential (negative) lithium host (anode). Lithium ions migrate through the electrolyte and then intercalate into the higher-potential (positive) lithium host (cathode). This process is reversible so upon charging, i.e. when a potential is applied in the opposite direction, lithium ions will intercalate back into the negative lithium host, allowing lithium ion batteries to be rechargeable. The
lithium ion battery is often referred to as a “rocking-chair battery” since lithium ions migrate back and forth between the anode and cathode upon cycling.\(^3\)

![Diagram of lithium ion battery](image)

**Figure 2.2** Schematic of lithium ion battery operating principles (Adapted from Tarascon and Armand).\(^2\)

### 2.1.2 Lithium Ion Battery Electrodes

Anode materials for lithium ion batteries are based on their standard reduction potential and energy density. For example, in the oxidation reaction of lithium (equation 2.1), pure lithium has a theoretical gravimetric capacity \((Q_e)\) of 3,861 mA·h·g\(^{-1}\) according to equation 2.2:

\[
Li \rightarrow Li^+ + e^-
\]  \(\text{(2.1)}\)

\[
Q = \frac{n_e \cdot F}{3.6A}
\]  \(\text{(2.2)}\)

where \(n_e\) is the number of electrons involved in the reaction, \(F\) is the Faraday constant (96,485 coulombs per mole of electrons), and \(A\) is the atomic weight in g·mol\(^{-1}\). The 3.6 term in the denominator converts coulombs (C) to milliampere hours (mA·h) according to equation 2.3.
The anodes currently used in lithium ion batteries have higher gravimetric capacities than their complimentary cathodes. Carbon, for example, is a common anode material because its ability to intercalate lithium at low potentials according to equation 2.4,

$$xLi + C_6 \rightarrow Li_xC_6$$

where $0 \leq x \leq 1$.\(^6\) Plugging in $n_e = 1$ mole of electrons per 6 moles of carbon into equation 2.2 yields a theoretical capacity for carbon ($Q_{\text{carbon}}$) of 372 mA·h·g\(^{-1}\). On the other hand, silicon can alloy with lithium to form Li\(_{22}\)Si\(_5\), incorporating as many as 4.4 moles of lithium per mole of silicon.\(^7\)–\(^10\) Thus, using equation 2.2, the specific insertion capacity of Si can be calculated, by setting $n_e = 4.4$ moles of electrons per mole of silicon, to be 4,199 mA·h·g\(^{-1}\). However, silicon is not used commercially because it undergoes a volume expansion of 400% upon lithiation, resulting in pulverization and capacity fading.\(^8\) Apparently this property can be circumvented; nano-architectured silicon shows less vulnerability to fracture due to stresses from volume changes and can be cycled with minimal capacity fading.\(^11\)

### Table 2.1 Comparison of cathode materials for Li-ion batteries (Adapted from Liu et al.)\(^{12}\)

<table>
<thead>
<tr>
<th>Cathode Material</th>
<th>Energy Density</th>
<th>Average Voltage</th>
<th>Gravimetric Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(_x)FePO(_x)F</td>
<td>0.414 W·h·g(^{-1})</td>
<td>3.6 V</td>
<td>115 mA·h·g(^{-1})</td>
</tr>
<tr>
<td>LiMn(_2)O(_4)</td>
<td>0.440 W·h·g(^{-1})</td>
<td>4.0 V</td>
<td>110 mA·h·g(^{-1})</td>
</tr>
<tr>
<td>LiFePO(_4)</td>
<td>0.495 W·h·g(^{-1})</td>
<td>3.3 V</td>
<td>150 mA·h·g(^{-1})</td>
</tr>
<tr>
<td>LiCoO(_2)</td>
<td>0.518 W·h·g(^{-1})</td>
<td>3.7 V</td>
<td>140 mA·h·g(^{-1})</td>
</tr>
<tr>
<td>LiCo(<em>{1/3})Ni(</em>{1/3})Mn(_{1/3})O(_2)</td>
<td>0.576 W·h·g(^{-1})</td>
<td>3.6 V</td>
<td>160 mA·h·g(^{-1})</td>
</tr>
<tr>
<td>LiNiO(_2)</td>
<td>0.630 W·h·g(^{-1})</td>
<td>3.5 V</td>
<td>180 mA·h·g(^{-1})</td>
</tr>
<tr>
<td>LiNi(<em>{0.5})Mn(</em>{0.5})O(_4)</td>
<td>0.686 W·h·g(^{-1})</td>
<td>4.7 V</td>
<td>146 mA·h·g(^{-1})</td>
</tr>
</tbody>
</table>
Cathode materials are lacking in capacity, compared to anode materials, and are hindering the performance of lithium batteries (Table 2.1).\textsuperscript{12} In some cases, the capacity of the cathode can be as low as 30\% (i.e., LiMnO\textsubscript{2}) the capacity of carbon. Thus, lithium batteries have the potential of providing more energy in smaller volumes and weights, but most of the currently used cathode materials are limiting these possible capacity increases.

Sulfur is a promising cathode material because of its high specific capacity and energy density.\textsuperscript{13-15} Sulfur reacts with lithium to form lithium sulfide according to equation 2.5.

\begin{equation}
2Li + S \rightarrow Li_2S
\end{equation}

Using equation 2.2 and setting \( \eta = 2 \) moles of electrons per mole of sulfur, \( Q_s \) is calculated to be 1,672 mA\cdot h\cdot g\textsuperscript{-1}. Theoretically, for every gram of sulfur in the cathode, 433 mg of lithium is required for the reaction in equation 2.5 to go to completion. Therefore, the theoretical gravimetric capacity of the lithium-sulfur battery with respect to the combined mass of sulfur and lithium is 1,167 mA\cdot h\cdot g\textsuperscript{-1}. With an average discharge voltage of approximately 2.2V, the energy density of the battery is 2,567 mW\cdot h\cdot g\textsuperscript{-1}.\textsuperscript{16}

Present-day lithium-sulfur batteries consist of solid-state sulfur composite cathodes, which incorporate a conductive carbon additive and an organic polymer binder.\textsuperscript{17} State-of-the-art lithium-sulfur batteries consist of cathodes in which sulfur is contained within an ordered nanostructured carbon framework to prevent capacity fading due to loss of active mass to the electrolyte.\textsuperscript{17,18} When the carbon is functionalized with polyethylene glycol, these cathodes exhibit reversible capacities of \( \sim 1100 \) mA\cdot h\cdot g\textsuperscript{-1} (with respect to sulfur mass). The discharge capacity of lithium metal-free batteries using high capacity silicon nanowire anodes and Li\textsubscript{2}S-containing ordered mesoporous carbon nanocomposites drops from \( \sim 420 \) mA\cdot h\cdot g\textsuperscript{-1}, initially, to \( \sim 230 \) mA\cdot h\cdot g\textsuperscript{-1}, within 20 cycles, when cycled at rate of C/3 (0.5 mA\cdot cm\textsuperscript{-2}).\textsuperscript{19}
2.1.3 Safety and Environmental Factors

One major concern in lithium battery systems is the safety of lithium electrolytes. Aside from the fact that the non-aqueous organic solvents are flammable, the salts themselves can be very harmful. LiAsF$_6$, for example, is generally no longer used in batteries because of its high toxicity, and has been replaced with LiPF$_6$.\textsuperscript{20} Although less toxic than LiAsF$_6$, LiPF$_6$ undergoes thermal decomposition at 50°C producing compounds that, in the presence of water, readily form HF which is highly toxic.\textsuperscript{21}

Another safety concern in lithium battery systems is electrode materials. Fires resulting from the formation of dendrites can be avoided by using a lithium host material as the anode.\textsuperscript{2} However, lithium host materials that function well as cathodes can be extremely hazardous to humans and the environment. LiCoO$_2$, for example, is toxic and cobalt, both metallic and ionic, has been found to cause deoxyribonucleic acid (DNA) breakage and inhibition of DNA repair in humans.\textsuperscript{22,23} Manganese is more benign than LiCoO$_2$, but its toxicity on the central nervous system has been linked to gait disorders and attention deficit hyperactivity disorder (ADHD) in children.\textsuperscript{24,25} Nickel is a seizure-inducing metal, which when in the Ni$^{2+}$ state is carcinogenic by a mechanism of binding to proteins and damaging DNA.\textsuperscript{26,27} Although exposure is unlikely, the threat of these materials should not be taken lightly; exposure threats can be immediate, i.e. the battery assembly line, or long-term, i.e. buildup of waste in trash dumps from improper disposal of batteries by consumers who fail to recycle used batteries.

There are far less worries with using sulfur as a cathode material because of its environmental abundance and nontoxicity.\textsuperscript{16,17} In fact, various polysulfides are listed for use as food flavors.\textsuperscript{28} Polysulfides can also undergo redox cycling to generate reactive oxygen species, which are more toxic to cancer cells than to healthy cells, exhibiting chemotherapeutic properties.\textsuperscript{28} On the
other hand, lithium and its salts are possible teratogens. Li₂S, which is the discharge product of the lithium-sulfur system, is toxic and upon contact with water can generate toxic gases.

Lithium battery resources are also of concern. In his article entitled “Is lithium the new gold?” Tarascon states that lithium just might become as precious as gold in this century and that the Andean countries in South America, which are abundant in lithium, could become the ‘new Middle-East.’²⁹ Traditionally, lithium was recovered from seawater, however the time and cost associated with this process is excessive.³⁰ Presently, roughly 83% of the lithium supply comes from brine lakes and salt pans, which are limited in size.³¹ In 2007 and 2008, the world production and usage of lithium was about 25,400 metric tons (t) and the demand is expected to be as high as 54,000 t, an amount currently beyond our production capabilities, by 2050.³² In Europe, roughly 20% of all batteries are recycled.³³ Lead-acid batteries contain 60% to 80% recycled lead and plastic because 96% of all lead-acid batteries are recycled.³⁴ This shows the impact that recycling of lithium ion batteries could have on the enormous demands for lithium that will be faced in the coming years.

2.2 3D Batteries

2.2.1 Advantages and Architectures

Micro-scale batteries (microbatteries) have not been able to keep up with complementary metal-oxide-semiconductor (CMOS) electronics. In particular, the lack of miniaturization can be realized in battery powered microelectromechanical systems (MEMS) in which the sizes of these devices usually depend on the size of the power supply. In most cases, integration of the power supply within the system is not possible. Table 2.2 shows that some of these battery-powered MEMS devices have batteries that are much larger than the microsystem.³⁵
It is apparent that the small footprint area allocated for the power supply in miniature devices creates a problem for traditional 2D batteries. For example, if the footprint area of the battery is decreased in order to integrate it into a device, there will be a decrease in the amount of stored energy resulting in increased current density, which usually leads to poor battery performance. In fact, reported areal energy densities for lithium thin-film batteries range from $2.5 \times 10^{-3}$ J mm$^{-2}$ to $\sim 2 \times 10^{-2}$ J mm$^{-2}$, which are lacking by two orders of magnitude in powering, for example, a smart dust mote for 1 day.$^{1,37,38}$ Increasing the film thickness of each electrode in order to obtain more energy would only lead to more problems. One problem is the mechanical integrity of the electrodes, which decreases as film thickness increases above 2 microns. Another problem is poor transfer kinetics caused by the limited planar interfacial area where the reduction-oxidation (redox) reactions take place. Therefore, as the thickness of an electrode is increased to obtain more energy (i.e. longer battery life), the film suffers from cracking which leads to less material available, resulting in less overall energy. Also, thicker electrodes mean that the diffusion path of redox active species to the reaction site is increased, resulting in power loss. The bottom line is that due to their 2D nature, traditional batteries can have either high energy density (i.e., thick-film) or high power density (thin-film), but compromise one property for the other.

<table>
<thead>
<tr>
<th>Application</th>
<th>System Volume (no battery) (mm$^3$)</th>
<th>Battery Volume (mm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micro-air vehicle</td>
<td>3.0 (no electrodes)</td>
<td>110</td>
</tr>
<tr>
<td>Environmental/biological monitoring</td>
<td>150</td>
<td>350</td>
</tr>
<tr>
<td>Biological potential monitoring</td>
<td>0.0073</td>
<td>326</td>
</tr>
<tr>
<td>Microelectronic pill</td>
<td>0.5</td>
<td>1,200</td>
</tr>
</tbody>
</table>

Table 2.2 Survey of battery powered microelectromechanical systems.$^{35}$
Figure 2.3 Examples of prospective 3D architectures for charge-insertion batteries: (a) interdigitated rod arrays; (b) interdigitated plate arrays; (c) concentric tube; (d) aperiodic “sponge” type architectures.

Figure 2.3 shows the different architectures of possible 3D batteries. The interdigitated rods (3a) and plates (3b) designs are filled with electrolyte, which is dead, or inactive, volume. On the other hand, the most promising of these is the concentric tube battery (3c), which minimizes the electrolyte volume. In this type of battery, an array of cylindrical anode rods is coated with a thin electrolyte separator film. The volume between the coated rods would then be filled with the cathode material. This design utilizes the amount of space available for the active mass (i.e. anode and cathode material) by minimizing the volume of the electrolyte separator. Figure 3d shows a
sponge-like cathode arranged in a continuous 3D network, which is coated with an ultrathin layer of ion-conducting dielectric (electrolyte), and the remaining free volume is filled with and interpenetrating, continuous anode. Using 3D designs, milliwatt-hour (mW·h) energies can be achieved in cubic millimeter batteries. 

Figure 2.4 Schematic of (a) 2D parallel plate and (b) concentric tube 3D batteries. 

A key advantage of 3D batteries is that at the microscopic level, transport between the anode and cathode remains one-dimensional, while the geometry allows for high energy density without sacrificing power density. By keeping both the thickness of the electrodes and the distance between them small, power losses due to diffusion are minimized. A comparison between 2D and 3D battery configurations is shown in Figure 2.4. Taking advantage of the “vertical” dimension enables the 3D battery to utilize more surface area, leading to higher power, while maintaining a small areal
footprint. The energy density is increased by simply increasing the length of the rods, $L$. Thus, there is no compromise between energy density and power density. $L$ is limited due to ohmic resistance along the rods, with the optimized value of $L$ being determined by a combination of parameters including the electronic and ionic conductivity of the electrode materials, the ionic conductivity of the electrolyte, and the electrode geometry.

### 2.2.2 Current 3D Battery Highlights

Table 2.3 summarizes the advances in 3D electrodes and 3D batteries. Nishizawa et al. demonstrated that nanotube morphologies formed in the pores of porous alumina templates improved the capacity retention and rate capabilities of LiMn$_2$O$_4$ during cycling.$^{40}$ This protocol stimulated much work on using “template synthesis” as a means of synthesizing nanotubes, nanowires, and nanorods of different positive electrode materials.$^{40,41}$ Success with these materials led researchers to use the same strategy for negative electrode materials.$^{42-46}$ Results for SnO$_2$ obtained by Li et al. established the promise of using nanowires as battery electrode materials.$^{47,48}$ Silicon nanowires, for example, have been demonstrated as anodes for lithium ion batteries with capacities greater than 3,000 mA·h·g$^{-1}$ for 10 cycles.$^{49}$ Cycling was improved further by using a carbon-silicon core-shell geometry, which exhibited areal and gravimetric capacities of 4.0 mA·h·cm$^{-2}$ and 2000 mA·h·g$^{-1}$, respectively, with minimal capacity fading for 50 cycles.$^{43}$
Table 2.3 Advances reported on the synthesis of 3D electrodes and 3D batteries (Adapted from Arthur et al.)\textsuperscript{39,40,42,43,47,50-56}

<table>
<thead>
<tr>
<th>Group (Year)</th>
<th>Chemistry</th>
<th>Cell Type</th>
<th>Gravimetric Capacity (mA·h·g\textsuperscript{-1})</th>
<th>Areal Capacity (mA·h·cm\textsuperscript{-2})</th>
<th>Power Density (mW·cm\textsuperscript{-2})</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nishizawa et al. (1997)</td>
<td>LiMn\textsubscript{2}O\textsubscript{4}</td>
<td>Positive electrode</td>
<td>134</td>
<td>0.103</td>
<td>---</td>
<td>3D tubular arrays; Current density = 0.1–1 mA·cm\textsuperscript{-2}</td>
</tr>
<tr>
<td>Wu et al. (2005)</td>
<td>Mn\textsubscript{2}O\textsubscript{4}</td>
<td>Negative electrode</td>
<td>970</td>
<td>0.233</td>
<td>---</td>
<td>Electrochemical deposition; Specific current = 85 mA·g\textsuperscript{-1}</td>
</tr>
<tr>
<td>Cui et al. (2009)</td>
<td>Carbon-Si Core-Shell nanowire</td>
<td>Negative electrode</td>
<td>2000</td>
<td>4.0</td>
<td>---</td>
<td>High surface area nanowires in 2D electrode arrangement; Cycled at C/5 rate</td>
</tr>
<tr>
<td>Li et al. (2000)</td>
<td>SnO\textsubscript{2}</td>
<td>Negative electrode</td>
<td>720</td>
<td>0.037</td>
<td>---</td>
<td>Templated nanowire array; Current density = 0.32 mA·cm\textsuperscript{-2} (8C)</td>
</tr>
<tr>
<td>Kotohoki et al. (2011)</td>
<td>LiCoO\textsubscript{2} \textendash Li\textsubscript{2}Mn\textsubscript{2}O\textsubscript{12}</td>
<td>Full Battery</td>
<td>&lt;1</td>
<td>0.0073</td>
<td>---</td>
<td>Honeycomb Li\textsubscript{0.35}Li\textsubscript{0.65}TiO\textsubscript{2} used as template and ceramic electrolyte</td>
</tr>
<tr>
<td>Teixidor et al. (2008)</td>
<td>Carbon</td>
<td>Negative electrode</td>
<td>---</td>
<td>0.350</td>
<td>---</td>
<td>Mixture of pyrolyzed SU-8* and MCMB* in post array</td>
</tr>
<tr>
<td>Cheah et al. (2009)</td>
<td>TiO\textsubscript{2}</td>
<td>Negative electrode</td>
<td>168</td>
<td>0.0112</td>
<td>---</td>
<td>Electrodeposited TiO\textsubscript{2} on Al nanorods; Current density = 1.0 μA·cm\textsuperscript{-2}</td>
</tr>
<tr>
<td>Shaijunon et al. (2010)</td>
<td>LiCoO\textsubscript{2}</td>
<td>Positive electrode</td>
<td>---</td>
<td>0.110</td>
<td>---</td>
<td>Spray-coated on Al nanorods; Cycled at C/5 rate</td>
</tr>
<tr>
<td>Nathan et al. (2005)</td>
<td>MCMB \textendash MoO\textsubscript{3}</td>
<td>Full Battery</td>
<td>---</td>
<td>1.0–2.0</td>
<td>0.35–1.75</td>
<td>Deposition of films in silicon or glass microchannel plate using centrifuge technique; Current density = 0.2–1.0 mA·cm\textsuperscript{-2}</td>
</tr>
<tr>
<td>Min et al. (2008)</td>
<td>Carbon \textendash PPyDBS\textsuperscript{*}</td>
<td>Full Battery</td>
<td>---</td>
<td>0.0106</td>
<td>0.06</td>
<td>Interdigitated design using pyrolyzed SU-8 electrodeposited with doped polypyrrole; Current density = 0.02–0.09 mA·cm\textsuperscript{-2}</td>
</tr>
<tr>
<td>Chamran et al. (2007)</td>
<td>Zinc \textendash Air</td>
<td>Full Battery</td>
<td>626</td>
<td>8.93</td>
<td>32.5</td>
<td>2D commercial cathode used; Current density = 0.42–28.25 mA·cm\textsuperscript{-2}</td>
</tr>
</tbody>
</table>

\* SU-8, epoxy photoresist from Microchem Corp.; MCMB, mesocarbon microbeads; PPyDBS, dodecylbenzene sulfonate doped polypyrrole.

Although there are several demonstrations of 3D electrodes showing performance gains over 2D electrodes, there are only a few demonstrations of fully functioning 3D batteries. One of the more elite 3D batteries is a zinc-air battery created by Chamran et al., which was comprised of a 3D zinc anode and a commercial cathode.\textsuperscript{56} This battery displays capacities of 8.93 mA·h·cm\textsuperscript{-2} and
626 mA·h·g\(^{-1}\) and a power density of 32.5 mW·cm\(^{-2}\). Of the lithium ion batteries, the 3D thin-film battery developed by Nathan et al. shows superiority over other 3D lithium ions batteries.\(^{54}\) This battery, which consists of mesocarbon microbeads (MCMB) anode and MoO\(_x\)S\(_y\) cathode films deposited on a microchannel plate, exhibits an areal capacity of 1.0–2.0 mA·h·cm\(^{-2}\) and a power density of 0.35–1.75 mW·cm\(^{-2}\) when cycled between 1.0–0.2 mA·cm\(^{-2}\). In any event, the development of 3D batteries is still in its infancy and much more research is required for advancing this technology.

### 2.3 Electrochemical Characterization

**Figure 2.5** 3-electrode electrochemical cell comprised of a working electrode, which is the monitored electrode, a counter electrode, and a reference electrode.

In a battery, energy is stored in the form of chemical bonds within the active mass of each electrode and the conversion of chemical energy into electrical energy is possible through redox reactions. Electrochemistry techniques provide a means of analyzing the chemical and electrical interactions at the interface of an electrode, revealing fundamental thermodynamic and kinetic properties of the redox active species. Electrochemical characterization is typically performed by
analyzing half-cell reactions in test tells composed of 3 electrodes: a counter electrode, a working electrode, and a reference electrode (Figure 2.5). In a half-cell reaction, a potentiostat is used to pass current between the counter and working electrodes, while monitoring the potential with respect to the reference electrode. The working electrode, which is the monitored electrode, is varied in potential to change the electron energy levels and induce reduction or oxidation of redox active species (Figure 2.6).

![Diagram of half-cell reactions](image)

**Figure 2.6** Representation of reduction (top) and oxidation (bottom) of species (A). Reduction is induced by applying a negative potential at the working electrode, which raises the electron energy level high enough for an electron to transfer into a vacant molecular orbital (MO) of species (A). Oxidation occurs when the energy of the electrons is lowered, i.e., by an applied positive potential, enough to the point where it is more favorable for electrons in the occupied MO to transfer to the working electrode. (Adapted from Bard)
Cyclic voltammetry (CV) is an extremely useful electrochemical characterization technique in which some of the information that can be obtained includes, but is not limited to, redox potentials, electrochemical reversibility, chemical reversibility, and determination of diffusion coefficients. In a CV experiment, the potentiostat applies a potential and measures the current response at each potential. The potential is swept linearly between 2 potentials (Figure 2.7a) and the rate at which this is done is the scan rate, \( \nu \).

A typical cyclic voltammogram of lithium polysulfide is depicted in Figure 2.7b. Positive and negative currents are assigned as oxidation and reduction, respectively. The peak currents for oxidation \( (i_{p,ox}) \) and reduction \( (i_{p,red}) \), at the oxidation \( (E_{p,ox}) \) and reduction \( (E_{p,red}) \) and \( (E_{p,red}) \) potentials, are obtained by subtracting the extrapolated baseline currents in order to subtract out non-faradaic currents. The peak-to-peak separation \( (\Delta E_p) \) between anodic and cathodic reactions (equation 2.6)

\[
\Delta E_p = E_{p,ox} - E_{p,red}
\]

(2.6)

carries information about the electrochemical reversibility, which is defined by

\[
\Delta E_p \approx \frac{2.3RT}{n_e F} \approx \frac{59mV}{n_e}
\]

(2.7)

where \( R \) is the gas constant, \( T \) is absolute temperature, \( n_e \) is the number of electrons transferred, and \( F \) is the Faraday constant. In an electrochemically reversible system, \( \Delta E_p \) decreases during repeated cycling until a steady-state pattern is reached, in which \( \Delta E_p = 58mV \) for a one-step, one-electron transfer process at 25°C.
Energy storage characteristics in battery materials are governed by thermodynamic formulations adapted to electrochemical reactions. The net Gibbs free energy ($\Delta G$) from an electrochemical reaction corresponds to the net available electrical energy according to equations 2.8 and 2.9

$$\Delta G = -n_e FE$$  \hspace{1cm} (2.8)$$

$$\Delta G^\circ = -n_e FE^\circ$$  \hspace{1cm} (2.9)$$

where $n_e$ is the number of electrons transferred in the reaction, $F$ is the Faraday constant, $E$ is the electromotive force (or cell potential), and $E^\circ$ and $\Delta G^\circ$ are the electromotive force and change in Gibbs free energy at standard temperature and pressure. The van’t Hoff isotherm, which leads to the relation between equilibrium constant, heat of reaction, and temperature, can be given in terms of free energy as
\[
\Delta G = \Delta G^\circ + RT \cdot \ln \left( \frac{a_p}{a_k} \right)
\]  
(2.10)

where \( R \) is the gas constant, \( T \) is the absolute temperature, and \( a_p \) and \( a_k \) are the activity of the products and reactants, respectively.\(^59\)\(^61\) For an electrochemical redox reaction,

\[
Ox + n_e e^- \Leftrightarrow Red
\]  
(2.11)

equations 2.8 and 2.9 can be combined with equation 2.10 to yield the Nernst equation,

\[
E = E^\circ + \frac{RT}{n_F} \ln \left( \frac{a_{Ox}}{a_{Red}} \right)
\]  
(2.12)

in which the activity coefficient approaches unity in dilute solutions and the activity of oxidized (\( a_{Ox} \)) and reduced (\( a_{Red} \)) species are usually replaced with the concentration of oxidized and reduced species, respectively.\(^57\)

Batteries are characterized using the Galvanostatic Cycling with Potential Limitation (GCPL) technique, in which the potentiostat applies a constant current to the battery and measures the voltage response with respect to time. Figure 2.8 shows a typical discharge curve of a battery discharged galvanostatically.\(^59\) In the absence of an external load, the potentiostat reads an open-circuit potential (\( V_{OC} \)), which can indicate the state of charge (or discharge) of the battery. As soon as a load is placed on the battery, i.e., when the GCPL begins, there is an immediate IR drop in potential caused by the internal resistance of the battery. The extent of IR drop and the height of the linear portion of the discharge curve are dependent on the applied current. As the current increases, the ohmic polarization increases and thus the discharge plateau drops. The larger the polarization in the charge and discharge curves, the larger the overpotential (\( \eta \)), which is the amount of additional potential/energy required to drive the reaction at a certain rate.\(^57\) Concentration polarization also increases with increasing discharge current, resulting in premature cell death. In
other words, a higher current results in an abortive discharge curve, where the battery’s “end of life” (Figure 2.8) occurs at a lower discharge capacity.

Figure 2.8  Typical discharge curve of a battery showing the influence activation, ohmic, and concentration polarizations on the discharge profile. (Adapted from Winter et al.)

Battery performance can be expressed in terms of capacity \((Q)\), energy \((U)\), and power \((P)\).

Capacity corresponds to the total amount of charge delivered (or stored) by the battery,

\[
Q = I \cdot t
\]  (2.13)

where \(I\) is the current (in Ampere) at which the battery is discharged (charged) and \(t\) is time (in hours). Capacity can be normalized by the mass of the redox active species, i.e., specific capacity, or by the electrode area, i.e., areal capacity. In microbattery applications, specific and areal capacities are usually given in units of mA·h·g\(^{-1}\) and mA·h·cm\(^{-2}\), respectively. One parameter which affects the amount of capacity obtained during discharge is the discharge rate, which can be defined as

\[
r_c = \frac{Q}{t}
\]  (2.14)
where \( r_c \) is termed the “C-rate.” For example, if a battery with \( Q = 1 \text{ mA·h} \) is discharged at \( r_c = 1\text{C} \), then the discharge current is 1 mA and the length of the discharge should theoretically be one hour. However, if the same battery is discharged at \( r_c = C/10 \), then the discharge current and length of discharge should be 100 \( \mu \text{A} \) and 10 hours, respectively. Batteries are typically measured at a C-rate of \( C/20 \).

Energy, \( U \), which is delivered by a battery upon discharging, can be calculated by

\[
U = \int_{0}^{t} E \cdot I \cdot dt
\] (2.15)

where \( E \) is the potential, \( I \) is the current, and \( t \) is time. Energy density can be normalized either by mass (i.e., mW·h·g\(^{-1}\)) or by volume (i.e., W·h·L\(^{-1}\)). Power, \( P \), describes the rate at which the energy can be released from a battery upon discharge. Power is given by

\[
P = E \cdot I
\] (2.16)

which can be obtained by multiplying the discharge voltage by the discharge current. Similar to energy density, gravimetric and volumetric power densities can be expressed in mW·g\(^{-1}\) and W·L\(^{-1}\), respectively.
Chapter 3 - Development of Li Battery using a Liquid Cathode

3.1 Introduction

This chapter discusses the development of a battery based on the lithium polysulfide \( \text{Li}_2\text{S}_n \) liquid cathode. Lithium polysulfides have been studied since the 1970s.\(^{62}\) They consist of anionic polysulfide chains \( \text{S}_n^{2-} \) of which each are counterbalanced by two lithium cations \( \text{Li}^+ \). These ions are quite soluble in aprotic solvents, up to 10 molar (10M), in organic solvents such as tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO).\(^{62}\) Both solubility and polysulfide chain length, \( n \), increase as the dielectric constant of the solvent decreases.

<table>
<thead>
<tr>
<th>Method</th>
<th>Reaction Type (Reactants)</th>
<th>Chemical Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Direct (Sulfur; Lithium)</td>
<td>( 2\text{Li} + \frac{n}{8} \text{S}_8 \rightarrow \text{Li}_2\text{S}_8 ) (3.1)</td>
</tr>
<tr>
<td>2</td>
<td>Electrochemical Reduction (Sulfur; Lithium Counter)</td>
<td>( 2e^- + \text{S}_8 \rightarrow \text{S}_8^{2-} ) (3.2.1) ( n\text{S}<em>8^{2-} \leftrightarrow \text{S}</em>{7n+1}^{2-} + (n-1)\text{S}^{2-} ) (3.2.2)</td>
</tr>
<tr>
<td>3</td>
<td>Direct (Sulfur, Lithium Sulfide)</td>
<td>( \text{Li}_2\text{S} + \frac{(n-1)}{8} \text{S}_8 \rightarrow \text{Li}_2\text{S}_8 ) (3.3)</td>
</tr>
</tbody>
</table>

Table 3.1 summarizes the methods of producing \( \text{Li}_2\text{S}_n \) reported by Rauh et al. The first method involves the direct reaction of lithium metal with elemental sulfur in THF or DMSO (3.1). This reaction can be very slow due to the low rate of lithium dissolution. The second method involves the electrochemical reduction of elemental sulfur (3.2.1) using lithium as a counter electrode. In THF this reduction occurs at 2.2V (vs. Li/Li\(^+\)) but could be as high as 2.7V in other
solvents, i.e. DMSO, dimethylformamide (DMF), and dimethylacetamide (DMAC). However, some of the reduced sulfur can be lost due to precipitation of lithium sulfide (Li₂S) through disproportionation reactions (3.2.2). The third method involves the reaction of Li₂S with elemental sulfur (3.3) in various solvents, of which THF and DMSO are best. One benefit of using this method is that the stoichiometry of lithium polysulfides can be precisely controlled. Another benefit is that the high surface area of the reactants (i.e., fine sulfur and Li₂S powders) allows the reaction to produce Li₂Sn much more rapidly.

Figure 3.1 Cyclic voltammogram of 4mM Li₂S₈, cathodic direction. Electrodes: glassy carbon, working; stainless steel, counter; porous Teflon-bonded carbon, reference. Electrolyte: 0.8M LiClO₄ in THF. Sweep rate: 50 mV·s⁻¹. Potential: vs. reference polysulfide electrode (RPSE).

The electrochemical reduction of sulfur is very complicated, composed of a series of electron transfer reactions. Yamin et al. have electrochemically characterized Li₂S₈ with cyclic
voltammetry (Figure 3.1), using glassy carbon, stainless steel, and porous Teflon-bonded carbon as the working, counter, and reference electrodes, respectively. CV analysis is summarized in Table 3.2. When sweeping in the cathodic direction (i.e., towards negative potentials), three reduction (or cathodic) peaks are observed. The first cathodic peak is attributed to the reduction of higher order polysulfides (i.e., \( n \geq 7 \)) to \( S_6^{2-} \) (3.4), while the second cathodic peak is attributed to the reduction of \( S_5^{2-} \) to \( S_5^{2-} \) (3.5). The third cathodic peak is attributed to the reduction of \( S_5^{2-} \) to both \( \text{Li}_2\text{S}_2 \) (3.6.1) and \( \text{Li}_2\text{S} \) (3.6.2). However, when the potential is swept in the anodic direction (i.e., towards positive potentials), only one oxidation (or anodic) peak is observed. In the literature, this anodic peak is attributed to the simultaneous oxidation of all polysulfides to elemental sulfur (3.7).

### Table 3.2 Summary of peak association with redox reaction from CV of 4mM Li\(_2\)S\(_8\) (Adapted from Yamin et al.)\(^{13}\)

<table>
<thead>
<tr>
<th>Peak</th>
<th>Sweep Direction</th>
<th>Redox Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cathodic</td>
<td>( S_n^{2-} + \left( \frac{n-6}{3} \right) e^- \rightarrow \frac{n}{6} S_6^{2-} ) (3.4)</td>
</tr>
<tr>
<td>2</td>
<td>Cathodic</td>
<td>( 5S_5^{2-} + 2e^- \rightarrow 6S_5^{2-} ) (3.5)</td>
</tr>
</tbody>
</table>
| 3    | Cathodic        | \( 10\text{Li}^+ + 2S_5^{2-} + 6e^- \rightarrow 5\text{Li}_2\text{S}_2 \) (3.6.1)  
\( 10\text{Li}^+ + S_5^{2-} + 8e^- \rightarrow 5\text{Li}_2\text{S} \) (3.6.2) |
| 4    | Anodic          | \( \text{Li}_2\text{S}_n \rightarrow S_8 \) (3.7) |

Energy in the \( \text{Li}_2\text{S}_n \) system is stored in the chemical bonds of the polysulfide chains. Thus, when reacted with lithium, the capacity obtained during discharge comes from the reduction of \( S_n^{2-} \) to shorter chain polysulfides and, ultimately, to \( S^{2-} \). Increasing the order of the polysulfide (i.e., increasing \( n \)) increases the amount of energy that can be stored in the liquid cathode. Table 3.3 lists the theoretical gravimetric capacities of various polysulfides according to
\[ S_n^{2-} + (2n-2)e^- \rightarrow nS^{2-} \]  \hfill (3.8)

where \( n \) is the polysulfide order and \( 2n-2 \) is the number of electrons required to reduce \( S_n^{2-} \) to \( S^{2-} \).

Based on equation 3.8, the capacity per sulfur atom, \( Q_{\text{atom}} \), can be calculated according to equation 3.9 and can be expressed in terms of mA·h·g\(^{-1}\) by multiplying \( Q_{\text{atom}} \) by the constant \( \beta \) (3.10), such that

\[ Q_{\text{atom}} = \frac{(2n-2)e^-}{n \cdot S_{\text{atom}}} = \frac{Q}{\beta} \]  \hfill (3.9)

\[ \beta = \frac{F}{3.6 \cdot A_S} = 835.85 \text{ mA·h·g}^{-1} \cdot S_{\text{atom}} \cdot (e^-)^{-1} \]  \hfill (3.10)

where \( Q \) is the discharge capacity in mA·h·g\(^{-1}\), \( F \) is the Faraday constant, \( A_S \) is the atomic weight of sulfur, and \( n \cdot S_{\text{atom}} \) is the number of sulfur atoms in the polysulfide chain. It can be seen that as the polysulfide order is increased, the theoretical capacity approaches that of elemental sulfur (i.e., 2 electrons per sulfur atom or 1672 mA·h·g\(^{-1}\)).

**Table 3.3 Theoretical discharge capacity of various lithium polysulfides**

<table>
<thead>
<tr>
<th>Cathode Composition</th>
<th>Discharge Capacity</th>
<th>Discharge Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( e^- S_{\text{atom}} )</td>
<td>(mA h g(^{-1}) sulfur)</td>
</tr>
<tr>
<td>Li_2S_6</td>
<td>1.67</td>
<td>1390</td>
</tr>
<tr>
<td>Li_2S_8</td>
<td>1.75</td>
<td>1460</td>
</tr>
<tr>
<td>Li_2S_{12}</td>
<td>1.83</td>
<td>1530</td>
</tr>
<tr>
<td>Li_2S_{20}</td>
<td>1.9</td>
<td>1590</td>
</tr>
<tr>
<td>Li_2S_{100}</td>
<td>1.98</td>
<td>1650</td>
</tr>
<tr>
<td>S</td>
<td>2</td>
<td>1672</td>
</tr>
</tbody>
</table>
3.2 Motivation

Although 3D battery development is still in its infancy, there are indeed 3D electrodes that show promising battery behavior. It has been shown that high-aspect-ratio carbon electrode arrays can be made via infiltration of a carbon slurry into a silicon mold, which is sacrificially etched away using XeF₂. However, creating a 3D electrode is but just a small step in fabricating a full 3D battery. One of the greatest challenges which hinder 3D battery advancement is the deposition of a conformal, electrolyte separator. For example, after fabricating a 3D carbon anode, an electrolyte separator must be deposited onto the carbon surface before applying, i.e., via sedimentation, the cathode material, i.e., LiCoO₂ (Figure 3.2a). Any areas where deposition of the separator is incomplete, i.e., a pinhole, will allow the cathode to be in contact with the carbon anode, causing an internal short.

There are two principal motivations for using lithium polysulfide as the cathode material. The first is the high capacity of the lithium-sulfur system (i.e., 1672 mA·h·g⁻¹). The second reason is that the use of lithium polysulfide eliminates the need for a separator. In other words, because Li₂Sₙ is electrically insulating, it can be in direct contact with lithium without shorting. This means that fabrication of a 3D battery using this liquid cathode requires only that a 3D anode and a cathode current collector (i.e. molybdenum) be present (Figure 3.2b).
Figure 3.2 Hypothetical scheme of 3D battery fabrication using (a) a solid-state LiCoO$_2$ cathode and (b) lithium polysulfide.
3.3 Experimental

3.3.1 Chemicals

Lithium sulfide (Li$_2$S) powder, 99.9% (12839, Alfa Aesar), was inserted into an argon (Ultra High Purity Ar, Air Liquide) filled glovebox and used as received. Sulfur, 99.98% (414980, Sigma-Aldrich), and lithium trifluoromethanesulfonate (lithium triflate), 99.995% (481548, Sigma-Aldrich), powders were dried separately on a Schlenk line by purging with argon three times and then raising the temperature to 120°C for 6 hours under vacuum. Inhibitor-free anhydrous tetrahydrofuran (THF), ≥99.9% (401757, Sigma-Aldrich), and anhydrous 1,3-dioxolane (DXL) with ~75 ppm butylated hydroxytoluene as inhibitor, 99.8% (271020, Sigma-Aldrich), were inserted into the glovebox and used as received.

Tetraethylene glycol dimethyl ether (TG), 99% (172405, Sigma-Aldrich), was dried on a Schlenk line by purging with argon three times and then raising the temperature to 105°C for 4 hours under vacuum. 4Å molecular sieves (208604, Sigma-Aldrich) were dried on a Schlenk line by purging with argon three times and then raising the temperature to 225°C for 24 hours. After placement into the glovebox, the TG was run through a column filled with the dry molecular sieves and collected in a dry amber jar at a rate of two drops per second.

3.3.2 Synthesis of Li$_2$S$_n$

Lithium polysulfides were synthesized inside an argon-filled glovebox by reacting stoichiometric amounts of Li$_2$S with sulfur at 55°C in a glass jar using THF as a solvent (Figure 3.3a). As the reaction proceeds, the opaque mixture becomes a red solution resembling human blood. Once the mixture is homogeneous, the solution must undergo a solvent exchange process in which TG replaces THF. After adding TG, the solution is stirred for one day at 55°C. The
temperature is then raised to 85°C and the solution is placed under vacuum (Figure 3.3b). The pressure is gradually decreased by controlling the flow of argon (in the glovebox) into the reaction jar using a 316L Stainless Steel Swagelok® Vernier Low-Flow Valve. Pressure decreases are done in small increments to avoid excessive boiling of the THF. Solvent exchange is complete when the bubble formation ceases while under full vacuum.

After the solvent exchange process, lithium triflate electrolyte salt is added to the lithium polysulfide solution such that the concentration of the electrolyte is equal to 0.8 M, regardless of the polysulfide concentration. After dissolution of the salt, DXL is added. The final solution is of blood-red color with moderate viscosity. This lithium polysulfide solution is referred to as the liquid cathode (or catholyte).

![Diagram](image.png)

**Figure 3.3** (a) Synthetic route of liquid cathode synthesis inside of an argon-filled glovebox. (b) Modified glovebox displaying custom vacuum system used to extract THF after addition of TG.
3.3.3 Battery Preparation

Batteries were constructed as shown in Figure 3.4 using molybdenum, 99.995% (10034, Alfa Aesar), and nickel, 99.5% (11453, Alfa Aesar), rods of ½” diameter as the cathode and anode current collectors, respectively. First, lithium foil, 99.9% (320080, Sigma-Aldrich), is polished using a polyethylene plate and then pressed onto the nickel rod. The nickel rod is then inserted into a polyethylene (PE) sleeve, followed by a PE spacer (■-ring), and a groove is cut out of the lithium to allow the spacer to be in direct contact with the nickel rod. Once the Ni rod is inserted into the PE sleeve, it is sealed by compression using a hose clamp. After adding the liquid cathode into the PE sleeve, the Mo rod must be inserted into the sleeve and then compressed until the Mo rod, PE spacer, and Ni rod are all in contact. This is done by hand using moderate force, but is very straightforward. Once the Mo rod is sealed by compression using a hose clamp, the battery is ready to be cycled.

Figure 3.4 Battery Cell Components and Construction
3.3.4 Measurements

Electrochemical measurements were recorded through EC-Lab software using a VMP3 Multi Potentiostat by Bio-Logic SA. Cyclic voltammetry (CV) experiments were carried out in an argon-filled glovebox using a three-electrode setup consisting of molybdenum working, lithium counter, and lithium reference electrodes; thus, all potentials in this chapter are referenced to Li/Li+. Three-neck round bottom flasks were sealed using rubber stoppers during all CV experiments to prevent solvent evaporation. All half-cells used a standard volume of 5 mL and were cycled between 0.5V and 4V vs. Li/Li+ at room temperature (15–20°C).

Galvanostatic Cycling with Potential Limitation (GCPL) experiments were carried out in an argon-filled glovebox on two-electrode battery cells, in which the molybdenum rod was the working electrode and the counter and reference wires from the potentiostat were both connected to the lithium-deposited nickel rod. All batteries had a liquid cathode volume loading between 40–50 μL and were cycled between 2.8V and 1.8V at room temperature.

3.4 Results and Discussion

3.4.1 Polysulfide Transport, 4mM Li₂S₁₂

First, CV experiments were carried out to show the redox behavior of lithium polysulfides using actual battery materials, i.e., molybdenum (cathode current collector) and lithium (anode). Cyclic voltammograms of 4mM Li₂S₁₂ catholyte (Figure 3.5) show similar redox behavior as seen in literature. At all attempted scan rates, three reduction peaks are observed, which are associated with the formation of $S_6^{2-}$ (1st reduction), $S_5^{2-}$ (2nd reduction), and $S_2^{2-} + S^{2-}$ (3rd reduction) as shown in equations 3.4–3.6.2. Similarly, when sweeping to anodic potentials, only one peak is observed, which is attributed to the oxidation of reduced polysulfides to sulfur (3.7).
Examination of the anodic ($E_{p,ox}$) and cathodic ($E_{p,red}$) peak potentials shows that $E_p$ varies with scan rate. $\Delta E_p$ between $E_{p,ox}$ and the first reduction peak ($E_{p,red}$), is more than 310 mV at a scan rate of $\nu = 5 \text{ mV} \cdot \text{s}^{-1}$. This indicates that the electrochemical reactions are sluggish and follow an irreversible process.\footnote{Plots of peak current ($i_p$) versus the square root of the scan rate ($\nu^{1/2}$) are shown in Figure 3.6. The linearity of the anodic (△) and cathodic (▽) peak currents with $\nu^{1/2}$ indicate a diffusion-limited faradaic process according to

$$i_p = FAC^*D^{1/2}\nu^{1/2}\left(\frac{amF}{RT}\right)^{1/2} \pi^{1/2} \chi(b\nu)$$

where $F$ is the Faraday constant, $A$ is the electrode surface area in cm$^2$, $C^*$ is the bulk concentration in mol·cm$^{-2}$, $D$ is the diffusion coefficient in cm$^2$·s$^{-1}$, $\nu$ is the scan rate in V·s$^{-1}$, $x$ is the transfer coefficient.}
coefficient, \( n \) is the number of electrons transferred, \( R \) is the gas constant, \( T \) is absolute temperature, and \( \chi(bt) \) is the normalized current for a totally irreversible system in CV.\(^{57}\)

Figure 3.6 Anodic and cathodic peak currents versus square root of scan rate from cyclic voltammograms of 4mM Li\(_2\)S\(_{12}\).

### 3.4.2 Proof of Concept – First Generation Battery

A proof of concept was demonstrated in which a battery was tested by pipetting 0.5 mL 4mM Li\(_2\)S\(_{12}\) catholyte into a glass vial of \( \frac{1}{2}'' \) inner diameter. The cathode current collector was molybdenum foil and the anode was lithium foil, both of which were folded at 90° angles and placed parallel to each other as shown in Figure 3.7. The surface area of each foil was approximately 0.6 cm\(^2\). Stainless steel wires were crimped to each foil and poked through a rubber septum turnover stopper which was sealed at the top of the glass vial to prevent solvent evaporation. The
working wire of the potentiostat was connected (via alligator clip) to the molybdenum electrode, while the counter and reference wires were clipped to the lithium electrode.

Battery performance of the first generation battery was characterized by galvanostatically cycling at 31.5 μA (~53 μA·cm⁻²). Multiplying the theoretical specific capacity of Li₂S₁₂ (Table 3.3) by the 942 μg of sulfur present in the catholyte yields a calculated theoretical capacity of 1.57 mA·h for this battery cell. Therefore, the current density at which the battery was cycled corresponds to a C-rate of C/50. Discharge (Figure 3.7a) and charge (Figure 3.7b) voltage profiles at this rate depict a chemically reversible system. The observed flat voltage plateaus, of which all cycles overlap, are indicative of a promising secondary battery system. However, although the voltage profiles appear hopeful, only ~1/3 of capacity is utilized (Figure 3.8a). Also, even at C-rates as low as C/50, the coulombic efficiency of the battery, which is the ratio of charge obtained during discharge over the charge put in during charging, is poor. By the fifth cycle, the discharge capacity reaches up to ~550 mA·h·g⁻¹, while the charge capacity increases to ~650 mA·h·g⁻¹, corresponding to a coulombic
efficiency of approximately 85%. This loss of capacity can be realized when plotting the voltage profile of a complete cycle (Figure 3.8b). After the battery discharges ("A" → "B") for 550 mA·h·g⁻¹, the following charge ("B" → "C") requires an additional 100 mA·h·g⁻¹ to return to the initial charged state (i.e., 4V). This loss is due to high internal resistances attributed to poor cell design, i.e. separation between lithium and molybdenum is ~5 mm. These results underscore the need for cell optimization.

![Figure 3.8](image)

**Figure 3.8** First generation Li₂S₁₂ battery. (a) Gravimetric and areal capacities during charging and discharging. (b) 5th cycle charge-discharge profiles. Catholyte: 4mM Li₂S₁₂, 0.8M LiSO₃CF₃ in TG/DXL (30/70 v/v). Current density: 53 μA·cm⁻².

### 3.4.3 Depth of Discharge – Li₂S₁₂ → Li₂S₃

One problem that plagues lithium-sulfur battery systems is the formation of Li₂S, which is the very same product that provides them with such high theoretical capacities. Both Li₂S and Li₂S₂ are insoluble in the catholyte. Therefore, after complete reduction of lithium polysulfide, if insoluble discharge products fail to reach the current collector (i.e. precipitation of Li₂S and Li₂S₂ away from
molybdenum) upon charging, then not all products can oxidize to higher order polysulfides. Thus, in theory, limiting the extent of discharge to produce mostly soluble polysulfides (i.e. \( n \geq 3 \)) should minimize the rate of sulfur loss via precipitation and enhance cycling capabilities. However, limiting the extent of polysulfide reduction comes at the price of capacity. Table 3.4 tabulates the theoretical capacity of various lithium polysulfides discharged to different states according to

\[
S_n^{2-} + \left( \frac{2n}{D} - 2 \right) e^- \rightarrow \left( \frac{n}{D} \right) S_D^{2-}
\]  

(3.12)

where \( n \) is the polysulfide order of the liquid cathode and \( D \) is the polysulfide order at the discharged state. Thus, the atomic capacity, \( Q_{\text{atom}} \), of the reduction of sulfur is calculated according to equation 3.13 and the theoretical discharge capacity, \( Q \), is calculated using equations 3.9 and 3.10.

\[
Q_{\text{atom}} = \frac{\left( \frac{2n}{D} - 2 \right) e^-}{n \cdot S_{\text{atom}}}
\]  

(3.13)

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Discharge Capacity (mA h ( S_n^{1 \text{~sulfur}} ))</th>
<th>( \text{Li}_2S_4 )</th>
<th>( \text{Li}_2S_2 )</th>
<th>( \text{Li}_2S )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(_2)S(_0)</td>
<td>279</td>
<td>557</td>
<td>1390</td>
<td></td>
</tr>
<tr>
<td>Li(_2)S(_8)</td>
<td>348</td>
<td>627</td>
<td>1460</td>
<td></td>
</tr>
<tr>
<td>Li(<em>2)S(</em>{12})</td>
<td>418</td>
<td>697</td>
<td>1530</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.4 Theoretical gravimetric discharge capacities of various lithium polysulfides

To test the effect of depth of discharge control, 4mM and 100mM Li\(_2\)S\(_{12}\) batteries were fabricated using the scheme shown in Figure 3.4. The specifications of each battery are shown in Figure 3.9. When cycling between Li\(_2\)S\(_{12}\) and Li\(_2\)S\(_3\), the theoretical capacities of the 4mM and 100mM batteries are 26 and 813 \( \mu \text{A} \cdot \text{h} \), respectively.
First, the 4mM Li$_2$S$_{12}$ battery was cycled using the GCPL technique at a rate of C/10 (2.9 μA·cm$^{-2}$), C/5 (5.8 μA·cm$^{-2}$), 1C (29 μA·cm$^{-2}$), and C/10 (2.9 μA·cm$^{-2}$). Plots of the charge-discharge profiles of the 4mM Li$_2$S$_{12}$ battery cycled at C/10 are shown in Figure 3.10. A clear benefit of this battery design is the gain in coulombic efficiency. By limiting the reduction reaction, we are obtaining 100% coulombic efficiency, compared to 85% in the first generation battery shown in Figure 3.8b. Another benefit is the decrease in ohmic polarization during cycling. Even when cycled at rates as high as C/10, the overpotential, which can be calculated by subtracting the potential of the charge and discharge plateaus, in this battery is about 215mV, compared to 705mV in the first generation battery cycled at C/50.

Figure 3.9 Specifications of (a) 4mM and (b) 100mM Li$_2$S$_{12}$ Batteries.

Figure 3.11 shows the cycling performance of the 4mM Li$_2$S$_{12}$ battery (■). When cycled at a current density of 2.9 μA·cm$^{-2}$ (C/10), 100% of the theoretical capacity (418 mA·h·g$^{-1}$) is attained. When the current density is doubled (C/5) the capacity drops by approximately 25% to ~300 mA·h·g$^{-1}$. After the 20$^{th}$ cycle, when the current density is increased to ten times that of the initial
discharge rate, the capacity decreases to less than 30% ($\sim 160$ mA·h·g$^{-1}$). However, by the 29th cycle, when the current density is lowered to the original rate (C/10), 100% of the capacity is recovered.

Figure 3.10 5th cycle charge-discharge voltage profiles of 4mM Li$_2$S$_{12}$ battery. C-rate, C/10; current density, 2.9 $\mu$A·cm$^{-2}$.

The decrease in capacity with increasing discharge rate that is observed in the 4mM Li$_2$S$_{12}$ battery is characteristic of a 2D battery. In other words, this behavior is expected in these batteries and 3D geometries are anticipated to remedy energy loss under high power (i.e. high current density) conditions. Evidence that capacity loss is due to electrode geometry lies within the final cycles of the battery, where the capacity is recovered when the discharge rate is decreased to C/10.

Similar to the 4mM battery, the 100mM battery was cycled at C/10 (90 $\mu$A·cm$^{-2}$) for 10 cycles. Plots of the charge-discharge profiles of the 5th cycle (Figure 3.12) show the degree of inefficiency of this battery. For example, compared to the theoretical capacity of 418 mA·h·g$^{-1}$, a
discharge capacity of only 250 mA·h·g⁻¹ is attained, which corresponds to a coulombic efficiency of about 60%. The overpotential of this battery is about 305 mV when cycled at C/10.

![Figure 3.11 Capacity retention during discharging of 4mM (■) and 100mM (○) Li₂S₁₂ batteries.](image)

One obvious problem with the 100mM Li₂S₁₂ battery is the overpotential, which is larger than that of the 4mM battery. It is difficult to have a precise comparison between the two batteries because of the difference in cell geometries (i.e., 20% larger spacer thickness in 100mM versus 4mM battery), which possibly causes the 100mM battery to have a slightly larger cell resistance. Also, although both batteries were cycled at the same C-rate (i.e., C/10), the current densities are significantly different (i.e., 2.9 μA·cm⁻² and 90 μA·cm⁻² for the 4mM and 100mM batteries, respectively). This factor of 31 increase in current density, along with greater cell resistance, are most likely the cause of the increased overpotential observed in the 100mM battery.

Another problem in the 100mM Li₂S₁₂ battery is the low gravimetric capacity. Over 10 cycles, the battery exhibits a discharge capacity of about 250 mA·h·g⁻¹, which is roughly 60% of the
theoretical capacity. The capacity shortcomings of this battery are associated with both the physical and chemical properties of the liquid cathode. It turns out that viscosity plays a major role in the degree of concentration polarization and that the increased viscosity of the 100mM battery hinders the diffusion of unreacted species towards the cathode current collector (i.e., Mo) upon discharging.

![Figure 3.12](image)

Figure 3.12 5th cycle charge-discharge voltage profiles of 100mM LiS₁₂ battery

Capacity loss due to coulombic inefficiency appears to be more prominent at higher concentrations of Li₂S₁₂. A polysulfide shuttle study reported by Mikhaylik and Akridge indicates that reduced sulfides do not fully oxidize to elemental sulfur upon charging.⁶⁶ In the study the authors state that instead, a polysulfide shuttle mechanism occurs, in which charged species from the sulfur cathode diffuse to the Li anode where they react parasitically to reform low-order polysulfides. So in the case of the 100mM Li₂S₁₂ battery, upon charging, the polysulfide shuttle mechanism appears to be preventing the complete charging of the reduced species to Li₂S₁₂, thus limiting the discharge capacity.
Figure 3.13  Areal capacity of 4mM (green squares) and 100mM (orange diamonds) Li$_2$S$_{12}$ batteries.

Although the discharge rates, with respect to sulfur mass, are the same (i.e., C/10), it is important to realize that areal current density in the 100mM battery is 31 times greater than in the 4mM battery. Since the geometry of each battery is planar (i.e., 2D batteries), the current density plays an important role in the utilization of sulfur capacity. Nevertheless, the 100mM battery produces areal discharge capacities as much as 28 times that of the 4mM battery, i.e., $0.812$ mA·h·cm$^{-2}$ compared to $0.029$ mA·h·cm$^{-2}$, at C/10 (Figure 3.13), clearly showing the benefit of increasing the lithium polysulfide concentration in the catholyte.
3.4.4 Lithium Polysulfide Stability

Lithium-sulfur battery systems are quite stable, with an estimated theoretical shelf life of at least 10 years at room temperature. Similarly, lithium polysulfide catholytes are very stable at low concentrations. The low dielectric constants of tetraglyme, reported in the literature between 7.8 and 5, and 1,3-dioxolane, 7.0, provide an environment in which polysulfide-solvent interactions are strong enough to keep Li₂S₁₂ dissolved in the catholyte at low concentrations.⁶⁷-⁷⁰ 4mM Li₂S₁₂ was stored for up to 16 months without any observable color change, precipitation, capacity loss, or change in redox behavior during cyclic voltammetry. On the other hand, when the concentration of Li₂S₁₂ is increased to 100mM, a very small amount of sulfur (and possibly Li₂S) precipitation is observed over time. Also, although the sulfur concentration of 100mM Li₂S₁₂ (i.e., 1.2M S) is a fraction of the maximum solubility (i.e., 10M S) reported in the literature by Rauh et al., 100mM appears to be very close to the solubility limit of the Li₂S₁₂ catholyte. For example, even a slight increase in the salt concentration (i.e., from 0.8M to 1.5M LiSO₃CF₃) results in the possible disproportionation of Li₂S₁₂ according to equation 3.14.⁶²

\[
\text{Li}_2\text{S}_{12} \rightarrow \text{Li}_2\text{S} + \left(\frac{7}{8}\right) \cdot \text{S}_8
\]  

\[ (3.14) \]

3.5 Summary

In this chapter, Li₂S₁₂ catholytes were synthesized and characterized using CV and GCPL electrochemical techniques. Cyclic voltammograms of dilute catholyte solutions show that the redox of lithium polysulfides involves electrochemically irreversible processes which are diffusion-controlled. Batteries were fabricated using Li₂S₁₂ liquid cathodes and cycled via GCPL technique, demonstrating chemical reversibility. The performance of each battery is summarized in Table 3.5. The enhancement in cell capacity is apparent with the evolution of battery design and the increase in
sulfur concentration, giving a good platform for the fabrication and testing of high capacity lithium polysulfide batteries.

Table 3.5 Summary of Li$_2$S$_{12}$ battery evolution

<table>
<thead>
<tr>
<th>Battery</th>
<th>Li$<em>2$S$</em>{12}$ Concentration</th>
<th>Mo – Li Separation (µm)</th>
<th>Catholyte Volume (µL)</th>
<th>Discharge Capacity</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Generation</td>
<td>4mM</td>
<td>~5000</td>
<td>500</td>
<td>465</td>
<td>490</td>
</tr>
<tr>
<td>Sealed</td>
<td>4mM</td>
<td>450</td>
<td>40</td>
<td>26</td>
<td>418</td>
</tr>
<tr>
<td>Sealed</td>
<td>100mM</td>
<td>570</td>
<td>51</td>
<td>488</td>
<td>250</td>
</tr>
</tbody>
</table>
Chapter 4 - High Capacity Liquid Cathodes

4.1 Motivation

High areal capacity electrodes are crucial in making a desirable microbattery. Therefore, it is necessary to increase the amount of sulfur in the catholyte. However, in any given solvent, lithium polysulfide solubility depends on the length of the polysulfide chains. This is apparent in the Li₂S₁₂ system, in which attempts of obtaining concentrations higher than 100mM were unsuccessful due to lithium polysulfide disproportionation.

Table 4.1 Theoretical capacity of 50 mL of various lithium polysulfides

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Compositional Range</th>
<th>Theoretical Capacity (mA h cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100mM</td>
<td>Li₂S₁₂ ⇌ Li₂S₃</td>
<td>0.89</td>
</tr>
<tr>
<td>100mM</td>
<td>Li₂S₅ → Li₂S₁₂ ⇌ Li₂S₃</td>
<td>0.45</td>
</tr>
<tr>
<td>500mM</td>
<td>Li₂S₆ → Li₂S₁₂ ⇌ Li₂S₃</td>
<td>2.2</td>
</tr>
<tr>
<td>1M</td>
<td>Li₂S₆ → Li₂S₁₂ ⇌ Li₂S₃</td>
<td>4.5</td>
</tr>
<tr>
<td>1.5M</td>
<td>Li₂S₆ → Li₂S₁₂ ⇌ Li₂S₃</td>
<td>6.7</td>
</tr>
</tbody>
</table>

In this chapter, an alternative approach is used to increase the sulfur content of the catholyte. The strategy is to synthesize a low order polysulfide, i.e. Li₂S₆, which should be more resistant to disproportionation than Li₂S₁₂ catholytes. The capacity would be significantly less if the catholyte were to be cycled between Li₂S₆ and Li₂S₃. However, by charging the Li₂S₆ to Li₂S₁₂ and then cycling between Li₂S₁₂ and Li₂S₃, the capacity is only slightly less. Any sulfur precipitation during charging is not a concern, since precipitation should occur at the cathode current collector and should be reduced upon discharging. Ultimately, larger quantities of sulfur should dissolve in the catholyte in the form of Li₂S₆ with capacity benefits of which are clear in Table 4.1. For
example, the theoretical capacity of 50 μL of 1.5M Li₂S₆ is 6.7 mA·h·cm⁻² when cycled between Li₂S₁₂ and Li₂S₃.

4.2 Experimental

4.2.1 Chemicals

Lithium sulfide (Li₂S), 99.9% (12839, Alfa Aesar), and anhydrous lithium nitrate (LiNO₃), 99.999% (44456, Alfa Aesar), powders were used as received. Sulfur, 99.98% (414980, Sigma-Aldrich), and lithium trifluoromethanesulfonate (or lithium triflate; LiSO₃CF₃), 99.995% (481548, Sigma-Aldrich), powders were dried separately on a Schlenk line by purging with argon three times and then raising the temperature to 120°C for 6 hours under vacuum. Inhibitor-free anhydrous tetrahydrofuran (THF), ≥99.9% (401757, Sigma-Aldrich), anhydrous 1,3-dioxolane (DXL) with ~75 ppm butylated hydroxytoluene as inhibitor, 99.8% (271020, Sigma-Aldrich), and anhydrous methyl acetate (MA), 99.5% (296996, Sigma-Aldrich), were used as received.

Tetraethylene glycol dimethyl ether (TG), 99% (172405, Sigma-Aldrich), was dried on a Schlenk line by purging with argon three times and then raising the temperature to 105°C for 4 hours under vacuum. 4Å molecular sieves (208604, Sigma-Aldrich) were dried on a Schlenk line by purging with argon three times and then raising the temperature to 225°C for 24 hours. After placement into the glovebox, the TG was run through a column filled with the dry molecular sieves and collected in a dry amber jar at a rate of two drops per second.
4.2.2 Synthesis of Li$_2$S$_6$

4.2.2.1 Li$_2$S$_6$ Catholyte

Li$_2$S$_6$ was synthesized in an argon filled glovebox according to the scheme shown in Figure 4.1. THF is added to lithium sulfide and sulfur powders, at a molar ratio of 1:5::Li$_2$S:S, in a glass vial and stirred at 55°C. Once the powders have reacted, TG is added. The THF is then extracted from the solution by evaporating under vacuum, while heating at 85°C. The remaining liquid is a viscous liquid cathode.

In a separate glass vial, lithium triflate, the electrolyte salt, is added to DXL and stirred for several hours. It should be noted that all liquid cathodes consist of 0.8M lithium triflate salt and a TG:DXL ratio of 30:70 by volume, unless otherwise noted. Once dissolved, the electrolyte solution is added to the lithium polysulfide. This final solution is the liquid cathode, or catholyte.

![Figure 4.1. Synthesis of lithium polysulfide (Li$_2$S$_6$) liquid cathode. Tetrahydrofuran (THF) is added to lithium sulfide (Li$_2$S) and sulfur in a glass jar. (1) Tetruglyme (TG) is added to the Li$_2$S$_6$ solution and (2) THF is removed at 85°C under vacuum. In a separate glass vial, lithium triflate, along with any other additives (3) is dissolved in 1,3-dioxolane (DXL). The two solutions are combined forming the Li$_2$S$_6$ liquid cathode, or catholyte.](image-url)
4.2.2 **Li$_2$S$_6$ Catholyte with additive**

Li$_2$S$_6$ catholytes were also synthesized with performance-enhancing additives. The additive(s), lithium nitrate (as 0.4M LiNO$_3$) and/or a combination of nitrate and MA, are added into the electrolyte salt/DXL solution (step 3 in Figure 4.1). After the additives dissolve, the electrolyte solution is combined with the Li$_2$S$_6$/TG solution to form the catholyte.

4.2.3 **Measurements**

Electrochemical measurements were recorded through EC-Lab software using a VMP3 Multi Potentiostat by Bio-Logic SA. Galvanostatic Cycling with Potential Limitation (GCPL) experiments were carried out in an argon-filled glovebox on two-electrode battery cells, in which the molybdenum rod was the working electrode and the counter and reference wires from the potentiostat were both connected to the lithium-deposited nickel rod. All batteries had a liquid cathode volume loading between 26–45 μL and were cycled between 2.8V and 1.8V at room temperature, unless otherwise noted. All batteries had a footprint area of 0.899 cm$^{-2}$. All battery capacity and energy density values, which are normalized by mass, are given in terms of grams of sulfur.

Overpotential, $\eta$, is calculated using the charge-discharge curves obtained from GCPL. Figure 4.2 shows a hypothetical plot of a Li–S battery being cycled galvanostatically, beginning with a discharge (A $\rightarrow$ B) and ending with a charge (B $\rightarrow$ C), where the capacity at A and B are 0% and 100%, respectively, for each cycle. The first overpotential that is considered is at the high voltage plateau and is calculated according to

$$\eta_H = V_C - V_{D,H} \quad (4.1)$$
where $V_{D,H}$ is the potential of the high voltage plateau from the discharge (red curve) and $V_c$ is potential of the charge (blue curve) at the corresponding capacity. Overpotentials are also considered at the low voltage plateau in the charged ($\eta_c$) and discharged ($\eta_d$) states. In the absence of the high voltage plateau, the overpotential at the charged state, $\eta_{c,L}$, is given by

$$\eta_{c,L} = V_c - V_{D,L}$$  \hspace{1cm} (4.2)$$

where $V_{c,L}$ and $V_{D,L}$ are the potentials of the charge and discharge profiles, respectively, at $Q_L$. The overpotential of the discharged battery, $\eta_{d,L}$, is given by

$$\eta_{d,L} = V_{c,L,0.95} - V_{D,L,0.95}$$  \hspace{1cm} (4.3)$$

where $V_{c,L,0.95}$ is potential of the charge (blue curve) taken at $Q = 95\%$ ($Q_{0.95}$) and $V_{D,L,0.95}$ is the potential of the low voltage plateau from the discharge (red curve) at $Q_{0.95}$.

Figure 4.2 Hypothetical charge-discharge voltage profiles of Li-S battery showing the relation between overpotential and the voltage plateaus. $\eta_H$ is the overpotential of the high voltage plateau. The overpotential of the battery at the charged state is $\eta_{c,L}$. $\eta_{d,L}$ is the overpotential at the discharged state, where the capacity at the end of discharge is defined as 100\% ($Q_{1.00}$) and $\eta_{d,L}$ is calculated at 95\% capacity ($Q_{0.95}$).
4.3 Results and Discussion

4.3.1 Effect of concentration on Li$_2$S$_6$ Batteries

4.3.1.1 100mM Li$_2$S$_6$ Battery

A 100mM Li$_2$S$_6$ battery was assembled according to the diagram shown in Figure 3.4, in which the thicknesses of the Li foil and PE spacer were 750 μm and 1.25mm, respectively (Figure 4.3). The catholyte volume was 45 μL, corresponding to 865 μg of sulfur, which in turn has a theoretical capacity of 362 μA·h when cycled between Li$_2$S$_{12}$ and Li$_2$S$_3$. Once the battery is assembled, the Li$_2$S$_6$ must first be charged to Li$_2$S$_{12}$, requiring ~121 μA·h. This is done galvanostatically by charging the battery at a current of 90 μA (100 μA·cm$^{-2}$) for approximately 1 hour and 21 minutes. The battery is then cycled using the GCPL technique.

![100mM Li$_2$S$_6$ Battery](image)

**Figure 4.3 Specifications of 100mM Li$_2$S$_6$ Battery**

Figure 4.4 shows the discharge profiles of the 100mM Li$_2$S$_6$ battery cycled 9 times at (a) 100 μA·cm$^{-2}$ (C/4), (b) 200 μA·cm$^{-2}$ (C/2), and (c) 500 μA·cm$^{-2}$ (1.24C). Below each graph are plots of the charge-discharge profiles of the 3rd cycle at a given current density. For example, the 3rd cycle at 100 μA·cm$^{-2}$ (cycle 3) is shown in Figure 4.4d, while the 3rd cycles at 200 μA·cm$^{-2}$ (cycle 12) and 500 μA·cm$^{-2}$ (cycle 21) are shown in Figure 4.4e and 4.4f, respectively.
Figure 4.4 Discharge profiles of 100mM Li$_2$S$_6$ battery at (a) 100 $\mu$A·cm$^{-2}$, (b) 200 $\mu$A·cm$^{-2}$, and (c) 500 $\mu$A·cm$^{-2}$. Charge (——) and discharge (—-—) profiles of the 3$^{rd}$ cycle at (d) 100 $\mu$A·cm$^{-2}$, (e) 200 $\mu$A·cm$^{-2}$, and (f) 500 $\mu$A·cm$^{-2}$ are shown below (a), (b), and (c), respectively.

One problem that is obvious with the 100mM Li$_2$S$_6$ battery is the capacity fading that is observed during the first 9 cycles. This is most likely due to the lack of charging caused by the polysulfide shuttling parasitic reactions with the lithium anode. According to the charge profile (Figure 4.4d), the battery should be fully charged because it is charged with the amount of charge equal to that of the theoretical capacity, i.e., the amount of charge is equal 418 mA·h·g$^{-1}$. However, by the 3$^{rd}$ cycle the battery discharges 252 mA·h·g$^{-1}$, which is only 60% of the theoretical capacity. By the 9$^{th}$ cycle, the discharge capacity and coulombic efficiency drop to 223 mA·h·g$^{-1}$ and 53%, respectively.
Figure 4.5 Capacity retention during discharging of 100mM Li$_2$S$_6$ battery at (♦) 100 μA·cm$^{-2}$ (C/4), (♦) 200 μA·cm$^{-2}$ (C/2), (♦) 500 μA·cm$^{-2}$ (1.24C), and (♦) 50 μA·cm$^{-2}$ (C/8).

Capacity fading ceases after the 10$^{th}$ cycle, however, the coulombic efficiency drops even further. At a current density of 200 μA·cm$^{-2}$ (Figure 4.4c) the discharge capacity is 171 mA·h·g$^{-1}$, which corresponds to a coulombic efficiency of 41%, while at 500 μA·cm$^{-2}$ (Figure 4.4f) the discharge capacity and coulombic efficiency are 142 mA·h·g$^{-1}$ and 34%, respectively. These low coulombic efficiencies indicate that the charge consumed by the polysulfide shuttle phenomenon could be as high as 66% at large discharge rates (i.e., 1.24C or 500 μA·cm$^{-2}$) and as low as 40% at lower current densities (i.e., 100 μA·cm$^{-2}$ or C/4).

Low voltage plateau overpotential is calculated using equations 4.2–4.3. When cycled at 100 μA·cm$^{-2}$ (Figure 4.4d), $\eta_{D,L}$ and $\eta_{C,L}$ are 335mV and 325mV, respectively. In other words, after discharging, when the battery is for all intents and purposes dead, the overpotential, $\eta_{D,L}$, is approximately 335mV, while towards the end of charging the overpotential for the low voltage
plateau drops to about 325mV. This drop in overpotential suggests that the internal resistance of the battery is lower at the charged state. At 200 \( \mu A \cdot cm^{-2} \) the overpotential increases from 380mV at the start of charging to 400mV towards the end of the charge. At 500 \( \mu A \cdot cm^{-2} \), \( \eta_{D,L} \) is 690mV, while \( \eta_{C,L} \) is 525mV. In the final cycles, when the current density is lowered to 50 \( \mu A \cdot cm^{-2} \), the overpotential decreases to \( \eta_{D,L} = 373mV \) and \( \eta_{C,L} = 340mV \). In general, the overpotential is larger at the start of charging and then decreases as the battery is charged, indicating that lithium polysulfide batteries have larger internal resistances when they are discharged.

![Figure 4.6 Discharge profiles of 100mM Li\(_2\)S\(_6\) battery taken from the 3\(^{rd}\) cycle at (▬) 100 \( \mu A \cdot cm^{-2} \) (C/4), (▬) 200 \( \mu A \cdot cm^{-2} \) (C/2), (▬) 500 \( \mu A \cdot cm^{-2} \) (1.24C), and (▬) 50 \( \mu A \cdot cm^{-2} \) (C/8).](image)

Figure 4.5 shows the cycling performance of the 100mM Li\(_2\)S\(_6\) battery. Capacity fading can be seen during the first 9 cycles during which the current density is 100 \( \mu A \cdot cm^{-2} \) (♦), with an initial discharge capacity of 331 m\( A \cdot h \cdot g^{-1} \) and a capacity of 223 m\( A \cdot h \cdot g^{-1} \) by cycle 9. At 200 \( \mu A \cdot cm^{-2} \) (♦) and 500 \( \mu A \cdot cm^{-2} \) (♦) the discharge capacity is steady at \( \sim 170 \) m\( A \cdot h \cdot g^{-1} \) and \( \sim 145 \) m\( A \cdot h \cdot g^{-1} \).
respectively. However, when the current density is lowered to 50 μA·cm$^{-2}$ ($\blacklozenge$) the discharge capacity is recovered and 418 mA·h·g$^{-1}$ is attained.

Another problem that the Li$_2$S$_6$ battery faces is the loss of the high voltage plateau when cycled at low current density (Figure 4.6). For example, while the overall capacity drops from $\sim 250$ mA·h·g$^{-1}$ to $\sim 170$ mA·h·g$^{-1}$ to $\sim 150$ mA·h·g$^{-1}$ when the current density is increased from 100 μA·cm$^{-2}$ (●) to 200 μA·cm$^{-2}$ (●) to 500 μA·cm$^{-2}$ (●), respectively, the high voltage plateau ($\sim 2.35V$) is preserved. However, when the current density is decreased to 50 μA·cm$^{-2}$ (●), the high plateau vanishes. This disappearance corresponds to a low charge state when the battery is charged at 50 μA·cm$^{-2}$.

Table 4.2 Discharge capacity of 100mM Li$_2$S$_6$ battery at various current densities

<table>
<thead>
<tr>
<th>Current Density (μA·cm$^{-2}$)</th>
<th>Discharge Capacity (mA·h·g$^{-1}$)</th>
<th>$Q_{H}/Q_{total}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>142</td>
<td>36 25%</td>
</tr>
<tr>
<td>200</td>
<td>171</td>
<td>28 16%</td>
</tr>
<tr>
<td>100</td>
<td>252</td>
<td>30 12%</td>
</tr>
<tr>
<td>50</td>
<td>418</td>
<td>--- ---</td>
</tr>
</tbody>
</table>

According to Mikhaylik and Akridge, the charge-shuttle factor, $f_c$ can be represented with the following equation:

$$f_c = \frac{k_s \cdot Q_{H} \cdot [S_{total}]}{I_C}$$  \hspace{1cm} (4.1)

where $k_s$ is the shuttle constant, $Q_{H}$ is the sulfur specific capacity related to the high voltage plateau, $[S_{total}]$ is the total sulfur concentration, and $I_C$ is the charge current. When the shuttle factor is greater than unity (i.e., at $k_s \cdot Q_{H} \cdot [S_{total}]/I_C > 1$) the cell never reaches complete charge and shows voltage leveling upon charging. As the shuttle factor approaches unity (i.e., by increasing $I_C$), there is a
slight increase in the slope of the high voltage plateau during charging. This appears to be the case with the 100mM Li₂S₆ battery, as can be seen in Table 4.2. As the Li₂S₆ battery is cycled from 100 μA·cm⁻² (Figure 4.4d) to 500 μA·cm⁻² (Figure 4.4f), the slope of the voltage plateau slightly increases during charging, indicating that although greater than unity, the shuttle factor is decreasing. Therefore, when discharged at 500 μA·cm⁻², the capacity from the high voltage plateau (Qₜₜ) accounts for 25% of the total discharge capacity (Qₐₜₜ). At 200 μA·cm⁻² and 100 μA·cm⁻², the fraction of Qₜₜ/Qₐₜₜ drops to 16% and 12%, respectively. Thus, the loss of Qₜₜ at 50 μA·cm⁻² appears to be caused largely by the polysulfide shuttle phenomenon.

### 4.3.1.2 500mM Li₂S₆ Battery

![500mM Li₂S₆ Battery Diagram](image)

**Figure 4.7 Specifications of 500mM Li₂S₆ Battery**

A 500mM Li₂S₆ battery was assembled according the diagram shown in Figure 3.4, in which the thicknesses of the Li foil and PE were identical to that of the 100mM Li₂S₆ battery in the previous section. The specifications of this battery are shown in Figure 4.7. The mass loading is 4.32 mg of sulfur, which in turn has a theoretical capacity of 1.81 mA·h when cycled between Li₂S₁₂ and Li₂S₃. Once the battery is assembled, the Li₂S₆ is charged to Li₂S₁₂, which requires ~603 μA·h. Thus, the battery is galvanostatically charged at a current of 90 μA (100 μA·cm⁻²) for approximately 6 hours and 42 minutes. The battery is then cycled using the GCPL technique.
Figure 4.8 Discharge profiles of 500mM Li$_2$S$_6$ battery cycled at (a) 100 $\mu$A·cm$^{-2}$, (b) 200 $\mu$A·cm$^{-2}$, (c) 500 $\mu$A·cm$^{-2}$, and (d) 1 mA·cm$^{-2}$. Charge (—) and discharge (―) profiles of the 3$^{rd}$ cycle at (e) 100 $\mu$A·cm$^{-2}$, (f) 200 $\mu$A·cm$^{-2}$, and (g) 500 $\mu$A·cm$^{-2}$ and the 9$^{th}$ cycle at (h) 1 mA·cm$^{-2}$ are shown to the right of (a), (b), (c), and (d), respectively.
Discharge profiles of the 500mM Li$_2$S$_6$ battery can be seen in Figure 4.8. This battery was cycled at (a) 100 μA·cm$^{-2}$ (C/20) for 3 cycles, (b) 200 μA·cm$^{-2}$ (C/10) for 6 cycles, (c) 500 μA·cm$^{-2}$ (C/4) for 9 cycles, and (d) 1 mA·cm$^{-2}$ (C/2) for 9 cycles. Cycling performance is shown in Figure 4.9. Aside from the first cycle, the battery does not exhibit capacity fading trends at any given discharge current density. For example, at 100 μA·cm$^{-2}$ (●), the discharge capacity at the 3rd cycle is slightly higher than that of the 2nd cycle. Even at a current density as high as 1 mA·cm$^{-2}$ (▲), capacity fading is not observed.

![Figure 4.9](image)

Figure 4.9 Capacity retention during discharging of 500mM Li$_2$S$_6$ battery at (●) 100 μA·cm$^{-2}$ (C/20), (▲) 200 μA·cm$^{-2}$ (C/10), (▲) 500 μA·cm$^{-2}$ (C/4), and (▲) 1 mA·cm$^{-2}$ (C/2).

One advantage in increasing the polysulfide concentration appears to be the slight drop in ohmic polarization at higher discharge rates. At 100 μA·cm$^{-2}$ (Figure 4.8e) the overpotential of the low voltage plateau at 5% charge, $\eta_{D,1}$, is 395mV (i.e., at the start of charging). As charging continues, the low voltage plateau overpotential, $\eta_{C,1}$, drops to 390mV (i.e., at $Q = 150$mA·h·g$^{-1}$).
This is slightly larger when compared to the $\eta_{D,L}$ and $\eta_{C,L}$ of 335mV and 325mV, respectively, in the 100mM battery. Similarly, at 200 $\mu$A·cm$^{-2}$ (Figure 4.8f), $\eta_{D,L}$ and $\eta_{C,L}$ are 440mV and 420mV, compared to 380mV and 400mV, respectively. However, at 500 $\mu$A·cm$^{-2}$ (Figure 4.8g) $\eta_{D,L}$ is 650mV, which is much lower than the 690mV overpotential that the 100mM battery exhibits when cycled at the same current density. At 1 mA·cm$^{-2}$ (Figure 4.8h), $\eta_{L,D}$ is 720mV, which close to the overpotential of the 100mM battery cycled at half the current density.

![Graph](image)

**Figure 4.10** Discharge profiles of 500mM Li$_2$S$_6$ battery taken from the 3rd cycle at (▬) 100 $\mu$A·cm$^{-2}$ (C/20), (▬) 200 $\mu$A·cm$^{-2}$ (C/10), and (▬) 500 $\mu$A·cm$^{-2}$ (C/4), and from the 9th cycle at (▬) 1 mA·cm$^{-2}$ (C/2).

Another advantage of increasing the concentration of the catholyte is the gain in discharge capacity of the high voltage plateau, $Q_{H}$, which can be seen in Figure 4.10. The high voltage plateau does not seem to appear until the battery is cycled at 500 $\mu$A·cm$^{-2}$, accounting for 42% of the total discharge capacity, $Q_{total}$ (Table 4.3). Interestingly, at 1 mA·cm$^{-2}$ the high voltage plateau seems
unaffected (i.e., $Q_{\text{f}}$ at 500 $\mu$A·cm$^{-2}$ and 1 mA·cm$^{-2}$, are 64 and 60 mA·h·g$^{-1}$, respectively), resulting in a $Q_{\text{f}}/Q_{\text{total}}$ of 65%. The high voltage plateau capacity gain can be explained by the shape of the charge profiles in Figures 4.8g and 4.8h, which indicate that the polysulfide shuttle factor appears to be $< 1$ at 500 $\mu$A·cm$^{-2}$ and 1 mA·cm$^{-2}$, respectively, for 500mM $\text{Li}_2\text{S}_6$ in this battery cell geometry (Figure 4.7).

Table 4.3  Discharge capacity of 500mM $\text{Li}_2\text{S}_6$ battery at various current densities

<table>
<thead>
<tr>
<th>Current Density ($\mu$A·cm$^{-2}$)</th>
<th>Discharge Capacity (mA h·g$^{-1}$) $Q_{\text{f}}$</th>
<th>$Q_{\text{f}}/Q_{\text{total}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>98</td>
<td>64</td>
</tr>
<tr>
<td>500</td>
<td>143</td>
<td>60</td>
</tr>
<tr>
<td>200</td>
<td>144</td>
<td>---</td>
</tr>
<tr>
<td>100</td>
<td>358</td>
<td>---</td>
</tr>
</tbody>
</table>

4.3.1.3  1.5M $\text{Li}_2\text{S}_6$ Battery

![1.5M $\text{Li}_2\text{S}_6$ Battery](image)

**Figure 4.11** Specifications of 1.5M $\text{Li}_2\text{S}_6$ Battery

- $V = 40 \mu$L
- $m_s = 11.7 \text{ mg Sulfur}$
- $C = 4.88 \text{ mAh}$  $\text{Li}_2\text{S}_{12} \rightarrow \text{Li}_2\text{S}_3$
- $C = 3.25 \text{ mAh}$  $\text{Li}_2\text{S}_6 \rightarrow \text{Li}_2\text{S}_3$
Figure 4.12  Discharge profiles of 1.5M Li$_2$S$_6$ battery at (a) 500 $\mu$A·cm$^{-2}$ and (b) 200 $\mu$A·cm$^{-2}$. Charge (▬) and discharge (▬) profiles of the 3$^{rd}$ cycle at (c) 500 $\mu$A·cm$^{-2}$ and (d) 200 $\mu$A·cm$^{-2}$ are shown below (a) and (b), respectively.

A 1.5M Li$_2$S$_6$ battery was assembled according the diagram shown in Figure 3.4, in which the specifications are shown in Figure 4.11. In this battery, the mass loading is 11.7 mg of sulfur, which in turn has a theoretical capacity of 4.88 mA·h when cycled between Li$_2$S$_{12}$ and Li$_2$S$_3$, requiring 1.63 mA·h to charge from Li$_2$S$_6$ to Li$_2$S$_{12}$. After assembly, the potentiostat was programmed to charge the battery at 1 mA·cm$^{-2}$ for 1 hour and 47 minutes, then cycle the battery 3 times at the following current densities: 1 mA·cm$^{-2}$ (cycles 1–3), 500 $\mu$A·cm$^{-2}$ (cycles 4–6), 200 $\mu$A·cm$^{-2}$ (cycles
7–9), 1 mA·cm$^{-2}$ (cycles 10–12), 500 μA·cm$^{-2}$ (cycles 13–15), and 200 μA·cm$^{-2}$ (cycles 16–18). However, this battery could neither charge nor discharge at 1 mA·cm$^{-2}$ and, thus, was unable to charge to Li$_2$S$_{12}$. As a result, the 1.5M Li$_2$S$_6$ battery could only be cycled between Li$_2$S$_6$ and Li$_2$S$_3$, in which the theoretical capacity is 3.25 mA·h.

![Figure 4.13](image)

**Figure 4.13** Capacity retention during discharging of 1.5M Li$_2$S$_6$ battery at (●) 1 mA·cm$^{-2}$ (C/3), (●) 500 μA·cm$^{-2}$ (C/7), and (●) 200 μA·cm$^{-2}$ (C/16).

Discharge profiles of the 1.5M Li$_2$S$_6$ battery can be seen in Figure 4.12. The battery shows significant capacity fading when cycled at 500 μA·cm$^{-2}$ (a), discharging about 48 minutes on the first cycle (cycle 4) and 25 minutes on the last cycle (cycle 15). Similar behavior is observed at 200 μA·cm$^{-2}$ (b). On the first cycle (cycle 7) the battery discharges for about 6 hours, but the discharge time drops to 4 hours by the final cycle (cycle 18). The overpotential at 500 μA·cm$^{-2}$,
which is obtained from Figure 4.12c, is 790mV and 580mV for $\eta_{DL}$ and $\eta_H$, respectively. At 200 $\mu$A·cm$^{-2}$ (Figure 4.12d), $\eta_{DL}$ and $\eta_H$ are 640mV and 320mV for the high voltage plateau.

Cycling performance of the 1.5M battery is shown in Figure 4.13. The specific capacity is much lower than the theoretical 279 mA·h·g$^{-1}$ (i.e., when cycled from Li$_2$S$_6$ → Li$_2$S$_3$). At 500 $\mu$A·cm$^{-2}$ the capacity drops by approximately 20%, from 31 to 25 mA·h·g$^{-1}$, within three cycles. When the current density is reduced to 200 $\mu$A·cm$^{-2}$ the capacity increases to 91 mA·h·g$^{-1}$, but rapidly decreases to 60 mA·h·g$^{-1}$ within three cycles. After repeating the scans at 500 $\mu$A·cm$^{-2}$ and 200 $\mu$A·cm$^{-2}$ the capacity stabilizes at approximately 16 and 62 mA·h·g$^{-1}$, respectively.

4.3.1.4 Li$_2$S$_6$ Battery Performance

Table 4.4 Performance summary of Li$_2$S$_6$ batteries

<table>
<thead>
<tr>
<th>Current Density</th>
<th>$Q_{DL}$ (mA h g$^{-1}$)</th>
<th>$Q_{total}$ (mA h g$^{-1}$)</th>
<th>$\eta_{DL}$ (mV)</th>
<th>$\eta_H$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100mM 500mM 1.5M</td>
<td>100mM 500mM 1.5M</td>
<td>100mM 500mM 1.5M</td>
<td>100mM 500mM 1.5M</td>
</tr>
<tr>
<td>50 $\mu$A cm$^{-2}$</td>
<td>--- --- ---</td>
<td>418 --- ---</td>
<td>373 --- ---</td>
<td>200 --- ---</td>
</tr>
<tr>
<td>100 $\mu$A cm$^{-2}$</td>
<td>30 --- ---</td>
<td>252 358 ---</td>
<td>335 395 ---</td>
<td>100 --- ---</td>
</tr>
<tr>
<td>200 $\mu$A cm$^{-2}$</td>
<td>28 --- 31</td>
<td>171 144 60</td>
<td>380 440 640</td>
<td>130 --- 330</td>
</tr>
<tr>
<td>500 $\mu$A cm$^{-2}$</td>
<td>36 60 22</td>
<td>142 143 25</td>
<td>690 650 790</td>
<td>220 350 570</td>
</tr>
<tr>
<td>1 mA cm$^{-2}$</td>
<td>--- 64 ---</td>
<td>--- 98 ---</td>
<td>--- 720 ---</td>
<td>--- 400 &gt;1000</td>
</tr>
</tbody>
</table>

Li$_2$S$_6$ battery performance is summarized in Table 4.4. At low current densities, overpotential increases with increasing Li$_2$S$_6$ concentration. Interestingly, this is only the case at current densities up to 200 $\mu$A·cm$^{-2}$. For example, when comparing the overpotential of dead
batteries (i.e., $\eta_{D,L}$) cycled at 500 $\mu$A·cm$^{-2}$, $\eta_{D,L}$ is lowest in the 500mM battery. Even when cycled at 1 mA·cm$^{-2}$, $\eta_{D,L}$ for the 500mM battery is only 4% larger than that of the 100mM battery discharged at one half the current density. In the case of charged batteries, the high voltage plateau overpotential, $\eta_{H}$, increases with increasing concentration.

Overpotential is directly related to a battery’s internal resistance. Thus, an estimate of the internal resistance of the battery, or cell resistance ($R_{cell}$), can be calculated according to

$$ R_{cell} = \frac{\Delta V}{\Delta I} $$ (4.2)

where $\Delta V$ is the overpotential (in Volts) and $\Delta I$ is the difference in current (in Amperes) between the charge and discharge scans. For example, the internal resistance of a dead battery can be calculated using $\eta_{D,L}$ and the difference between the charge current, $I_C$, and discharge current, $I_D$, according to equation 4.3.

$$ R_{cell} = \frac{\eta_{D,L}}{I_C - I_D} $$ (4.3)

Figure 4.14   Cell resistance versus current density of 100mM (■), 500mM (▲), and 1.5M (●) Li$_2$S$_6$ batteries in the charged (a) and discharged (b) states.
$R_{\text{cell}}$ is plotted as a function of current density in Figure 4.14. Apparently, the resistance of the battery is less in the charged state (a) than in the discharged state (b), regardless of current density. Both states exhibit a drop in resistance as the current density is increased. At any given current density, charged batteries exhibit increasing resistance with increasing $Li_2S_6$ concentration, similar to dead batteries. However, there appears to be a crossover point, around 450 μA·cm$^{-2}$, where the resistance of the 500mM battery decreases beyond that of the 100mM battery as the current density is increased. This implies that there may be benefits in using the 500mM $Li_2S_6$ system, over 100mM and 1.5M systems, in high current applications.

The internal resistance of a battery is expressed by

$$R_{\text{cell}} = R_i + R_e + R_{IF}$$ (4.4)

where $R_i$, $R_e$, and $R_{IF}$ are the ionic, electronic, and interfacial resistance, respectively, in the cell. The dependence of internal resistance on $Li_2S_6$ concentration is interesting because it is somewhat counterintuitive. For example, the sulfur concentration of the 100mM, 500mM, and 1.5M $Li_2S_6$ batteries are 0.6M, 3M, and 9M (wrt sulfur), respectively. According to Chang et al., the ionic conductivity of 0.5M LiSO$_3$CF$_3$ in TG/DXL (30/70 v/v) steadily increases from 1.5 to 4.3 mS·cm$^{-1}$ as the concentration of $Li_2S_8$ is increased from 0 to 4.5M (wrt sulfur), respectively. Beyond 4.5M S, the ionic conductivity steadily decreases and at about 6.9M S the ionic conductivity drops to approximately 2.1 mS·cm$^{-1}$. Based on these findings, the ionic conductivity, $\sigma_i$, of the $Li_2S_6$ batteries should behave in the following manner: ($R_{i,100mM} > R_{i,500mM}$) and ($R_{i,1.5M} > R_{i,500mM}$). However, $R_{cell}$ increases as follows: ($R_{cell,100mM} < R_{cell,500mM} < R_{cell,1.5M}$). Since $R_i$ should be negligible, because Mo and Li are metals, the increase in $R_{cell}$ with increasing concentration is most likely caused by the increase in interfacial resistance as the sulfur concentration increases. For example, a thicker layer of insulating products could form on the Mo and Li when cycling batteries with higher concentrations.
Also, it is possible that sulfur concentration may play a role in the solid-electrolyte interphase (SEI) formation, in which case low concentration batteries could have a less resistive SEI layer.

Figure 4.15 Areal Capacity of (a) 100mM (squares) and 500mM (triangles) and (b) 1.5M (circles) Li2S6 batteries cycled at 100 μA·cm⁻² (black), 200 μA·cm⁻² (red), 500 μA·cm⁻² (blue), and 1 mA·cm⁻² (green).

Figure 4.15a shows a comparison between the areal discharge capacities obtained from the 100mM (squares) and 500mM (triangles) Li2S6 batteries cycled at 100 μA·cm⁻² (black), 200 μA·cm⁻² (red), and 500 μA·cm⁻² (blue). The 500mM battery shows superior performance over the 100mM battery. At a current density of 100 μA·cm⁻², the 500mM battery yields an areal capacity of 2 mA·h·cm⁻² on the first discharge, which is approximately 6.7 times the capacity of the 100mM battery. By the 3rd cycle, the areal capacity of the 500mM battery drops to 1.72 mA·h·cm⁻², yet exhibits 7.1 times the capacity of the 100mM battery. However, at 200 μA·cm⁻² and 500 μA·cm⁻² the capacity of the 500mM battery drops to only 3.8 times and 3.1 times, respectively, the capacity of the 100mM battery. When the 500mM battery is cycled at 1 mA·cm⁻², the areal capacity approaches that which is obtained at 500 μA·cm⁻², exhibiting double the capacity of the 100mM battery cycled at one tenth the current density.
Battery performance can be realized by observing the coulombic efficiency, \( \varepsilon \), which is defined as

\[
\varepsilon = \frac{Q_d}{Q_c} \times 100
\]

(4.5)

where \( Q_d \) is the capacity (or charge) obtained during discharging and \( Q_c \) is the capacity (or charge) consumed during charging. Figure 4.16 shows the coulombic efficiency of the (a) 100mM, (b) 500mM, and (c) 1.5M Li\textsubscript{2}S\textsubscript{6} batteries. In the 100mM battery, the coulombic efficiency at 100 \( \mu \text{A}\cdot\text{cm}^{-2} \) is quite low (i.e., 54\% < \( \varepsilon \) < 64\%) and decreases with increasing current density. On the other hand, the 500mM battery is much more efficient when cycling at same current density (i.e., 85\% < \( \varepsilon \) < 100\%). At 200 \( \mu \text{A}\cdot\text{cm}^{-2} \), the coulombic efficiency drops to about 35\%. Intriguingly, the coulombic efficiency increases when the current density is increased beyond 200 \( \mu \text{A}\cdot\text{cm}^{-2} \). For example, at 500 \( \mu \text{A}\cdot\text{cm}^{-2} \) and 1 mA\cdot\text{cm}^{-2}, the coulombic efficiency increases to about 48\% and 63\%, respectively. These results are concurrent with the internal resistance (Figure 4.14b), which show that \( R_{\text{cell}} \) of the 500mM battery decreases beyond \( R_{\text{cell}} \) of the 100mM when cycled above 200 \( \mu \text{A}\cdot\text{cm}^{-2} \). The combination of larger \( \sigma \) and lower \( R_{\text{cell}} \) and \( f_c \) make the 500mM battery more efficient when cycled at higher current densities.
Compared to the 500mM battery, the performance of the 1.5M battery (Figure 4.15b) is far from impressive, with an areal capacity of only \(\sim 0.8 \text{ mA}\cdot\text{h} \cdot \text{cm}^{-2}\) at 200 \(\mu\text{A}\cdot\text{cm}^{-2}\). This battery exhibits poor rate capabilities, due to its high internal resistance (Figure 4.14). At 500 \(\mu\text{A}\cdot\text{cm}^{-2}\), the discharge capacity drops to 0.2 \(\text{mA}\cdot\text{h} \cdot \text{cm}^{-2}\), while at 1 \(\text{mA}\cdot\text{cm}^{-2}\) the overpotential is too large for the battery to cycle. The coulombic efficiency (Figure 4.16c) is higher than that of the lower concentration batteries, suggesting that capacity limitations in the 1.5M battery are mostly a result of large concentration polarization resulting from relatively high viscosity of 1.5M Li\(_2\)S\(_6\).

### 4.3.2 Polysulfide Shuttle Suppression

#### 4.3.2.1 State-of-charge

One way to increase cycling efficiency is to suppress the parasitic reactions that take place via the polysulfide shuttle phenomenon during battery charging. The use of LiNO\(_3\) as an electrolyte additive has been found to prevent the polysulfide shuttle mechanism in solid-state lithium–sulfur batteries.\(^{73,74}\) It turns out that LiNO\(_3\) forms a protective SEI layer on the surface of the lithium anode, protecting the lithium from reacting with polysulfides.\(^{74-76}\) As a result, electric charge is not wasted during charging and the state-of-charge (SOC) of the battery is increased.

A 100mM Li\(_2\)S\(_6\) battery, containing 0.4M LiNO\(_3\) additive, was assembled according the diagram shown in Figure 3.4, in which the thicknesses of the Li foil and PE spacer were 800 \(\mu\text{m}\) and 1.15mm, respectively (Figure 4.17). The catholyte volume was 31 \(\mu\text{L}\), correlating to 605 \(\mu\text{g}\) of sulfur, which in turn has a theoretical capacity of 253 \(\mu\text{A}\cdot\text{h}\) when cycled between Li\(_2\)S\(_{12}\) and Li\(_2\)S\(_6\). Once the battery is assembled, the Li\(_2\)S\(_6\) must first be charged to Li\(_2\)S\(_{12}\), requiring \(\sim 84.3 \mu\text{A}\cdot\text{h}\). This
is done galvanostatically by charging the battery at 500 μA for approximately 10 minutes. The battery is then cycled using the GCPL technique.

**100mM Li$_2$S$_6$ (LiNO$_3$ additive) Battery**

![Diagram of battery configuration]

- $V = 31 \mu$L
- $m_s = 605 \mu$g Sulfur
- $C = 253 \mu$Ah

Figure 4.17 Specifications of 100mM Li$_2$S$_6$ battery with LiNO$_3$ additive

Figure 4.18 shows the discharge profiles of the 100mM Li$_2$S$_6$ battery with LiNO$_3$ additive. This battery was cycled 3 times at (a) 100 μA·cm$^{-2}$ (C/2.8), (b) 200 μA·cm$^{-2}$ (C/1.4), (c) 500 μA·cm$^{-2}$ (1.8C), (d) 2 mA·cm$^{-2}$ (7.1C), and (e) 50 μA·cm$^{-2}$ (C/5.6). To the right of each graph are plots of the charge-discharge profiles of the 3$^{rd}$ cycle. For example, the 3$^{rd}$ cycle at 100 μA·cm$^{-2}$ (cycle 3) is shown in f, while the profiles of the 3$^{rd}$ cycle at 200 μA·cm$^{-2}$ (cycle 6), 500 μA·cm$^{-2}$ (cycle 9), 2 mA·cm$^{-2}$ (cycle 12), and 50 μA·cm$^{-2}$ (cycle 15) are shown in g, h, i, and j, respectively.

Suppression of the polysulfide shuttle mechanism with the addition of LiNO$_3$ is apparent in Figure 4.19. For the first 6 cycles, the discharge capacity is 100% the theoretical (i.e., 418 mA·h·g$^{-1}$) when cycled at 100 μA·cm$^{-2}$ (▲) and 200 μA·cm$^{-2}$(▲). At 500 μA·cm$^{-2}$ (▲) the capacity drops slightly, to about 408 mA·h·g$^{-1}$, while at 2 mA·cm$^{-2}$ (▲) it drops significantly to about 60 mA·h·g$^{-1}$. However, once the current density is decreased to 50 μA·cm$^{-2}$ (▲), the discharge capacity is completely recovered.
Figure 4.18 Voltage profiles of 100mM Li$_2$S$_6$ battery with nitrate (as 0.4M LiNO$_3$) additive.
The coulombic efficiency (Figure 4.19) shows that 100% of the charge capacity is utilized when the battery is discharged at 100 \( \mu \text{A} \cdot \text{cm}^{-2} \) (○) and 200 \( \mu \text{A} \cdot \text{cm}^{-2} \) (●). At 500 \( \mu \text{A} \cdot \text{cm}^{-2} \) (●) the coulombic efficiency drops slightly (i.e., 96% \( \leq \varepsilon \leq 98\% \)). The coulombic efficiency for the cycles at 2 \( \text{mA} \cdot \text{cm}^{-2} \) is not shown because the discharge capacities were slightly larger than the charge capacities (i.e., \( \varepsilon > 100\% \)). This is common when high current cycling is preceded by a low-rate charge. Nevertheless, the large coulombic efficiency at 2 \( \text{mA} \cdot \text{cm}^{-2} \) indicates that the capacity loss at high current densities is due to excessive concentration polarization. In the final cycles, when the current density is decreased to 50 \( \mu \text{A} \cdot \text{cm}^{-2} \) (●), the coulombic efficiency is 100%.

Figure 4.19 Capacity retention (triangles) during discharging of 100mM Li\textsubscript{2}S\textsubscript{6} battery with LiNO\textsubscript{3} additive at 100 \( \mu \text{A} \cdot \text{cm}^{-2} \) (▲), 200 \( \mu \text{A} \cdot \text{cm}^{-2} \) (▲), 500 \( \mu \text{A} \cdot \text{cm}^{-2} \) (▲), 2 \( \text{mA} \cdot \text{cm}^{-2} \) (▲), and 50 \( \mu \text{A} \cdot \text{cm}^{-2} \) (▲). Coulombic efficiency (circles) is shown on the right vertical axis.
Battery performance is summarized in Table 4.5. Contrary to the additive-free 100mmM battery, the addition of LiNO$_3$ yields increases in capacity at the high voltage plateau ($Q_{H}$). Also, the ratio of $Q_{H}/Q_{total}$ is quite large (i.e., 57%) at the lowest current density, indicating that LiNO$_3$ is preventing polysulfide shuttling during charging. $Q_{H}/Q_{total}$ reaches a minimum value of 26% at 200 $\mu$A·cm$^{-2}$, and increases to 50% as the current density is increased to 2 mA·cm$^{-2}$. The large capacity observed in the high voltage plateau region corresponds to complete charging of Li$_2$S$_6$ to Li$_2$S$_{12}$.

Table 4.5 Highlights of 100mM Li$_2$S$_6$ Battery with LiNO$_3$ additive

<table>
<thead>
<tr>
<th>Current Density (µA·cm$^{-2}$)</th>
<th>Discharge Capacity (mA·h·g$_{S}^{-1}$)</th>
<th>$Q_{H}/Q_{total}$</th>
<th>$\eta_{DL}$ (mV)</th>
<th>$\eta_{H}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>60</td>
<td>50%</td>
<td>850</td>
<td>500</td>
</tr>
<tr>
<td>500</td>
<td>408</td>
<td>35%</td>
<td>640</td>
<td>180</td>
</tr>
<tr>
<td>200</td>
<td>418</td>
<td>26%</td>
<td>440</td>
<td>85</td>
</tr>
<tr>
<td>100</td>
<td>418</td>
<td>45%</td>
<td>300</td>
<td>35</td>
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<td>50</td>
<td>418</td>
<td>57%</td>
<td>285</td>
<td>22</td>
</tr>
</tbody>
</table>

Overpotential in the 100mM Li$_2$S$_6$ battery with LiNO$_3$ additive, which is taken from Figure 4.18 (f–j), is for the most part less than in the 100mM battery without any additive. For example, $\eta_{DL}$ at 50, 100, 200, and 500 $\mu$A·cm$^{-2}$ is 285, 300, 440, and 640mV, respectively, with LiNO$_3$, compared to 373, 335, 380, and 680mV without LiNO$_3$. In the charged state, $\eta_{H}$ at 50, 100, 200, and 500 $\mu$A·cm$^{-2}$ is 22, 35, 85, and 180mV with LiNO$_3$, compared to 200, 100, 130, and 220mV, respectively, without LiNO$_3$. 

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Cell resistance of the 100mM Li$_2$S$_6$ battery with (triangles) and without (squares) LiNO$_3$ is plotted versus current density in Figure 4.20, using the overpotential values listed in table 4.5. For the most part, $R_{\text{cell}}$ at the discharged state is smaller with LiNO$_3$ (▲) than without (■). At the charged state, $R_{\text{cell}}$ is much less with LiNO$_3$ (△) than without (□). For example, at 50 $\mu$A·cm$^{-2}$, $R_{\text{cell}}$ for the LiNO$_3$ and LiNO$_3$-free batteries are 220Ω and 2.3kΩ, respectively.

Figure 4.21 shows the discharge capacity (a) and energy density (b), with respect to sulfur mass, of 100mM Li$_2$S$_6$ batteries, with (▲) and without (■) LiNO$_3$. At low current density (i.e., 50 $\mu$A·cm$^{-2}$), the capacity of both batteries is 418 mA·h·g$^{-1}$, but the energy density is 21% larger in the battery with LiNO$_3$. As current density increases, both capacity and energy density are improved in the LiNO$_3$ battery. At 500 $\mu$A·cm$^{-2}$, the additive-free battery exhibits 35% the capacity and one-third the energy density of the battery with LiNO$_3$. 

Figure 4.20  Cell resistance versus current density of 100mM Li$_2$S$_6$ battery with (triangles) and without (squares) LiNO$_3$ in the charged (open) and discharged (filled) states.
4.3.2.2 Depth of discharge

Increases in capacity and energy with the addition of LiNO₃ indicate that the polysulfide shuttle mechanism is being suppressed during battery charging. This means that the amount of charge input is effectively increasing the SOC of the battery, i.e., increasing the polysulfide order to \( n = 12 \). However, another strategy to increase the amount of capacity obtained from the battery is to vary the depth of discharge (DOD). This can be done by allowing the reduction of lithium polysulfides to proceed beyond \( \text{Li}_2\text{S}_3 \), i.e., \( n < 3 \). For example, if the battery could be cycled between \( \text{Li}_2\text{S}_{12} \) and \( \text{Li}_2\text{S}_{2.26} \), then discharge capacity would be 600 mA·h·g⁻¹.

To demonstrate capacity gains by controlling the DOD of a 100mM \( \text{Li}_2\text{S}_6 \) with LiNO₃ additive, a battery was assembled in which the catholyte volume was 40 \( \mu \text{L} \) (i.e., 779 \( \mu \text{g} \) sulfur). Figure 4.22 shows the discharge profiles of the battery cycled at 100 \( \mu \text{A} \cdot \text{cm}^{-2} \) with various potential windows; the upper limit was 2.8V, while the lower limit was (a) 1.8V, (b) 1.7V, and (c) 1.6V.
Figure 4.22 Discharge profiles of 100mM Li$_2$S$_6$ battery with LiNO$_3$ additive cycled at 100 $\mu$A·cm$^{-2}$ with upper potential limit of 2.8V and lower potential limit of (a) 1.8V, (b) 1.7V, and (c) 1.6V.

Figure 4.23 Voltage profiles of 100mM Li$_2$S$_6$ battery with LiNO$_3$ additive taken from 3$^{rd}$ cycle with the following cutoff voltages: 1.8V (■), 1.7V ( ■), and 1.6V ( ■).
Although the discharge plots in Figure 4.22 show good reversibility (i.e., overlapping curves), the charge-discharge profiles at each potential window scan (Figure 4.23) indicate otherwise. The charge profiles of the 3<sup>rd</sup> cycle at 1.8V (▬), 1.7V (▬), and 1.6V (▬) cutoff potentials all overlap for the duration of the charge (i.e., 600 mA·h·g<sup>‒1</sup>). However, the discharge profiles do not overlap and the coulombic efficiency is less than unity.

Cycling performance can be seen in Figure 4.24. Both capacity (a) and energy density (b) fading are observed during cycling. During the first 6 cycles, when the low-potential cutoff is 1.8V, the capacity decreases from 593 to 537 mA·h·g<sup>‒1</sup>. Beyond 1.8V, the discharge capacity continues to drop until plateauing at about 530 mA·h·g<sup>‒1</sup>. Similarly, the energy density is 1282 mW·h·g<sup>‒1</sup> (with respect to sulfur mass) on the first cycle and plateaus at 1128 mW·h·g<sup>‒1</sup>, i.e., when the low-potential cutoff voltage is lowered below 1.8V.

![Figure 4.24](image_url)  

Figure 4.24  (a) Charge capacity (open squares) and discharge capacity (closed squares) and (b) energy density retention of 100mM Li<sub>2</sub>S<sub>6</sub> battery containing LiNO<sub>3</sub> additive cycled with 1.8V (■), 1.7 (■), and 1.6V (■) low potential cutoff.

Because of the amount of insoluble products, i.e., Li<sub>2</sub>S and Li<sub>2</sub>S<sub>2</sub>, associated with discharging beyond 418 mW·h·g<sup>‒1</sup>, the effect of charging current density on the oxidation of these byproducts
was tested. Figure 4.25a shows the charging capacity at 200 μA·cm\(^{-2}\) (○), 500 μA·cm\(^{-2}\) (▽), 1 mA·cm\(^{-2}\) (△), 300 μA·cm\(^{-2}\) (★), and 100 μA·cm\(^{-2}\) (►) of the 100mM Li\(_2\)S\(_6\) battery with LiNO\(_3\) additive, in which the discharge capacity was maintained throughout the experiment at 100 μA·cm\(^{-2}\) (squares). Above 200 μA·cm\(^{-2}\), the battery does not accept a full charge (i.e., \(Q_c < 600\) mA·h·g\(^{-1}\)) and the charge capacity decreases with increasing current density. On the other hand, the coulombic efficiency (Figure 4.25b) increases from 81% to 96% when the charging current is increased from 200 μA·cm\(^{-2}\) to 1 mA·cm\(^{-2}\). When the charging current is decreased to 100 μA·cm\(^{-2}\), the coulombic efficiency drops to 75%.

Since the discharge current is fixed at 100 μA·cm\(^{-2}\), the charging current must be limiting the discharge capacity. When charged at low current, both the charge and discharge capacities are high, but the coulombic efficiency is low. At high charging current, the efficiency is high, but large concentration polarization is resulting in a premature SOC, which limits the discharge capacity.
In Figure 4.25a, when the charging current density is lowered to the original 100 μA·cm⁻² (▷), the discharge capacity (◼) does not recover to ~537 mA·h·g⁻¹, but is just shy of 450 mA·h·g⁻¹. One explanation for this is that discharging beyond Li₂S₃ results in capacity fading due to the excessive precipitation of LiS and Li₂S₂ from the liquid cathode. Another explanation is that LiNO₃ could have been consumed during the potential cutoff tests during the first 20 cycles. It turns out that in solid-state lithium sulfur batteries, LiNO₃ is believed to undergo an irreversible reduction at 1.6V, on the carbon (cathode) surface, and that the reduction products unfavorably affect the capacity and reversibility of the battery.⁷⁷ This could also be the case in the liquid cathode, in which LiNO₃ was reduced when the low-potential cutoff was set to 1.6V.

Figure 4.26 shows the capacity retention of a 100mM Li₂S₆ battery with LiNO₃ additive cycled at 100 μA·cm⁻². The discharge capacity (◼) reaches a maximum of 573 mA·h·g⁻¹ on the third cycle.
cycle. Assuming a charged state of \( n = 12 \), i.e., \( \text{Li}_2\text{S}_{12} \) is the longest stable polysulfide, equation 3.12 becomes

\[
S_{12}^{2-} + \left( \frac{24}{D} - 2 \right) e^- \rightarrow \left( \frac{12}{D} \right) S_D^{2-}
\]

(4.6)

and the atomic capacity, in terms of electrons per sulfur atom, is given by equation 4.7.

\[
Q_{\text{atom}} = \frac{\left( \frac{24}{D} - 2 \right) e^-}{12 \cdot S_{\text{atom}}}
\]

(4.7)

Substituting 4.7 into 3.9 gives the polysulfide order at the discharged state, \( D \), according to

\[
D = 24 \cdot \left[ \left( \frac{12 \cdot S_{\text{atom}}}{e^-} \right) \left( \frac{Q_D}{\beta} \right) + 2 \right]^{-1}
\]

(4.8)

where \( Q_D \) is the discharge capacity in mA·h·g\(^{-1}\), and \( \beta = 835.85 \) mA·h·g\(^{-1}·S_{\text{atom}}·(e^-)^{-1} \). According to equation 4.8, \( D = 2.35 \) for the third discharge, indicating that the battery discharges to \( \text{Li}_2\text{S}_{2.35} \). After 12 cycles, the discharge capacity plateaus to approximately 510 mA·h·g\(^{-1}\), which corresponds to a liquid cathode in the \( \text{Li}_2\text{S}_{2.35} \) state.

Although discharge capacity values are impressive, capacity gains through the deepening of the DOD come at the expense of coulombic efficiency (\( \eta \)). For example, when the DOD is limited to \( \text{Li}_2\text{S}_3 \), the coulombic efficiency is 100\% when discharged at current densities up to 200 \( \mu \text{A}·\text{cm}^{-2} \) (Figure 4.19). When discharging to \( \text{Li}_2\text{S}_{2.33} \), however, the coulombic efficiency plateaus at approximately 85\% when discharged at 100 \( \mu \text{A}·\text{cm}^{-2} \) (Figure 4.26a). Since \( \text{LiNO}_3 \) has been shown to suppress the polysulfide shuttle mechanism, the coulombic inefficiency must be due to the resistive nature of the sulfide and disulfide precipitates at the current collector/catholyte interface; the resulting energy loss would be given off in the form of heat. X-ray photoelectron spectroscopy of the Mo surface would verify the presence of sulfur (i.e., S 2p\(_{3/2}\) binding energy of 163.9 eV) and/or lithium sulfide (i.e., S 2p\(_{3/2}\) binding energy of 162.1 eV).\(^{78}\)
Despite the drop in coulombic efficiency when discharged beyond Li$_2$S$_3$, the 100mM Li$_2$S$_6$ battery with LiNO$_3$ additive displays an impressive amount of energy storage and delivery. Figure 4.26b shows the energy density of the battery cycled at 100 $\mu$A·cm$^{-2}$. By the 3$^{rd}$ cycle, when the battery discharges to Li$_2$S$_{2.35}$, the energy density is greater than 1240 mW·h·g$^{-1}$. Eventually, the amount of energy discharged by the battery decreases to approximately 1110 mW·h·g$^{-1}$. However, the energy density exhibited by the battery is consistent and is much larger than the energy density of commercially available cathodes.

### 4.3.3 High order Polysulfide Charge State

Another method of increasing the energy density of the liquid cathode is to increase the limit of the polysulfide order during battery charging. For this to be possible, the high order polysulfide must be stable in the electrolyte, i.e., polysulfide-solvent interactions must be stronger than polysulfide-polysulfide interactions. While the limit of stable polysulfides approaches $n = 12$ in cyclic ether solvents, stable polysulfides as large as $n = 100$ can be obtained in methyl acetate (MA).$^{62}$ Although the concentration of Li$_2$S$_{100}$ is limited to 15mM (i.e., 1.5M S), the ability to increase the liquid cathode’s SOC beyond Li$_2$S$_{12}$ is important in obtaining larger, reversible capacities. For example, if one were able to charge lithium polysulfide to Li$_2$S$_{100}$, then to obtain 600 mA·h·g$^{-1}$ one would only need to deepen the DOD to Li$_2$S$_{2.71}$. In comparison to cycling between Li$_2$S$_{12}$ to Li$_2$S$_{2.26}$ in the absence of MA, the use of MA should increase the cyclability of the polysulfide by lessening the DOD and, thus, decreasing the amount of insoluble sulfides produced upon discharging.

A 100mM Li$_2$S$_6$ battery, containing 0.4M LiNO$_3$ additive and 10% MA, was assembled according to the diagram shown in Figure 3.4, in which the thicknesses of the Li foil and PE spacer were 770 $\mu$m and 1.10mm, respectively (Figure 4.27). The catholyte volume was about 30 $\mu$L.
correlating to 571 µg of sulfur. The TG/DXL volumetric ratio was maintained at 30/70 (i.e., TG:DXL:MA::27:63:10 v/v). Once the battery is assembled, the Li$_2$S$_6$ must first be charged to Li$_2$S$_{100}$, requiring ~150 µA·h. This is done galvanostatically by charging the battery at 89.9 µA for approximately 1 hour and 40 minutes. The battery is then cycled using the GCPL technique.

![Figure 4.27 Specifications of 100mM Li$_2$S$_6$ Batteries with nitrate additive (as 0.4M LiNO$_3$) and MA.](image)

Figure 4.27 Specifications of 100mM Li$_2$S$_6$ Batteries with nitrate additive (as 0.4M LiNO$_3$) and MA.

Figure 4.28 shows the capacity (a) and energy density (b) of the 100mM Li$_2$S$_6$ battery with LiNO$_3$ additive and 10% MA cycled at 100 µA·cm$^{-2}$. The battery exhibits 100% coulombic efficiency when cycled to a low-potential cutoff of 1.8V ( ■ ) and 1.7V ( ■ ), with charge and discharge capacities of 600 mA·h·g$^{-1}$ throughout. However, when the low-potential cutoff is decreased further to 1.6V ( ■ ), the discharge capacity drops to about 430 mA·h·g$^{-1}$, corresponding to a coulombic efficiency of ~72%.

With the addition of MA, the polysulfide order in the charged state is assumed to be 100. Thus, equation 3.12 becomes

\[
S_{100}^{2-} + \left( \frac{200}{D} - 2 \right) e^- \rightarrow \left( \frac{100}{D} \right) S_D^{2-}
\]

and the atomic capacity, $Q_{\text{atom}}$, in terms of electrons per sulfur atom, is given by equation 4.10.
Substitution of 4.10 into 3.9 gives the polysulfide order at the discharged state, \( D \), according to equation 4.11.

\[
D = 200 \left[ \frac{\left( \frac{100 \cdot S_{\text{atom}}}{e^-} \right) \left( \frac{Q_D}{\beta} \right) + 2}{e^-} \right]^{-1}
\]  

(4.11)

According to equation 4.11, the lithium polysulfide order at the discharged state is calculated to be 2.71 at the 1.8V and 1.7V low-potential cutoffs. However, at a low-potential cutoff of 1.6V, \( D \) is 3.74, suggesting that irreversibility is occurring below 1.7V, either from LiNO\(_3\) or MA reduction.

![Figure 4.28](image)

Figure 4.28 (a) Charge (open squares) and discharge (closed squares) and (b) energy density retention of 100mM Li\(_2\)S\(_6\) battery containing LiNO\(_3\) additive with MA (10%) cycled with 1.8V (■), 1.7 (□), and 1.6V (□) low potential cutoff.

Although capacity data might suggest that the battery performs worse only when the low-potential cutoff is decreased below 1.7V, the energy density (Figure 4.28b) suggests otherwise. For
example, during battery cycling within the normal operating potential window of 2.8V–1.8V (⊙), the energy density is steadily decreasing. This steady decrease is also seen when the low-potential cutoff is set to 1.7V (⊙). Given that the coulombic efficiency is 100% within these potential windows, the drop in energy density is a result of increased overpotential, which must be caused by the formation of a growing passivation layer, suggesting that 10% MA might be excessive. Nevertheless, the increase in the charged polysulfide order is evident in the initial energy density exhibited by the battery, i.e., 1321 mW·h·g⁻¹ with 10% MA compared to 1282 mW·h·g⁻¹ without MA (Figure 4.24b).

Figure 4.29 5th cycle charge (dotted lines) and discharge (solid lines) profiles of 100mM Li₂S₆ batteries with nitrate additive (as 0.4M LiNO₃) with no MA (●), 5% MA (●), and 10% MA (●). Current density: 100 μA·cm⁻². Electrolyte: 0.8M LiSO₃CF₃ in TG/DXL (30/70 v/v).

To test the effect of MA content on energy fading, a battery was assembled according to the specifications in Figure 4.27, in which the MA content was reduced by one half. The TG/DXL
volumetric ratio was maintained at 30/70 (i.e., TG, 28.5%; DXL, 66.5%; MA, 5%, v/v). Figure 4.29 shows the 5th cycle voltage profiles of 100mM Li$_2$S$_6$ batteries with different MA concentrations. All batteries, which contain nitrate additive (as 0.4M LiNO$_3$) and a salt concentration of 0.8M LiSO$_3$CF$_3$, were cycled at 100 μA·cm$^{-2}$. Apparently, a decrease in the high voltage plateau is accompanied by the presence of MA. Interestingly, the addition of MA results in an increase in overpotential (▬), but when the MA content is increased to 10% (▬) the overpotential decreases. Nevertheless, there is a gain in capacity and coulombic efficiency with the addition of MA.

![Figure 4.30](image)

**Figure 4.30** (a) Charge (☐) and discharge (■) capacity and coulombic efficiency (○) and (b) energy density (with respect to sulfur mass) of 100mM Li$_2$S$_6$ battery with nitrate additive (as 0.4M LiNO$_3$) and 5% MA. Current density: 100 μA·cm$^{-2}$. Electrolyte: 0.8M LiSO$_3$CF$_3$ in TG/DXL (30/70 v/v).

Figure 4.30 shows the capacity (a) and energy density (b) of the 5% MA battery cycled at 100 μA·cm$^{-2}$. Both the charge (☐) and discharge capacity (■) is 600 mA·h·g$^{-1}$ for the first 11 cycles. Assuming a charged state of $n = 100$, the polysulfide order at the discharged state is calculated, using equation 4.11, to be 2.71. After the 11th cycle, the discharge capacity begins to drop, reaching about 460 mA·h·g$^{-1}$ by the 18th cycle, corresponding to a discharged state consisting of Li$_2$S$_{3.51}$. While the
charging capacity is constant at 600 mA·h·g⁻¹ for the first 18 cycles, it drops continuously in the following cycles. Beyond 20 cycles, the charge and discharge capacities quickly diminish and the battery dies by the 30th cycle.

The energy density of the 5% MA battery can be seen in Figure 4.30b. Behaving analogously to the discharge capacity, the energy density oscillates between 1210 and 1235 mW·h·g⁻¹ for the first 11 cycles and then begins to drop, reaching <1000 mW·h·g⁻¹ by the 14th cycle. The decrease in MA content, i.e., to 5%, appears to stabilize the energy density in the early cycles, compared to the 10% MA battery. On the other hand, the energy density is significantly increased in the 10% MA battery, which suggests the presence of a greater concentration of Li₂S₁₀₀ compared to the 5% battery. In any case, the MA is limiting the cyclability of the lithium polysulfide battery when discharging beyond Li₂S₃ to obtain 600 mA·h·g⁻¹.

4.4 Summary

Sulfur loading is increased to 9M S by synthesizing catholytes of Li₂S₆, compared to 1.2M S with Li₂S₁₂ (Chapter 3). Battery areal capacity is increased to as high as 2 mA·h·cm⁻² using 500mM Li₂S₆, compared to 0.8 mA·h·cm⁻² using 100mM Li₂S₁₂ (Chapter 3), when cycled between Li₂S₁₂ and Li₂S₃. The internal resistance of the batteries increases with Li₂S₆ concentration as follows: R₁₀₀mM < R₅₀₀mM < R₁.₅M, which is most likely a result of viscosity increases with increasing concentration. The 500mM Li₂S₆ battery outperforms the 100mM and 1.5M Li₂S₆ batteries at most current densities, indicating that the lithium polysulfide system is complex, depending on many factors other than the internal resistance. The capacity increases as follows: Q₁.₅M < Q₁₀₀mM < Q₅₀₀mM. Shortcomings in capacity in the 1.5M battery are mainly due to large internal resistance. In the 100mM battery, the lack of charging, due to the polysulfide shuttle mechanism, is overwhelmingly limiting the capacity.
The polysulfide shuttle mechanism is suppressed with the addition of LiNO$_3$ additive, allowing the batteries to completely charge to Li$_2$S$_{12}$. With LiNO$_3$ additive the coulombic efficiency of the 100mM Li$_2$S$_6$ battery is improved to 100% at current densities between 50 and 200 $\mu$A·cm$^{-2}$ (compared to 57%, at 100 $\mu$A·cm$^{-2}$, and 42%, at 200 $\mu$A·cm$^{-2}$, without LiNO$_3$) and to 97% at 500 $\mu$A·cm$^{-2}$ (compared to 35% without LiNO$_3$). As a result, capacity gains at current densities between 100 and 500 $\mu$A·cm$^{-2}$ range from 66% to 187%, respectively, with the addition of LiNO$_3$. Similarly, energy density gains between 21% (at 50 $\mu$A·cm$^{-2}$) to 200% (at 500 $\mu$A·cm$^{-2}$) are observed when LiNO$_3$ is added to 100mM Li$_2$S$_6$.

Depth of discharge experiments (in catholytes with nitrate additive) indicate that as lithium polysulfide reduction is allowed to proceed beyond Li$_2$S$_3$, further gains in capacity and energy are observed, but at the expense of coulombic efficiency (Table 4.6). Based on the maximum discharge capacity of the 100mM Li$_2$S$_6$ battery with nitrate additive, the lithium polysulfide is reduced to as low as Li$_2$S$_{2.55}$. The reversible discharge capacity suggests that the reduction of lithium polysulfide proceeds to Li$_2$S$_{2.57}$.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Target Capacity (mA h g$^{-1}$)</th>
<th>Discharge Capacity (mA h g$^{-1}$)</th>
<th>Coulombic efficiency</th>
<th>Energy Density (mW h g$^{-1}$)</th>
<th>Energy Density (mW h cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>---</td>
<td>418</td>
<td>266</td>
<td>64%</td>
<td>474</td>
</tr>
<tr>
<td>(b)**</td>
<td>LiNO$_3$</td>
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<td>418</td>
<td>100%</td>
<td>944</td>
</tr>
<tr>
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<td>559</td>
<td>86%</td>
<td>1209</td>
</tr>
<tr>
<td>(d)</td>
<td>LiNO$_3$ 5% MA</td>
<td>600</td>
<td>600</td>
<td>100%</td>
<td>1226</td>
</tr>
<tr>
<td>(e)</td>
<td>LiNO$_3$ 10% MA</td>
<td>600</td>
<td>600</td>
<td>100%</td>
<td>1279</td>
</tr>
</tbody>
</table>

* Values listed are the averages over the first 5 cycles  
** Values listed are the averages over 3 cycles  

Discharge capacity, coulombic efficiency, and energy density are increased with the addition of MA (Table 4.6). The average increases in discharge capacity and coulombic efficiency with the
addition of MA (compared to batteries without MA) are 7% and 14%, respectively, for batteries with 5% and 10% MA. 5% MA increases the average energy density by 1.4%, while 10% MA increases it by 5.8%. These increases in discharge capacity, coulombic efficiency, and energy density indicate that the presence of MA is allowing more reduction to occur at the cathode, suggesting that there are “more charged,” longer polysulfide chains (i.e., \( \text{Li}_2\text{S}_{100} \)) in the charged state. However, MA-containing liquid cathodes have poor cyclability at both 5% and 10% MA.
Chapter 5 - Three-dimensional Li$_2$S$_n$ Batteries

5.1 Introduction

In chapters 3 and 4, secondary lithium batteries based on using lithium polysulfide liquid cathodes are demonstrated. Batteries with an areal capacity as high as 2 mA·h·cm$^{-2}$ are obtained using 500mM Li$_2$S$_6$ (Chapter 4). With the addition of LiNO$_3$, cycling efficiency is improved, resulting in capacity and energy density gains over batteries without LiNO$_3$.

However, when cycled at high rates, 2D lithium polysulfide batteries exhibit energy loss. In an attempt to increase the amount of energy, the volume loading of polysulfides is increased. However, lower capacities are achieved due to increased cell resistance resulting from larger separation distances between the lithium and cathode current collector. Also, the kinetic barriers that are associated with 2D battery designs have an adverse effect on the energy density during large power consumption. By creating a 3D battery, these kinetic barriers should be minimized. Therefore, at a given current density, larger capacities should be obtained in 3D batteries compared to 2D batteries with similar volume loading.

Carbon is a common anode material in lithium-ion batteries that can be fabricated into 3D architectures using carbon-microelectromechanical systems technology and infiltration through micromachined silicon.$^{55,56,79}$ However, in a high-capacity cathode system, such as that of lithium polysulfide, it is more beneficial to use a pure lithium anode which has a theoretical capacity of 3,861 mA·h·g$^{-1}$, compared to 372 mA·h·g$^{-1}$ in carbon. This is extremely challenging since the fabrication techniques used to make 3D architectures involve exposing the workpiece to atmosphere, which is unacceptable for lithium.

One method used to overcome the challenges of fabricating a 3D lithium anode is to plate lithium on the surface of a preexisting 3D current collector. For example, 3D arrays of lithium can
be fabricated by electrodepositing nickel though a silicon mold and then sacrificially etching the silicon. The 3D nickel current collector can then be inserted into an inert atmosphere glovebox where lithium can be plated onto the nickel from a lithium electrolyte solution. However, the high costs associated with this process, both materials and labor, tend to make it unappealing in many cases. As a result, different methods of creating 3D lithium anodes have been developed and are discussed in this dissertation.

In this chapter, two methods of forming 3D lithium anodes, using polystyrene as the mold, are discussed. In the first method, a 3D nickel current collector array is fabricated using a polystyrene mold and the nickel is inserted into a glovebox, where lithium is electrodeposited onto the nickel. The second method that is discussed involves the plating of lithium through a polystyrene mold or template, in which both lithium plating and mold removal take place within the glovebox. Two processes have been developed to fabricate polystyrene molds/templates: 1) micromachining of a polystyrene disk and 2) microprinting of polystyrene paint.

5.2 Lithium-plated 3D Nickel array

5.2.1 Experimental

5.2.1.1 Chemicals

Lithium sulfide (Li$_2$S), 99.9% (12839, Alfa Aesar), and anhydrous lithium salts, lithium nitrate (LiNO$_3$), (44456, Alfa Aesar), lithium perchlorate (LiClO$_4$), 99.99% battery grade (634565, Sigma-Aldrich), and lithium hexafluorophosphate (LiPF$_6$), 98% (11529, Alfa Aesar), were placed in an argon-filled glovebox and used as received. Sulfur, 99.98% (414980, Sigma-Aldrich), and lithium trifluoromethanesulfonate (or lithium triflate, LiSO$_2$CF$_3$), 99.995% (481548, Sigma-Aldrich),
powders were dried separately on a Schlenk line by purging with argon three times and then raising the temperature to 120°C for 6 hours under vacuum.

Inhibitor-free anhydrous tetrahydrofuran (THF), ≥99.9% (401757, Sigma-Aldrich), anhydrous 1,3-dioxolane (DXL) with ~75 ppm butylated hydroxytoluene as inhibitor, 99.8% (271020, Sigma-Aldrich), anhydrous propylene carbonate (PC), 99.7% (310328, Sigma-Aldrich), anhydrous ethylene carbonate (EC), 99% (676802, Sigma-Aldrich), anhydrous dimethyl carbonate (DMC), ≥99% (517127, Sigma-Aldrich), and anhydrous toluene, 99.8% (244511, Sigma-Aldrich), were inserted into an argon-filled glovebox and used as received. Tetraethylene glycol dimethyl ether (or tetraglyme, TG), 99% (172405, Sigma-Aldrich), was dried on a Schlenk line by purging with argon three times and then raising the temperature to 105°C for 4 hours under vacuum. 4Å molecular sieves (208604, Sigma-Aldrich) were dried on a Schlenk line by purging with argon three times and then raising the temperature to 225°C for 24 hours. After insertion into the glovebox, the TG was run through a column filled with the dry molecular sieves and collected in a dry amber jar at a rate of two drops per second.

Aqueous electrolyte salts, nickel(II) chloride (NiCl₂), 98% (339350, Sigma-Aldrich), and nickel(II) sulfate hexahydrate (NiSO₄·6H₂O), 99-102% (31483, Sigma-Aldrich), and boric acid (H₃BO₃), 95% (A74, Fisher Scientific), were used as received.

### 5.2.1.2 Lithium polysulfide synthesis

4mM Li₂S₁₂

Lithium polysulfides were synthesized in an argon glovebox. Lithium foil was polished using a polyethylene block and cut into small pieces, a few millimeters in size, and added to a glass jar. Sulfur powder was added to the jar, such that the molar ratio of Li:S was 1:6. 10 mL of THF was added in a glass vial and the mixture was stirred for several weeks. Once the lithium and sulfur have
reacted, TG was added. The solution was transferred to a Schlenk line flask, sealed, removed from the glovebox, and heated on an argon Schlenk line at 85°C for 2 hours to remove the THF. While under vacuum, the flask was reinserted into the glovebox. Lithium triflate was added to the solution, followed by DXL, and stirred for several hours. This final solution is the 4mM Li₂S₁₂ catholyte and is composed of 0.8M LiSO₃CF₃ in TG/DXL (30/70 v:v).

100mM Li₂S₆

Li₂S₆ was synthesized according to the scheme shown in Figure 4.1. THF is added to lithium sulfide and sulfur powders, at a molar ratio of 1:5::Li₂S:S, in a glass vial and stirred for several hours. TG is added after the powders have reacted. The THF is then extracted from the solution by evaporating under vacuum, while heating at 85°C. The remaining liquid is a viscous liquid cathode.

In a separate glass vial, LiSO₃CF₃ and lithium nitrate (LiNO₃) salts are added to DXL and stirred for several hours. The electrolyte solution is added to the lithium polysulfide. This final solution is the 100mM Li₂S₆ catholyte and consists of 0.8M LiSO₃CF₃ and 0.4M LiNO₃ in TG/DXL (30/70 v:v).

5.2.1.3 3D Nickel

Silicon mold fabrication

Silicon molds were provided by Professor Chang-Jin Kim from the Department of Mechanical and Aerospace Engineering, University of California, Los Angeles. Typical fabrication consists of a deep reactive-ion etching (DRIE) step, in which holes with the desired dimensions can be formed throughout the entire thickness of a silicon wafer.⁶⁴
**Polystyrene mold fabrication**

A birch wood rod, ½” in diameter (9683K17, McMaster-Carr), is drilled and tapped on one end. On the other end, a disc of polystyrene, cut from a polystyrene petri dish (0875713, Fisher Scientific), is mounted using hot glue. The rod is then screwed onto a precision x–y stage, which is mounted on the base of a micro-drill press, and the polystyrene (PS) disk is drilled using water as a coolant (Figure 5.1). The PS disk is then deburred by polishing both sides of the PS mold.

![Figure 5.1 Polystyrene (PS) mold fabrication using water-cooled micro-drilling process. Mold thickness, h, determines maximum post height in 3D array.](image)

**Electrodeposition**

Silicon and polystyrene molds are mounted onto the surface of a polished nickel rod using hot glue. The nickel rod is screwed onto a stainless steel (type 18–8) threaded (8–32) rod and the surfaces of the stainless steel and nickel are coated with a protective film of hot glue. The nickel electrode is assembled into a three-electrode cell with two sheets of nickel foil serving as the counter
and reference electrodes (Figure 5.2). A nickel electrolyte solution, consisting of 240 g·L⁻¹ NiSO₄·6H₂O, 20 g·L⁻¹ NiCl₂, and 20 g·L⁻¹ H₃BO₃, is added to the cell and nickel is electrodeposited via constant current (through silicon) or pulsed (through polystyrene) deposition. Electrodeposition of nickel through silicon molds is done at a current density of 10 mA·cm⁻² while sonicking in a bath to remove hydrogen bubbles formed during deposition. When electrodepositing through polystyrene, Triton X-114 (Union Carbide Chemicals) surfactant is added to the electrolyte solution to help wet the walls of the through-holes in the mold. A typical pulse cycle consists of a 15 mA·cm⁻² pulse for 50 ms and a -1 mA·cm⁻² pulse for 250 ms. After deposition, excess nickel is removed via wet polishing and the PS mold is removed by dissolving in toluene.

![Figure 5.2 Scheme of obtaining a 3D nickel post array by electrodepositing nickel through a drilled polystyrene (PS) mold and then removing the mold by dissolving in toluene.](image)

5.2.1.4 Lithium deposition

3D nickel current collectors are inserted into an argon glovebox and mounted in three-electrode configurations. Each lithium-deposition cell consists of a 3D nickel array (working
electrode) and two sheets of lithium foil, one serving as the counter electrode and the other as the reference electrode (Figure 5.3a). A lithium electrolyte solution, consisting of 1M LiPF₆ in PC, is added to the cell and lithium is electrodeposited onto the 3D nickel array via pulse deposition.

Lithium-deposited samples are rinsed in first PC then EC to remove LiPF₆. A final rinse in DXL is carried out prior to installation in the battery cell (Figure 5.3b).

![Image](image_url)

**Figure 5.3** (a) Electrodeposition of lithium onto a 3D nickel array and (b) cross-section showing integration in 3D battery.

### 5.2.1.5 Measurements

Electrochemical measurements were recorded through EC-Lab software using a VMP3 Multi Potentiostat by Bio-Logic SA. Galvanostatic Cycling with Potential Limitation (GCPL) experiments were carried out in an argon-filled glovebox on two-electrode battery cells, in which the molybdenum rod was the working electrode and the counter and reference wires from the potentiostat were both connected to the lithium-deposited nickel rod. All batteries were cycled at room temperature.
5.2.2 Results and Discussion

5.2.2.1 3D Nickel current collectors

Figure 5.4 shows 3D nickel arrays obtained via electrodeposition through silicon (a) and PS molds machined with 330 μm (b) and 750 μm (c) drill bits. The specifications of the 3D arrays are listed in Table 5.1. Nickel arrays deposited through etched silicon (3D-Ni_{25, Si}) have a diameter, d, of 25 μm and a height, h, of 75 μm, yielding an aspect ratio (ratio of height to diameter) of 4:1. The pitch, P, which is the distance between nearest neighboring posts and is measured from the center of each post, is 100 μm. The resulting 3D array areal density and volume normalized per square centimeter footprint area, are 17,556 posts·cm\(^{-2}\) and 0.862 mm\(^3\)·cm\(^{-2}\), respectively, providing a surface area 2.28 times that of the anode of the 2D battery.

Table 5.1 Summary of electrodeposited 3D Ni arrays

<table>
<thead>
<tr>
<th>Current Collector</th>
<th>Diameter, d (μm)</th>
<th>Pitch, P (μm)</th>
<th>Height, h (μm)</th>
<th>Aspect Ratio (d:h)</th>
<th>Areal Density (posts cm(^{-2}))</th>
<th>Array Volume (mm(^3) cm(^{-2}))</th>
<th>Surface Area (3D/2D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3D-Ni_{25, Si}</td>
<td>25</td>
<td>75</td>
<td>100</td>
<td>4:1</td>
<td>17,556</td>
<td>0.862</td>
<td>238%</td>
</tr>
<tr>
<td>3D-Ni_{400, PS}</td>
<td>400</td>
<td>1200</td>
<td>800</td>
<td>2:1</td>
<td>77</td>
<td>7.7</td>
<td>254%</td>
</tr>
<tr>
<td>3D-Ni_{800, PS}</td>
<td>800</td>
<td>1200</td>
<td>800</td>
<td>1:1</td>
<td>77</td>
<td>31</td>
<td>410%</td>
</tr>
</tbody>
</table>

Micromachined polystyrene molds yield posts with slightly larger diameter (i.e., 330 μm and 750 μm drill bits produce holes with diameters of approximately 400 μm and 800 μm, respectively). Local heating during drilling, due to friction, increases the temperature far above the glass transition temperature of polystyrene, allowing polymer chains flow, even when cooled with water. 3D nickel current collectors fabricated using PS molds drilled with 330 μm (3D-Ni_{400, PS}) and
Figure 5.4 Angle (left) and top (right) views of 3D nickel arrays on nickel rods fabricated via electrodeposition through silicon (a) and PS (b and c) molds drilled with (b) 330 μm and (c) 750 μm drill bits. (a) Diameter, 25 μm; pitch, P, 75 μm. (b) Diameter, 400 μm; pitch, P, 1200 μm. (c) Diameter, 800 μm; pitch, P, 1200 μm.
750 μm (3D-Ni_{800,PS}) drill bits have an identical pitch and areal density of 1200 μm and 77 posts·cm^{-2}, respectively. As a result, 3D-Ni_{400,PS} is one quarter of the volume of 3D-Ni_{800,PS} and 3D-Ni_{800,PS} has 1.6 times the surface area of 3D-Ni_{400,PS}.

5.2.2.2 3D-Ni_{25,Si} 4mM Li_{2}S_{12} Battery

![Figure 5.5](image.png)

Figure 5.5 Voltage profiles (a) and capacity retention (b) of 3D 4mM Li_{2}S_{12} battery using lithium-coated 3D-Ni_{25,Si} as the anode.

Lithium was deposited in excess in 3D-Ni_{25,Si}. Using the lithium-deposited 3D-Ni_{25,Si} anode, a 4mM Li_{2}S_{12} 3D battery was assembled as shown in Figure 3.4. This battery was cycled three times at each of the following current densities: 1.8 μA·cm^{-2}, 3.6 μA·cm^{-2}, 7.1 μA·cm^{-2}, and 14.2 μA·cm^{-2}. Figure 5.5 shows the voltage profiles (a) and capacity retention (b) of the 3D battery. Due to the large separation of this un-optimized battery (i.e., 1.5 mm spacer), the overpotential is quite large and the potential cutoffs are widened (i.e., 4V to 1.5V). It should be noted that according to cyclic voltammetry, no side reactions or electrolyte degradation occur within this potential window.
Nevertheless, 100% coulombic efficiency (▲) is observed for the first nine cycles. The coulombic efficiency drops to around 85% when the current density is increased to 14.2 μA·cm$^{-2}$.

![Ragone plot](image)

**Figure 5.6** Ragone plot of 3D-Li$_2$S$_{12}$ battery with lithium-plated 3D-Ni$_{25,51}$ anode (▲) and 2D-Li$_2$S$_{12}$ battery with lithium foil anode (■). Catholyte: 4mM Li$_2$S$_{12}$, 0.8M LiSO$_3$CF$_3$ in TG/DXL (30/70 v/v).

A Ragone plot comparing 3D and 2D 4mM Li$_2$S$_{12}$ batteries is shown in Figure 5.6. The 2D battery (■) shows more prominent energy density fading with increasing loads. On the Ragone plot, the 3D battery (▲) points are much more vertical, indicating that the energy density is not significantly dropping when the current is increased. When the current density in the 2D battery is doubled, from 2.9 to 5.8 μA·cm$^{-2}$, the energy density drops by 31%, i.e., from 58 to 40 μW·h·cm$^{-2}$. However, when the current density in the 3D battery is increased by a factor of eight, from 1.8 to 14.2 μA·cm$^{-2}$, the energy loss is only 23%, i.e., from 79 to 61 μW·h·cm$^{-2}$. The ability of 3D batteries to maintain high energy density with increasing current density underlies one of the principal benefits of 3D batteries.
After cycling, the battery was disassembled and the 3D anode was soaked and rinsed with DXL to wash off any lithium polysulfides. After the DXL evaporated, the anode was removed from the glovebox and stored in air. Figure 5.7 shows an image of the 3D anode after one week of air exposure. An interesting observation is that the film of lithium around each post appears to be unharmed by the atmosphere. This is most likely due to the formation of a protective layer, consisting mostly of lithium sulfide, which is formed during battery cycling. Another interesting observation is that, regardless of how rough the electrodeposited lithium is, the lithium appears smoother after cycling in lithium polysulfide. The polysulfide shuttle mechanism creates an intrinsic property in the lithium-sulfur system in which lithium dendrites are oxidized during battery charging, thus protecting the cell from overcharge. Based on the image in Figure 5.7, in 3D architectures, lithium anodes with porous morphologies are densified after constant stripping and plating during battery cycling and the polysulfide shuttle mechanism appears to be aiding in the conformality of the lithium film.
5.2.2.3 3D-Ni_{400,PS} and 3D-Ni_{800,PS} 100mM Li$_2$S$_6$ batteries

3D 100mM Li$_2$S$_6$ batteries were assembled according to Figure 3.4. Figure 5.8 shows the charge (open squares) and discharge (closed squares) profiles of batteries with lithium-deposited 3D-Ni$_{400,PS}$ (a) and 3D-Ni$_{800,PS}$ (b) anodes. Each battery was cycled at 100 μA·cm$^{-2}$ (■), 200 μA·cm$^{-2}$ (■), 500 μA·cm$^{-2}$ (■), and 2 mA·cm$^{-2}$ (not shown). The 3D-Ni$_{400,PS}$ battery (a) appears to outperform the 3D-Ni$_{800,PS}$ battery (b) as far as areal capacity, i.e., 758 μA·cm$^{-2}$ versus 281 μA·cm$^{-2}$, respectively. However, it should be noted that because of the asymmetry of the nickel post array in the 3D-Ni$_{800,PS}$ current collector, the volume could not be determined accurately until visually inspecting it outside of the glovebox after battery cycling. Thus, the estimation of the catholyte volume in the battery was underestimated and the battery could have been cycled up to ~600 μA·h·cm$^{-2}$ based on the final anode volume.

![Figure 5.8](image)

Figure 5.8 Charge (open squares) and discharge (closed squares) voltage profiles of 3D Li$_2$S$_6$ batteries with lithium-plated 3D-Ni$_{400,PS}$ (a) and 3D-Ni$_{800,PS}$ (b) anodes. Catholyte: 100mM Li$_2$S$_6$, 0.4M LiNO$_3$ and 0.8M LiSO$_3$CF$_3$ in TG/DXL (30/70 v/v).
The cycling performance of the 3D batteries can be seen in Figure 5.9. Capacity (○) fading in the 3D-Ni$_{400}$PS battery (a) is apparent, dropping slightly at each current density. At 100 μA·cm$^{-2}$, the coulombic efficiency (►) drops 20% by the third cycle. When the current density is increased by a factor of 5, the capacity drops by about 75% and the coulombic efficiency rises to about 96%. At 2 mA·cm$^{-2}$, the battery does not cycle.

![Figure 5.9](image.png)

**Figure 5.9** Charge (○) and discharge (●) capacity retention and coulombic efficiency (►) of 3D Li$_2$S$_6$ batteries using lithium-plated 3D-Ni$_{400}$PS (a) and 3D-Ni$_{800}$PS (b) anodes. Catholyte: 100mM Li$_2$S$_6$, 0.4M LiNO$_3$ and 0.8M LiSO$_3$CF$_3$ in TG/DXL (30/70 v/v).

The 3D-Ni$_{800}$PS battery (Figure 5.9b) appears to perform slightly better than the 3D-Ni$_{400}$PS battery. The Coulombic efficiency is 100% for the first six cycles and decreases to about 95% when the battery is cycled at 500 μA·cm$^{-2}$. This battery cycles at 2 mA·cm$^{-2}$, but only exhibits about 10% of the capacity. When the current density is decreased to 50 μA·cm$^{-2}$, the capacity is recovered and the coulombic efficiency increases to 100%.
Figure 5.10  Cell resistance of charged 2D (▲), 3D-Ni_{400,PS} (■) and 3D-Ni_{800,PS} (⊙) batteries. Catholyte: 100mM Li_{2}S_{6}, 0.4M LiNO_{3} and 0.8M LiSO_{3}CF_{3} in TG/DXL (30/70 v/v).

At each current density, the overpotential is larger in the 3D-Ni_{400,PS} battery than in the 3D-Ni_{800,PS} battery, which is due to larger internal resistance in the former. Figure 5.10 shows cell resistance values, which are calculated using equation 4.3, plotted as a function of current density. At low current density (100 μA·cm^{-2}) the cell resistance of the 3D-Ni_{800,PS} battery is 75% that of the 3D-Ni_{400,PS} battery, i.e., 500Ω versus 660Ω. When the current density is increased to 500 μA·cm^{-2}, the cell resistance of the 3D-Ni_{800,PS} battery is 82% that of the 3D-Ni_{400,PS} battery, i.e., 250Ω versus 305Ω. In both cases, the transition from a 2D anode to a 3D anode results in decreased cell resistance in the Li_{2}S_{6} battery.

Reasons for the lower cell resistance and improved rate capability of the 3D-Ni_{800,PS} battery over the 3D-Ni_{400,PS} battery lies within the structure of the 3D anodes. Since post height, pitch, and separation distance between the anode and cathode current collectors are the same in each anode,
the difference in performance must be due to post diameter. For example, as the post diameter is increased from 400 to 800 μm, the surface area increases, compared to using a flat lithium anode, from 254% to 410%. Thus, the cell resistance of the 100mM Li2S6 batteries depends on the anode geometry and increases in the following manner: $R_{\text{cell}}(\text{3D-Ni}_{800,\text{PS}}) < R_{\text{cell}}(\text{3D-Ni}_{400,\text{PS}}) < R_{\text{cell}}(\text{2D})$. However, the areal capacity is lower in the larger diameter nickel array anode because there is less volume available for active mass, due to occupation of volume by the nickel.

Figure 5.11 Ragone plot of Li2S6 batteries with 3D-Ni$_{400,\text{PS}}$ (■), 3D-Ni$_{800,\text{PS}}$ (○), and lithium foil (▲) anodes. Catholyte: 100mM Li$_2$S$_6$, 0.4M LiNO$_3$ and 0.8M LiSO$_3$CF$_3$ in TG/DXL (30/70 v/v).

Figure 5.11 shows a Ragone plot comparing the 3D-Ni$_{400,\text{PS}}$ (■) and 3D-Ni$_{800,\text{PS}}$ (○) batteries with the 2D battery (▲). Disappointingly, it can be seen that the 100mM Li$_2$S$_6$ 3D batteries do not exhibit performance gains over the 2D battery (▲). However, a close look at the cross-sections of each cell (Figure 5.12) helps reveal the reason for this. The 3D-Ni$_{400,\text{PS}}$ battery (b) has more available
volume for catholyte, hence higher energy density when discharged at low currents. The $3D\text{-Ni}_{800,PS}$ battery (c) has more surface area, resulting in lower cell resistance and higher rate capabilities than the $3D\text{-Ni}_{400,PS}$ battery. The 2D battery outperforms the 3D batteries because the electrode separation is smaller and the electric field between the anode and cathode is more uniform throughout the entire area of the electrodes.

![Diagram](image)

**Figure 5.12** Specifications of 100mM Li$_2$S$_6$ batteries with lithium foil (a), $3D\text{-Ni}_{400,PS}$ (b), and $3D\text{-Ni}_{800,PS}$ (c) anodes showing cell geometry and distances between cathode current collector (Mo) and lithium surfaces.

Finite element analysis of 3D lithium ion microbatteries in the “trench” design (see interdigitated parallel plate architecture in Figure 2.3b) shows that lithiation and delithiation starts directly at the electrode plate tips. It turns out that current distribution, which controls the concentration gradient, is concentrated at the plate tips because of the small radius of curvature at the tips. This appears to be the case in the 3D lithium polysulfide batteries. The current distribution is concentrated at the post tips, limiting the rate capabilities of the 3D batteries. This is apparent in Figure 5.7, which shows the discharged 3D lithium anode having no lithium at the post tips, indicating that most of the reaction occurs at the tip of the post in the presence of excess lithium.
Catholyte stability in the 3D battery is apparent in Figure 5.13, which shows the open-circuit potential (OCP) of the 3D-Ni_{400,PS} battery taken after the 51\textsuperscript{st} discharge. After 5 days the OCP of the discharged battery plateaus at 2.11V and maintains this potential for approximately 50 days. OCP stability serves as evidence that the concentrations of reductants and oxidants are constant, indicating that the SEI layer on the 3D lithium anode is inhibiting self-discharge at room temperature.

Figure 5.13 Open-circuit potential of discharged 3D-Ni_{400,PS} Li_{2}S_{6} battery versus time. OCP recorded after 51 cycles. Catholyte: 100mM Li_{2}S_{6}, 0.4M LiNO\textsubscript{3} and 0.8M LiSO\textsubscript{3}CF\textsubscript{3} in TG/DXL (30/70 v/v).
5.3 Electroplated 3D Lithium

5.3.1 Motivation

To this point, the process of fabricating 3D current collector arrays via deposition of nickel through a micromachined polystyrene mold has been developed and proven to be successful. However, 3D nickel current collectors are limiting the capacity of the battery because of the volume occupied by nickel, which is not involved in the electrochemical reaction within the cell, but only provides electrical contact to the lithium anode.

One way to increase the amount of energy available in the lithium polysulfide battery is to increase the volume available for the liquid cathode. This can be done by eliminating the nickel array. Since polystyrene molds allow electrodeposition and mold removal to take place within the glovebox, they enable us to fabricate 3D arrays of pure lithium. Because lithium is a metal, i.e. high electrical conductivity, posts with high aspect ratios could be fabricated without any concerns of a potential drop along the post.

5.3.2 Experimental

5.3.2.1 Micro-printed polystyrene templates

Polystyrene (PS) beads, average $M_w \sim 192,000$ (430102, Sigma-Aldrich), are dissolved in toluene to form a PS-paint solution with a concentration of $20 \, \text{g}_{\text{PS}} \cdot \text{L}^{-1}$. A nickel rod is machined, using a lathe, to yield square, parallel surfaces. On one end (bottom) of the nickel rod, a hole is drilled, using a $\#29$ drill bit, and the hole is tapped, using an 8–32 tap. The other end (top) of the nickel rod is wet-sanded, using de-ionized water, on a polishing wheel using a series of 120, 240, 400, 600, 800, 1200, and 2400 grit silicon carbide paper. The surface is then polished on a neoprene
wheel with 1, 0.3, and 0.05 μm alumina powder to give the nickel rod surface a mirror finish. PS paint is loaded into a GIX Microplotter II (SonoPlot, Inc.) and a pattern, designed using SonoDraw software, is printed onto the polished surface of the nickel rod (Figure 5.14). It should be noted that the roughness of the nickel surface must be less than 10 microns to prevent damage to the microprinter tip. The nickel rod is allowed to dry in air for two days before handling.

![Diagram of Microprinting Process](image)

Figure 5.14 Polystyrene template formation on nickel rod via microprinting of PS-paint.

5.3.2.2 Lithium deposition

An 18–8 stainless steel 8–32 threaded rod is softened by heating with a propane torch, until red hot, and bent at a 45° angle using vice grips. The PS-templated nickel rod is screwed onto the bent stainless steel rod and hot glue is used to insulate the surface of the nickel and stainless steel to
prevent contact with electrolyte during electrodeposition. The nickel is inserted into an argon glovebox and mounted in a three-electrode configuration along with two sheets of lithium foil, one serving as the counter electrode and the other as the reference electrode (Figure 5.15). A lithium electrolyte solution is added to the cell and lithium is electrodeposited through the PS-template via pulsed deposition. Lithium-deposited samples are rinsed in PC then DMC to remove LiPF₆. The nickel rod is soaked in toluene to remove the PS-template. A final rinse in DXL is carried out prior to installation in the battery cell.

Figure 5.15 Fabrication scheme of 3D lithium square post array via electrodeposition of lithium through PS-template and template removal via dissolving in toluene.

### 5.3.3 Results and Discussion

#### 5.3.3.1 3D Lithium square post arrays

A proof-of-concept experiment was demonstrated using PS checkered-pattern templates formed on polished nickel surfaces via microprinting. In this case, the PS squares were
approximately 600 μm by 600 μm and the exposed nickel was about 500 μm by 500 μm (Figure 5.16a). After microprinting, the templated nickel rod is placed into a lithium deposition cell (Figure 5.15) with an electrolyte consisting of 0.25M LiClO₄ in EC/DMC (50/50 v/v). Lithium is deposited galvanostatically using a pulse sequence of -430 μA·cm⁻² for 10 ms followed by a rest period (no current) of 50 ms, which is repeated one million times. After lithium deposition, lithium salts are washed off using DMC and the nickel rod is soaked in toluene to dissolve the PS-template.

Figure 5.16 (a) Checkered-pattern PS-template deposited on polished nickel surface via microprinting of PS-paint and (b) 3D lithium square post array after PS-template removal.

Figure 5.16b shows the square lithium posts after removal of the PS template. Each lithium post has a length and width of about 500 μm and a height of roughly 50 μm, indicating an aspect ratio of 1:10. The deposited lithium is very porous and dendritic because of the electrolyte that was
used. When using 1M LiPF$_6$ in PC, the lithium posts are denser and the surface is smoother. This is in agreement with Gireaud et al., who have electrodeposited relatively smooth lithium films at both low (1 mA·cm$^{-2}$) and high (50 mA·cm$^{-2}$) current densities using LiPF$_6$ in EC/DMC (50/50 v/v).$^{84}$ It should be noted that the lithium posts are white in color only because the images are taken in air. It should be also noted that in this design, when larger aspect ratios are attempted, merging of post corners is anticipated and the resulting interconnected rows of posts are expected to limit catholyte mobility in the lateral direction (i.e., parallel to nickel surface). Nevertheless, patterned lithium architectures have been fabricated via electrodeposition through printed PS templates using a process that is carried out within an inert atmosphere glovebox.

### 5.3.3.2 3D Lithium array 100mM Li$_2$S$_6$ battery

PS-paint was printed onto a polished nickel rod with the pattern shown in Figure 5.17. After the PS is dry, the nickel rod is assembled in a lithium deposition cell, according to Figure 5.15, and 1M LiPF$_6$ in PC is added. Lithium is galvanostatically deposited using ON/OFF pulses of -1 mA·cm$^{-2}$ for 10 ms / rest for 50 ms. After 16 million pulses, the nickel rod is soaked and rinsed with DMC to remove any remaining LiPF$_6$. The PS-template is dissolved using toluene and the resulting battery anode array is referred to as 3D-Li$_{Square,200}$.
Figure 5.17 Isolated-post PS-template showing perpendicular rows of PS lines (black), 200 μm thick, printed on a polished nickel rod.

Table 5.2 Electrodeposited square-post lithium anode array, 3D-Li_{Square,200}, specifications

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length x Width x Height (μm)</td>
<td>200 x 200 x 200</td>
</tr>
<tr>
<td>Pitch, P (μm)</td>
<td>400</td>
</tr>
<tr>
<td>Areal Density (posts cm(^2))</td>
<td>625</td>
</tr>
<tr>
<td>Array Volume (mm(^3) cm(^{-2}))</td>
<td>5.4</td>
</tr>
<tr>
<td>Li Capacity (mA h cm(^{-2}))</td>
<td>11.1</td>
</tr>
<tr>
<td>Surface Area (3D/2D)</td>
<td>125%</td>
</tr>
</tbody>
</table>

Characteristics of the square-post lithium anode array, 3D-Li_{Square,200}, are summarized in Table 5.2. The posts are cubic with an edge length of 200 μm, thus, the square posts have an aspect ratio of 1:1. These posts are completely isolated from each other, allowing catholyte to flow freely between them. With the given post geometry, the areal post density and total volume of the posts are 625 posts per cm\(^2\) and 5.4 mm\(^3\) per cm\(^2\), respectively. Based on the amount of lithium deposited, assuming 100% coulombic efficiency, the available anodic areal capacity within the posts is 11.1 mA·h·cm\(^{-2}\). If the aspect ratio were to be increased to 5:1, the capacity of the lithium anode would increase to 55.5 mA·h·cm\(^{-2}\).
Figure 5.18 Cross-section of 3D-Lisquare,200 100mM Li$_2$S$_6$ battery. Electrolyte: 0.4M LiNO$_3$ and 0.8M LiSO$_3$CF$_3$ in TG/DXL (30/70 v/v).

Figure 5.19 Top view of 3D-Lisquare,220 anode in 3D 100mM Li$_2$S$_6$ battery (a) before initial charge and (b) after charging to Li$_2$S$_{12}$. 
A battery was assembled according to Figure 3.4 using the 3D-Li\textsubscript{Square,200} anode. Two washers (inner diameter: \(\frac{3}{8}''\); outer diameter: \(\frac{1}{2}''\)) are punched out of a 210 \(\mu\text{m}\) thick PE sheet, using \(\frac{3}{8}''\) and \(\frac{1}{2}''\) hole punches, and stacked to be used as spacers in the 3D battery assembly (Figure 5.18). The molybdenum–nickel separation is 420 \(\mu\text{m}\), allowing for about 28 \(\mu\text{L}\) of volume available for the catholyte. With the addition of 100mM Li\textsubscript{2}S\textsubscript{6} into the 3D battery, 0.54 mg of sulfur is present, corresponding to a theoretical capacity of 0.224 mA·h when cycled between Li\textsubscript{2}S\textsubscript{12} and Li\textsubscript{2}S\textsubscript{3}. Prior to cycling, Li\textsubscript{2}S\textsubscript{6} is charged to Li\textsubscript{2}S\textsubscript{12}, during which lithium deposits onto the bare nickel in between the lithium posts, i.e., where the PS template used to be, further increasing the surface area of the anode. Since no efforts were made in insulating the nickel rod surface outside of the lithium post array footprint area (Ni rod surface in Figure 5.19a) the footprint area increases from 0.36 cm\(^2\) before charging (a) to 0.71 cm\(^2\) after charging to Li\textsubscript{2}S\textsubscript{12} (b). Similarly, after charging the liquid cathode, the surface area of lithium, \(A_{Li}\), increases from 0.45 cm\(^2\) to 1.07 cm\(^2\).

Figure 5.20 shows the charge (open squares) and discharge (closed squares) profiles of the 3D-Li\textsubscript{Square,200} 100mM Li\textsubscript{2}S\textsubscript{6} battery. The capacity decreases by 45\% (from 340 to 188 mA·h·g\(^{-1}\)) when the current density is increased from 127 to 253 \(\mu\text{A}·\text{cm}^{-2}\). When the current density is increased to 634 \(\mu\text{A}·\text{cm}^{-2}\), the capacity decreases to about 15\% (i.e., 50 mA·h·g\(^{-1}\)) of the capacity obtained at 127 \(\mu\text{A}·\text{cm}^{-2}\). One obvious benefit is the large amount of the high voltage plateau discharge capacity. For example, at 127 \(\mu\text{A}·\text{cm}^{-2}\) the capacity of the high discharge plateau is roughly 59\% of the total capacity. Larger high voltage plateaus mean more power; therefore, the 3D-Li array shows promise.
Figure 5.20 Charge (open squares) and discharge (closed squares) profiles of the 3D-Li\textsubscript{Square,200} Li\textsubscript{2}S\textsubscript{6} battery taken from the 3\textsuperscript{rd} cycle at 127 ( ), 253 ( ), and 634 μA cm\textsuperscript{-2} ( ). Catholyte: 100mM Li\textsubscript{2}S\textsubscript{6}, 0.4M LiNO\textsubscript{3} and 0.8M LiSO\textsubscript{3}CF\textsubscript{3} in TG/DXL (30/70 v/v).

Figure 5.21 Capacity retention (a) and coulombic efficiency (b) of 3D Li\textsubscript{2}S\textsubscript{6} battery with 3D-Li\textsubscript{Square,200} anode. Catholyte: 100mM Li\textsubscript{2}S\textsubscript{6}, 0.4M LiNO\textsubscript{3} and 0.8M LiSO\textsubscript{3}CF\textsubscript{3} in TG/DXL (30/70 v/v).
Capacity retention can be seen in Figure 5.21a. Capacity fading is apparent with increasing current density. For example, at 127, 253, and 634 \( \mu \text{A} \cdot \text{cm}^{-2} \), the areal capacity is about 0.21, 0.11, and 0.04 mA·h·cm\(^{-2} \), respectively. At 2.5 mA·cm\(^{-2} \), the battery does not cycle. When the current is decreased to 63 \( \mu \text{A} \cdot \text{cm}^{-2} \), the capacity is recovered. However, the coulombic efficiency (Figure 5.21b) does not recover but, rather, drops significantly to 76% (from an initial 88%).

![Graph showing Ragone plot](image)

**Figure 5.22** Ragone plot of 3D Li\(_2\)S\(_6\) batteries using 3D-Ni\(_{400,PS}\) (■), 3D-Ni\(_{800,PS}\) (▲), and 3D-Li\(_{\text{Square,200}}\) (○) anodes. Catholyte: 100mM Li\(_2\)S\(_6\), 0.4M LiNO\(_3\) and 0.8M LiSO\(_3\)CF\(_3\) in TG/DXL (30/70 v/v).

Figure 5.22 shows a Ragone plot comparing the 3D lithium square post array battery to batteries with the lithium-plated 3D nickel current collector array anodes. The poor delivery of energy during high power cycling is apparent in the 3D-Li\(_{\text{Square,200}}\) battery (○). This indicates that the 3D-Li\(_{\text{Square,200}}\) anode is a poor candidate for the 3D liquid cathode battery. A major reason for its poor performance is the low surface area of the 3D lithium array (Figure 5.19). However, this can
be remedied by increasing the aspect ratio of the posts. For example, if the aspect ratio were to be increased to 5:1, the surface area would be 525% that of the footprint area, compared to 125% at the present aspect ratio of 1:1.

5.4 Summary

In this chapter, 3D lithium polysulfide batteries were demonstrated using two types of 3D anodes: lithium-plated 3D nickel current collector arrays and 3D lithium square post arrays. Early designs incorporating lithium-plated nickel array anodes were expensive and time-consuming, due to the nature of the silicon mold fabrication techniques used to form the nickel array. As a result, a new method of forming molds using polystyrene was developed. Polystyrene molds were micromachined, nickel was deposited through the molds via electrodeposition, and the molds were dissolved using toluene. Lithium was then electrodeposited onto the nickel array using pulsed deposition and batteries were assembled using these anodes.

Lithium-plated 3D nickel current collector anodes were successfully fabricated and incorporated into battery cells. The 3D-Ni_{400,PS} Li_2S_6 battery exhibited higher areal capacity due to the relatively large volume available for the liquid cathode resulting from smaller diameter posts (i.e., 400 μm). On the other hand, the 3D-Ni_{800,PS} Li_2S_6 battery exhibited less capacity fading and better rate capabilities because of the larger surface area resulting from larger diameter posts (i.e., 800 μm).

Another benefit of the developed polystyrene molds is the ability to electrodeposit through the mold and remove the mold within an inert atmosphere glovebox. This allows the fabrication of pure lithium 3D architectures. By microprinting polystyrene paint onto nickel and then depositing lithium through the template and dissolving the template inside the glovebox, 3D lithium square-post arrays were successfully fabricated. However, the lithium square-post array Li_2S_6 battery
exhibited capacity fading and poor rate capabilities. This is most likely caused by the small amount of surface area resulting from the combination of low aspect ratio (i.e., 1:1) and small diameter (i.e., 200 μm). Although capacity retention and higher rate capabilities are anticipated with larger aspect ratio posts, interdigitating the molybdenum current collector is believed to increase the rate capabilities of the 3D Li₂S₉ battery.
Chapter 6 - Li₂S₆ Sol-gel Batteries

6.1 Introduction

6.1.1 Motivation

A novel polysulfide-based gel cathode has been synthesized using the sol-gel process. One motivation behind using sol-gel processing is that lithium polysulfide can be contained within a solid-state silica matrix, which means that more battery configurations could be produced using simpler processes. For example, compared to using a liquid cathode, forming a leak-free battery with the polysulfide gel cathode would require fewer steps and parts. The assembly of such a sol-gel cathode would be analogous to forming an epoxy coating on a surface; the sol would be mixed with the liquid cathode and applied to a lithium anode where it would be sandwiched in between the lithium and a molybdenum current collector and allowed to gel. Since the silica matrix is electrically insulating, the gel cathode would behave analogously to the liquid cathode and would not short with lithium.

Another motivation of using a sol-gel cathode is the possible formation of a protective SEI layer that would prevent polysulfide shuttling analogously to LiNO₃. Umeda et al. have shown that by dipping lithium into TEOS, an electrochemically stable protective film can be formed on the surface of lithium, in which lithium can be plated and stripped at 1 mA·cm⁻² without any change in cell impedance for 100 cycles. The authors state that the protective silicate film is initiated at the surface of the lithium metal, where the concentration of hydroxyl groups is high, according to

\[ \text{LiOH} + \text{Si(OR)}_4 \rightarrow \text{LiO-Si(OR)}_3 + \text{ROH} \]  \hspace{1cm} (6.6)

where R is an ethyl group. Hence, a liquid cathode sol should behave similarly when gelled in the presence of a lithium anode.
6.1.2 Sol-gel processing

Sol-gel chemistry allows vitreous silica (SiO₂) to be synthesized at room temperature through chemical reactions, as opposed to traditional glass formation methods that require the melting and quenching of molten silica. Through the sol-gel process, silica can be synthesized using a number of tetraalkoxysilane (Si(OR)₄) precursors, of which Si(OCH₃)₄ (tetramethoxysilane or TMOS) and Si(OCH₂CH₃)₄ (tetraethoxysilane or TEOS) are most commonly used. When reacted with water, these precursors undergo two simultaneous reactions, hydrolysis (6.1) and condensation (6.3–6.5).[^86]

**Hydrolysis**

\[
\text{Si(OR)₄ + H₂O} \rightarrow \text{HO–Si(OR)₃ + ROH} \quad (6.1)
\]

\[
\vdots
\]

\[
\rightarrow \text{Si(OH)₄ + 4ROH} \quad (6.2)
\]

**Condensation**

\[
\text{Si(OH)₄ + Si(OH)₄} \rightarrow (\text{OH})₃\text{Si–O–Si(OH)₃} + \text{H₂O} \quad (6.3)
\]

\[
(\text{OR})₃\text{Si–OH} + \text{HO–Si(OR)₃} \rightarrow (\text{OR})₃\text{Si–O–Si(OR)₃} + \text{H₂O} \quad (6.4)
\]

\[
(\text{OR})₃\text{Si–OH} + \text{Si(OR)₄} \rightarrow (\text{OR})₃\text{Si–O–Si(OR)₃} + \text{ROH} \quad (6.5)
\]

Hydrolysis generally involves the use of a catalyst (i.e., acid) for the tetraalkoxysilane precursor and water to undergo a bimolecular nucleophilic substitution (SN₂) reaction, of which an alcohol (ROH) is the byproduct. Repeating hydrolysis an additional three times on the same alkoxysilane molecule produces a solution of fully hydrolyzed silanes in alcohol, or “sol” (6.2). Condensation generally occurs in the presence of hydrolyzed silane molecules (6.3–6.5). Hydrolyzed
(fully or partially) silane molecules condense together forming Si–O–Si bridges, in which a three-dimensional SiO₂ network is formed, producing water and/or alcohol as byproduct(s).

Figure 6.1 depicts an overview of sol-gel processing. Depending on the drying technique, different gels can be formed for various applications. By coating the sol onto a substrate and allowing the solvent(s) to evaporate, xerogel films are formed. If these materials are sintered, dense films can result. By casting the sol into a mold, wet gels are formed. If the system is sealed, the gel
remains wet. However, by allowing the solvents to evaporate, xerogels can be formed. Wet gels can also form aerogels through solvent extraction. The ideal gel for the lithium polysulfide cathode is a wet gel, which is a porous, three-dimensional SiO$_2$ matrix infiltrated with catholyte.

Sols made via the acid catalyzed sol-gel route contain water and alcohol and will therefore react with lithium metal. These reactions must be avoided. Thus, a non-aqueous synthesis must be used, which produces neither byproduct, leaving a non-hydrolytic sol-gel route as the method of choice for synthesizing the polysulfide gel cathode. Metal oxides (including silica) can be formed via non-hydrolytic sol-gel routes through the reaction of: (I) metal halide with alcohol (6.7),$^{87-89}$ (II) metal halide with metal alkoxide (6.8),$^{88-90}$ and (III) metal alkoxide with carboxylic acid (6.9).$^{88,91,92}$

\[
\begin{align*}
M-X + ROH & \rightarrow M-OH + RX \\
M-X + M-OR & \rightarrow M-O-M + RX \\
M-OR + R'COOH & \rightarrow MO-O-CR' + ROH
\end{align*}
\] (6.7) (6.8) (6.9)

This research deals with the formation of a Li$_2$S$_6$ sol-gel (polysulfide gel) cathode via a non-hydrolytic sol-gel route using the first method listed above (6.7).

6.2 Experimental

6.2.1 Chemicals

Lithium sulfide (Li$_2$S) powder, 99.9% (12839, Alfa Aesar), was inserted into an argon (Ultra High Purity Ar, Air Liquide) filled glovebox and used as received. Sulfur, 99.98% (414980, Sigma-Aldrich), and lithium trifluoromethanesulfonate (lithium triflate, LiSO$_3$CF$_3$), 99.995% (481548, Sigma-Aldrich), powders were dried separately on a Schlenk line by purging with argon three times and then raising the temperature to 120°C for 6 hours under vacuum. Inhibitor-free anhydrous tetrahydrofuran (THF), ≥99.9% (401757, Sigma-Aldrich), and anhydrous 1,3-dioxolane (DXL) with
~75 ppm butylated hydroxytoluene as inhibitor, 99.8% (271020, Sigma-Aldrich), were placed into the glovebox and used as received.

Tetraethylene glycol dimethyl ether, or tetruglyme, (TG), 99% (172405, Sigma-Aldrich), was dried on a Schlenk line by purging with argon three times and then raising the temperature to 105°C for 4 hours under vacuum. 4Å molecular sieves (208604, Sigma-Aldrich) were dried on a Schlenk line by purging with argon three times and then raising the temperature to 225°C for 24 hours. After placement into the glovebox, the TG was run through a column filled with the dry molecular sieves at a rate of two drops per second.

Silicon tetrachloride (SiCl₄) precursor, 99.998% (289388, Sigma-Aldrich), and anhydrous tert-butanol, ≥99.5% (471712, Sigma-Aldrich), were used as received.

6.2.2 500mM Li₂S₆ Synthesis

Li₂S₆ was synthesized in an argon filled glovebox according to the scheme shown in Figure 4.1. THF is added to lithium sulfide and sulfur powders, at a molar ratio of 1:5::Li₂S:S, in a glass vial and stirred for several hours. Once the powders have reacted, TG is added. The THF is then extracted from the solution by evaporating under vacuum, while heating at 85°C. The remaining Li₂S₆ in TG is a viscous solution.

In a separate glass vial, LiSO₃CF₃ salt is added to DXL and stirred for several hours. Once dissolved, the electrolyte solution is added to the lithium polysulfide. This final solution is the liquid cathode, or catholyte, and is composed of 500mM Li₂S₆ and 0.8M LiSO₃CF₃ in TG/DXL (30/70 v/v).
6.2.3 Sol-gel Synthesis

Lithium polysulfide-containing gels were synthesized using a modified version of the non-hydrolytic sol-gel route reported by Vioux et al.\textsuperscript{87,89} Inside of an argon filled glovebox, SiCl\textsubscript{4} is slowly added to a mixture of tert-butanol and tetraglyme inside of a Schlenk-type flask; a typical molar ratio of SiCl\textsubscript{4}:tert-butanol:tetraglyme is 1.0:1.5:0.43. The solution is sealed using a rubber turnover septum stopper and allowed to react for 18 hours while stirring. The flask is then removed from the glovebox, installed on a vacuum line, and heated at 95°C under vacuum (~500 mTorr) to evaporate any unreacted precursors and/or trace water molecules. The flask is brought to 1 atm, by purging the vacuum line with nitrogen, and inserted into the glovebox. This solution is called the “sol.” Once synthesized, one part sol and one part catholyte are mixed together in a glass vial to form a polysulfide-sol. The polysulfide-sol is then cast into the battery cell for electrochemical characterization. The remaining polysulfide-sol is left to gel in the glass vial for characterization of its physical properties.

6.2.4 Battery Preparation

3-electrode batteries were constructed as shown in Figure 6.2 using molybdenum, 99.995% (10034, Alfa Aesar), and nickel, 99.5% (11453, Alfa Aesar), rods of ½” diameter as the cathode and anode current collectors, respectively. First, lithium foil, 99.9% (320080, Sigma-Aldrich), is polished using a polyethylene plate and pressed onto the nickel rod. The nickel rod is then inserted into a modified polyethylene (PE) sleeve, followed by a PE spacer (■-ring), both of which are cut to allow contact between the polysulfide gel and the lithium reference electrode. The molybdenum rod is then inserted into the sleeve and polysulfide-sol is injected into the cell through the PE sleeve and
-ring. A polished sheet of lithium foil is wrapped around the PE sleeve, sealing the cell, and a hose clamp is tightened around the lithium foil to ensure a tight seal.

Figure 6.2 3-electrode battery cell components and construction

### 6.2.5 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is a technique in which a sinusoidal signal (usually potential) is passed through a cell to provide information about both the electrolyte and the interface under steady-state conditions. Signal amplitude is generally on the order of 10mV, to keep the system close to equilibrium, while signal frequency, $f$, is varied over a broad range (usually 100 kHz – 100 mHz) to determine the electrical characteristics of the interface. Thus, electrochemical cells can be described as having common circuit elements, resistors, capacitors, and inductances, with a complex impedance of magnitude $Z$ according to

$$Z = Z_{\text{real}} + jZ_{\text{imag}} \quad (j = \sqrt{-1})$$

(6.10)

where $Z_{\text{real}}$ and $Z_{\text{imag}}$ are the real and imaginary impedance components, respectively.
The Warburg impedance, which is depicted in the equivalent circuit in Figure 6.3b, represents the diffusive constraints in electroactive species and is a function of frequency according to

$$Z(\omega) = \frac{\sigma}{\omega^{1/2}} - \frac{j\sigma}{\omega^{1/2}}$$  \hspace{1cm} (6.11)

where $\sigma$ is a constant and $\omega$ is the angular frequency. Contributions of the Warburg impedance on electron transfer limitations, due to limitations in mass transport of electroactive species at low frequencies, can be realized by

$$Z(\omega) = R_s + R_{ct} \left[ 1 + \frac{\lambda}{\sqrt{2\omega}} \right] - \frac{j R_{ct} \lambda}{\sqrt{2\omega}} C_d - \frac{jR_s\lambda}{\sqrt{2\omega}}$$  \hspace{1cm} (6.12)
where $R_s$ is the solution resistance, $R_{ct}$ is the charge transfer resistance, $\lambda = k_f \cdot D_O^{-1/2} + k_b \cdot D_R^{-1/2}$, $k_f$ and $k_b$ are the forward and backward electron-transfer rate constants, and $D_O$ and $D_R$ are the diffusion coefficients for the oxidant O and reductant R for the reaction $O + ne^- \leftrightarrow R$. Figure 6.4 shows computer simulations of equation 6.12. The Nyquist plot (a) shows the effect of polarization resistance on the real, $Z'(\omega)$, and imaginary, $Z''(\omega)$, impedance. For comparison purposes, a circuit comprised of a single 1 kΩ resistor would appear as a single point on the $Z'$ axis, while a capacitor would appear as a vertical line parallel to the $Z''$ axis and intersecting the $Z'$ axis at the value equal to the contact resistance. At low frequencies, the Warburg contribution dominates and the phase angle in the Nyquist (a) and Bode (c) plots approaches 45°.

Figure 6.4 Nyquist (a) and Bode (b and c) plots simulated using equation 6.12. (Adapted from Park et al.) Contribution of Warburg impedance (●) is shown for the case of $R_{ct} = 2$ kΩ. $R_s$, 10 Ω; $C_d$, 20 μF; $R_{ct}$ (●), 100 Ω; $R_{ct}$ (★), 500 Ω; $R_{ct}$ (△), 1 kΩ; $R_{ct}$ (◆), 2 kΩ.
From the Nyquist plot (Figure 6.4a), the time constant, $\tau$, can be obtained according to

$$R_\alpha \cdot C_d = \frac{1}{\omega_c} = \frac{1}{2\pi \cdot f_c} = \tau \quad (6.13)$$

where $\omega_c$ is the critical angular frequency at which $Z''(\omega)$ is maximum. The time constant of a given electrochemical reaction indicates how fast the reaction takes place. Bode plots express the magnitude of the impedance as a function of $\omega$ (Figure 6.4b), indicating values of solution resistance at high frequency and the sum of solution and charge transfer resistances at low frequency. Bode plots of phase shift, $\Phi$, as a function of $\omega$ (Figure 6.4c) show transitions between resistance ($\Phi = 0^\circ$) and capacitance ($\Phi = -90^\circ$) dominating contributions to impedance.

### 6.2.6 Measurements

Electrochemical measurements were carried out at room temperature in an argon glovebox using a three-electrode cell (Figure 6.2) consisting of molybdenum working, lithium counter, and lithium reference electrodes; thus, all potentials in this chapter are referenced to Li/Li$^+$. Cyclic voltammetry (CV) and Galvanostatic Cycling with Potential Limitation (GCPL) experiments were recorded through EC-Lab software using a VMP3 Multi Potentiostat by Bio-Logic SA. EIS measurements were recorded using a 1252a Frequency Response Analyzer in conjunction with a 1287 Potentiostat/Galvanostat (Solartron Analytical). All three-electrode battery cells used a standard volume of about 100 $\mu$L, with a molybdenum–lithium (counter) separation of about 1 mm. In CV experiments, battery half-cells were cycled between 0.5V and 4V vs. Li/Li$^+$. In EIS experiments, battery half-cells were characterized using the Potentio Electrochemical Impedance Spectroscopy (PEIS) technique, in which the amplitude of the potential wave was 10mV and the frequency was varied between $10^{-1} - 10^5$ Hz. GCPL experiments were carried out on the three-electrode battery cells by removing the reference wire from the lithium reference foil and connecting
it to the lithium-deposited nickel rod. Thus, two-electrode batteries were cycled between 2.8V and 1.8V.

6.3 Results and Discussion

6.3.1 Polysulfide gel physical properties

Polysulfide gels synthesized via the modified non-hydrolytic sol-gel route resemble coagulated human blood. Typically, one part catholyte is added to one part sol, the resulting polysulfide-sol is swirled for a few seconds, and gelation occurs within an hour (the polysulfide gel). It should be noted that the sol does not gel without addition of the catholyte. Also, the sol gels within 45 minutes when either catholyte (with LiSO₃CF₃) or Li₂S₆-TG solution is added, indicating that the polysulfide is inducing gelation. To the touch, the polysulfide gels feel viscoelastic. Thus, the polysulfide gels are dark red, soft, and can be elastically deformed. One important observation is that the gels remain red, which is indicative of the lithium polysulfide stability in the gel. Earlier versions of the polysulfide gels used non-hydrolytic sols of slightly higher water content which caused the gel color to change from dark red to yellow, which is an indication of sulfur precipitation.

<table>
<thead>
<tr>
<th>Li₂S₉ Concentration</th>
<th>Gel composition (volume ratio)</th>
<th>BET Surface Area (m² g⁻¹)</th>
<th>Pore Volume (BJH model) (cm³ g⁻¹)</th>
<th>Pore Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250 mM</td>
<td>Sol:Catholyte::1:2</td>
<td>518.8 ±10.3</td>
<td>0.254</td>
<td>1.96</td>
</tr>
</tbody>
</table>

BET analysis of polysulfide ambigels, which are soaked in a series of solvents (i.e., THF → DXL → acetone → pentane), are summarized in Table 6.1. The analysis indicates that the
polysulfide gels are very porous. The BET surface area, pore volume (BJH method), and pore diameter are 518.8 m\(^2\)·g\(^{-1}\) (± 10.3 m\(^2\)·g\(^{-1}\)), 0.254 cm\(^3\)·g\(^{-1}\), and 1.96 nm, respectively.

### 6.3.2 Electrochemical activity

A 250mM Li\(_2\)S\(_6\) sol-gel battery was fabricated by mixing 1 part sol to 1 part 500mM Li\(_2\)S\(_6\) catholyte, containing 0.8M LiSO\(_3\)CF\(_3\) in TG/DXL (30/70 v/v), and injecting the polysulfide-sol into the three-electrode battery cell shown in Figure 6.2. The cell is then sealed with a sheet of lithium foil which also serves as the reference electrode. The impedance of the polysulfide sol-gel cathode showing the sol-to-gel transition can be seen in Figure 6.5. Table 6.2 summarizes the EIS analysis of the polysulfide gel cathode using the equivalent circuits shown in Figure 6.5a, where CPE is a constant phase element. Initially, the polysulfide-sol (□) has an R\(_s\) and R\(_ct\) of 103 Ω and 1570 Ω, respectively. Gelation occurs after about 45 minutes and approximately 2 hours after gelation (○), R\(_s\) and R\(_ct\) increase to 200 Ω and 1960 Ω, respectively. This increase in resistance is very small, considering that the cathode has transitioned from a liquid to a solid phase, indicating that the gel is behaving similar to a liquid sol. After the battery is galvanostatically cycled (two-electrode GCPL) for about 5 weeks, excess electrolyte was added to the cathode by soaking 0.8M LiSO\(_3\)CF\(_3\) in TG/DXL (30/70 v/v) into the polysulfide gel and the impedance analysis (three-electrode EIS) of the polysulfide gel cathode (▲) shows that the molybdenum-polysulfide gel interface becomes more complex (Figure 6.5a), with an R\(_2\) and R\(_3\) of 97 Ω and 1230 Ω, respectively. The solution resistance drops slightly to 182 Ω. Even with excess lithium salt, R\(_s\) is similar in the gel before and after cycling, indicating that the solution impedance is most likely limited by the pore diameter (1.96 nm) of the silica matrix.
Figure 6.5 Nyquist (a) and Bode (b) plots of 250mM Li$_2$S$_6$ sol-gel cathode in the sol (□) and gel (○) phases and after battery cycling (△). Dotted lines in (a) indicate equivalent circuit model fit. Electrodes: molybdenum, working; lithium, counter; lithium, reference. Electrolyte: 0.4M LiSO$_2$CF$_3$. 
Table 6.2 Summary of EIS analysis of polysulfide gel cathode

<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 6.6 shows a cyclic voltammogram of the polysulfide gel after the sol-gel transition. At a scan rate of 1 mV·s$^{-1}$, both oxidation and reduction peaks are observed, indicating that Li$_2$S$_6$ is electrochemically active within the silica matrix. The peak-to-peak separation is about 1.2V, indicating an electrochemically irreversible system. However, the capacity of the oxidation and reduction peaks are 0.19 and 0.17 A·s·cm$^{-2}$, respectively, indicating some chemical reversibility.

Figure 6.6  Cyclic voltammogram of 250mM Li$_2$S$_6$ sol-gel battery after gelation, cathodic direction. Electrodes: molybdenum, working; lithium, counter; lithium, reference. Electrolyte: 0.4M LiSO$_3$CF$_3$. Sweep rate: 1 mV·s$^{-1}$.
6.3.3 **Polysulfide gel battery performance**

Two-electrode GCPL discharge profiles of the polysulfide gel battery in the three-electrode battery cell are shown in Figure 6.7. At a current density of 100 μA·cm⁻² (a) the IR drop and ohmic polarization are large. The large cell resistance is associated with long diffusion paths, due to the dimensions of the three-electrode battery cell, and the small pore diameter of the silica matrix. In this case, a discharge capacity of only 17 μA·h·cm⁻² is achieved over 5 cycles. When the current density is reduced by a factor of two (b), both high and low voltage plateaus are present over the four discharge cycles and the capacity increases significantly to as high as 750 μA·h·cm⁻². At 10 μA·cm⁻² (c) the discharge capacity increases further to roughly 1 mA·h·cm⁻².

![Figure 6.7](image)

**Figure 6.7** GCPL discharge profiles of 250mM Li₂S₆ sol-gel battery at (a) 100 μA·cm⁻², (b) 50 μA·cm⁻², and (c) 10 μA·cm⁻². Electrodes: molybdenum, working; lithium, counter/reference. Electrolyte: 0.4M LiSO₃CF₃.

Figure 6.8 shows a Ragone plot of the polysulfide gel battery (○). For comparative purposes, the 500mM (●) and 100mM (▲) Li₂S₆ liquid cathode batteries are also shown. At low discharge rates, the energy density of polysulfide gel battery is 2.3 mW·h·cm⁻², which is comparable to the liquid cathode batteries. At high discharge rates, the power density of polysulfide gel battery is comparable to the liquid cathode batteries. For example, at 100 μA·cm⁻², the power density of the polysulfide
gel, 500mM Li$_2$S$_6$ liquid, and 100mM Li$_2$S$_6$ liquid cathode batteries are 0.19 mW·cm$^{-2}$, 0.20 mW·cm$^{-2}$, and 0.19 mW·cm$^{-2}$, respectively. On the other hand, the energy density of the polysulfide gel at 100 $\mu$A·cm$^{-2}$ is 0.03 mW·h·cm$^{-2}$, which is far less than the liquid cathodes. This is mainly due to the cell geometry of the polysulfide gel battery. However, it is also likely that the silica matrix plays a major role in the rate capabilities of the polysulfide gel and that catholyte diffusion could be restricted by narrow pores.

![Figure 6.8](image)

**Figure 6.8** Ragone plot of batteries with polysulfide gel (●), 500mM Li$_2$S$_6$ liquid (○), and 100mM Li$_2$S$_6$ liquid (○) cathodes. Electrodes: molybdenum, working; lithium, counter/reference. Electrolyte: 0.4M LiSO$_3$CF$_3$.

### 6.4 Summary

Lithium polysulfide has been incorporated into a silica matrix using a non-hydrolytic sol-gel route. The resulting polysulfide gel cathode is encapsulated within a porous silica matrix. Cyclic
voltammetry indicates that, although the polysulfide gel shows electrochemical irreversibility, the lithium polysulfide is electrochemically active within the silica matrix. GCPL shows that the polysulfide gel battery is secondary in nature. In first-generation polysulfide gel batteries, up to 1 mA·h·cm⁻² is obtained.
Chapter 7 - Conclusions

Three-dimensional (3D) battery architectures have emerged as a new direction for powering microelectromechanical systems and other small autonomous devices. Although there are few examples to date of fully functioning 3D batteries, these power sources have the potential to achieve high power density and high energy density in a small footprint. With the limited advances made in the fabrication of components designed for these devices, there remain several technical challenges. Probably one of the most challenging tasks in the mass-production of 3D batteries is the formation of a conformal, electrolyte separator coating on the 3D electrode, which becomes progressively challenging with increasing aspect ratio. This problem can be solved using a lithium polysulfide liquid cathode, which has been shown to be stable in direct contact with the lithium anode without creating an electrical short, thus eliminating the need for a conformal electrolyte separator. In fact, even after high power cycling, the open-circuit potential of lithium polysulfide batteries appears to be stable for months, indicating that self-discharge within the battery is very low.

The first part of this dissertation deals with the synthesis, electrochemical characterization, and battery performance of lithium polysulfide liquid cathodes (Chapter 3). Although cyclic voltammetry indicates that lithium polysulfide redox is electrochemically irreversible, galvanostatic cycling with potential limitation shows that Li$_2$S$_{12}$ batteries are secondary in nature, exhibiting discharge capacities as high as 0.8 mA·h·cm$^{-2}$, using 100mM Li$_2$S$_{12}$ (1.2M S), when the liquid cathode is cycled between Li$_2$S$_{12}$ and Li$_2$S$_3$. By synthesizing Li$_2$S$_6$, sulfur loading is increased to 9M S (Chapter 4). The discharge capacity is increased to as high as 2 mA·h·cm$^{-2}$, using 500mM Li$_2$S$_6$ (3M S), when the battery is cycled at 0.1 mA·cm$^{-2}$. Further concentration of Li$_2$S$_6$ increases the sulfur loading but at the expense of cell resistance, which leads to shortcomings in the discharge capacity.
Lithium nitrate is effective at suppressing the polysulfide shuttle mechanism, allowing the liquid cathode to charge to Li$_2$S$_{12}$, thus increasing the coulombic efficiency to 100% (at current densities between 50 and 200 μA·cm$^{-2}$) when the battery is cycled between Li$_2$S$_{12}$ and Li$_2$S$_3$. Further gains in capacity and energy are observed when batteries are cycled beyond Li$_2$S$_3$, but at the expense of coulombic efficiency. With the addition of methyl acetate, the discharge capacity, coulombic efficiency, and energy density are increased because of the oxidation of some of the polysulfide chains to Li$_2$S$_{100}$. MA-containing liquid cathodes produce batteries that perform exceptionally for up to 11 cycles.

The next part of this dissertation deals with the fabrication of 3D batteries using Li$_2$S$_6$ liquid cathodes and 3D lithium anodes (Chapter 5). Initially, 3D anode current collectors were fabricated by electrodepositing nickel onto the negative battery terminal through a silicon mold and then sacrificially etching the silicon mold. Lithium was then electrodeposited onto the 3D nickel current collector array to form the 3D anode. However, the resources and labor associated with the process of forming the silicon molds are excessive. As a result, a new, quicker, and simpler method of forming 3D nickel current collectors was developed. This method consists of forming polymer molds using micromachining techniques, electrodepositing nickel onto the negative battery terminal, and dissolving the polymer mold using a solvent. An advantageous benefit of the developed process is the ability to form 3D architectures using moisture/air sensitive elements such as alkali metals. A second process was developed in which a polymer paint is printed onto the negative battery terminal and a 3D array of pure lithium is grown via electrodeposition, after which the template is removed via dissolving in an organic solvent.

3D batteries were demonstrated using anodes fabricated from silicon molds and the developed polystyrene molds. Table 7.1 compares commercial primary lithium thick-film (Panasonic ML414S) and thin-film (ST EFL700A39) batteries to our secondary 3D 100mM Li$_2$S$_6$
batteries (3D-Ni_{PS,400}, 3D-Ni_{PS,800}, and 3D-Ni_{Square,200}). Even with lower nominal voltage, the lithium-plated 3D Li_{2}S_{6} batteries (3D-Ni_{PS,400} and 3D-Ni_{PS,800}) generate higher power densities than both the commercial Panasonic and ST batteries. Typically, the areal energy density of these 3D batteries lies between that of the thick-film and the thin-film batteries. It should be noted, however, that the values listed for the 3D batteries are based on discharge current densities that are >9 times and >3 times larger than those of those listed for the Panasonic and ST batteries, respectively. It should also be noted that the values listed for our lithium polysulfide batteries (Table 7.1) do not take the mass or volume of the packaging into consideration. Nevertheless, the performances of the Li_{2}S_{6} batteries indicate a promising secondary battery system. However, further optimization is required to increase the volumetric energy density without compromising the power density. For example, the 2D 0.5M Li_{2}S_{6} battery (Table 7.1) shows outstanding energy storage/delivery behavior and incorporating it in a 3D battery could have a significant impact on increasing the volumetric, as well as the areal, energy density.

Table 7.1 Energy and Power densities of lithium polysulfide batteries compared to commercial primary lithium batteries.

<table>
<thead>
<tr>
<th></th>
<th>Panasonic (ML1415S)</th>
<th>ST (EFL700A39)</th>
<th>100mM Li_{2}S_{6} 3D Batteries (3D-Ni_{PS,400}) (3D-Ni_{PS,800}) (3D-Ni_{Square,200})</th>
<th>0.5M Li_{2}S_{6} (2D Battery)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
<td>1.45 mm</td>
<td>0.2 mm</td>
<td>1.2 mm</td>
<td>0.5 mm</td>
</tr>
<tr>
<td>Voltage</td>
<td>3.0 V</td>
<td>3.9 V</td>
<td>2.2 V</td>
<td>2.2 V</td>
</tr>
<tr>
<td>Current Density</td>
<td>0.053 mA·cm^{-2}</td>
<td>0.15 mA·cm^{-2}</td>
<td>0.5 mA·cm^{-2}</td>
<td>0.5 mA·cm^{-2}</td>
</tr>
<tr>
<td>Areal Energy Density</td>
<td>21.2 mW·h·cm^{-2}</td>
<td>0.49 mW·h·cm^{-2}</td>
<td>0.52 mW·h·cm^{-2}</td>
<td>0.55 mW·h·cm^{-2}</td>
</tr>
<tr>
<td></td>
<td>76 J·cm^{-2}</td>
<td>1.76 J·cm^{-2}</td>
<td>1.9 J·cm^{-2}</td>
<td>2.0 J·cm^{-2}</td>
</tr>
<tr>
<td>Volumetric Energy</td>
<td>146 mW·h·cm^{-3}</td>
<td>24 mW·h·cm^{-3}</td>
<td>4.4 mW·h·cm^{-3}</td>
<td>4.7 mW·h·cm^{-3}</td>
</tr>
<tr>
<td>Density</td>
<td>527 J·cm^{-3}</td>
<td>16 J·cm^{-3}</td>
<td>16 J·cm^{-3}</td>
<td>17 J·cm^{-3}</td>
</tr>
<tr>
<td>Power Density</td>
<td>0.13 mW·cm^{-2}</td>
<td>0.60 mA·cm^{-2}</td>
<td>1.1 mW·cm^{-2}</td>
<td>1.0 mW·cm^{-2}</td>
</tr>
</tbody>
</table>
The final part of this dissertation focused less on 3D batteries and was geared more towards the use of the sol-gel process to make gel cathodes in which the liquid lithium polysulfide catholyte is confined within the solid matrix of a three-dimensional silica network. This is a unique concept for a few reasons. One reason is that the liquid cathode can flow freely within the pores, making the polysulfide gel cathode electrochemically active, as is shown by cyclic voltammetry and galvanostatic cycling data of polysulfide gel batteries. Another reason is that when it comes to transitioning this technology from the laboratory bench top to the manufacturing sector, the integration of a sol-gel cathode into a battery cell seems to be much more straightforward and require fewer processes than the integration of a liquid cathode. Finally, the formation of a silane SEI during gelation could possibly increase the stability of the lithium anode and prevent the polysulfide shuttle mechanism from limiting the coulombic efficiency. Although the latter has not been shown thus far, polysulfide gel batteries have been fabricated and galvanostatically cycled, demonstrating rechargeability. However, further investigation is needed to understand the nature of gelation and the feasibility of commercializing a long shelf-life, profitable battery using the polysulfide gel cathode.
Chapter 8 - Future Work

One milestone that truly needs to be achieved to unleash the unrevealed energy and power generation capabilities of the 3D liquid cathode battery is to fabricate a battery with interdigitated current collectors. A simple and achievable model is the parallel plate architecture, of which a proof-of-concept would be demonstrated using current collectors fabricated from either silicon or polymer molds. For example, a silicon mold could be formed, with the pattern shown in Figure 8.1, using CMOS technology to form trenches throughout the entire thickness of a silicon wafer. The mold would then be mounted to an insulating substrate, for example a glass slide, using hot glue. If a thin layer (~200 nm) of nickel were to be deposited on the glass surface through the trenches, then nickel and molybdenum could separately be electrodeposited, filling the anode and cathode trenches, respectively. The silicon would then be etched using xenon difluoride, leaving an interdigitated array of molybdenum and nickel current collector plates (Figure 8.2). Lithium would then be electrodeposited on the nickel and the injection of Li$_2$S$_6$ catholyte would form a complete 3D battery.

Figure 8.1 Specifications of proposed interdigitated parallel-plate mold. Continuous black region is the mold material; shaded gray regions are the through holes/trenches where current collector is to be deposited.
Table 8.1 lists the dimensions of the interdigitated plates based on the mold design shown in Figure 8.1. The internal footprint area, which will contain the anode (lithium) and cathode \((\text{Li}_2\text{S}_6)\), is 1 cm\(^2\). If a 1 mm thick silicon mold were to be used, then the aspect ratio of the anode and cathode current collector plates would be 100:1 and 50:1, respectively. Because of the parallel plate design, the thickness of the battery (i.e., height) could be very large (i.e., 1 mm) without increasing the diffusion distances of electroactive redox species between the anode and cathode current collectors. As a result, the surface area of each current collector array would be 18.6 times larger than the internal footprint area.

<table>
<thead>
<tr>
<th>Current Collector</th>
<th>Plate Length, L (mm)</th>
<th>Plate Width, W (mm)</th>
<th>Plate Height, h (mm)</th>
<th>Aspect Ratio (h:W)</th>
<th>Pitch, P (mm)</th>
<th>Areal Density (plates cm(^{-2}))</th>
<th>Plate Volume (mm(^3) cm(^{-2}))</th>
<th>Surface Area (cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>9.25</td>
<td>0.01</td>
<td>1</td>
<td>100:1</td>
<td>0.1</td>
<td>100</td>
<td>9.25</td>
<td>18.6</td>
</tr>
<tr>
<td>Cathode</td>
<td>9.25</td>
<td>0.02</td>
<td>1</td>
<td>50:1</td>
<td>0.1</td>
<td>100</td>
<td>18.5</td>
<td>18.6</td>
</tr>
</tbody>
</table>

Table 8.2 lists the specifications of two different 3D \(\text{Li}_2\text{S}_6\) interdigitated plate batteries, a 5 mA·h \((\alpha)\) and an 8.2 mA·h \((\beta)\) battery. It should be noted that these values are based on the cycling between \(\text{Li}_2\text{S}_{12}\) and \(\text{Li}_2\text{S}_3\). In battery \(\alpha\), the amount of lithium required would form a ~1.3 \(\mu\)m lithium film on the nickel surface, leaving 70 \(\mu\)L of volume available for the catholyte. Thus, a 0.89M \(\text{Li}_2\text{S}_6\) liquid cathode would be used. Similarly, battery \(\beta\) would have a ~2.1 \(\mu\)m film of lithium and incorporate 68 \(\mu\)L of 1.5M \(\text{Li}_2\text{S}_6\) catholyte. Although the performance of 2D 1.5M \(\text{Li}_2\text{S}_6\) batteries have been unsatisfactory (Chapter 4), the small separation between the lithium anode and molybdenum current collector (i.e., ~33 \(\mu\)m) in battery \(\beta\) should be sufficiently small enough to accommodate the sluggish diffusion resulting from the high viscosity of the catholyte.
Figure 8.2 Proposed interdigitated parallel-plate design for 5 mA·h·cm$^{-2}$ and 8.2 mA·h·cm$^{-2}$ 3D liquid cathode batteries, in which the catholyte would be confined to the left side of the white dotted line. Green, cathode current collector; red, anode current collector. Active footprint area, 1 cm$^2$.

Because of the large aspect ratio of the mold features, formation of the interdigitated plates will be challenging for a few reasons. One reason is because depositing the seed layer might be difficult. The seed layer consists of an adhesion layer, usually titanium, and a nickel layer. If deposition is done via sputtering, particles could deposit non-uniformly on the glass substrate and along the mold walls. On the other hand, if deposition is done via evaporation, then condensation could occur at the mold openings, clogging the holes and preventing the atoms from ever reaching the substrate. The second reason why this design may be challenging is that the electrodeposition of molybdenum is more difficult at these high aspect ratios, than with nickel, and might require some effort to form smooth molybdenum plates. Nevertheless, formation of the current collector plates is possible and with the demonstration of the proposed 3D interdigitated lithium polysulfide battery, perhaps there will be overwhelming proof that efforts in fabricating 3D batteries are worth the time and money.
Table 8.2 Specifications of 5 mA·h and 8.2 mA·h 3D interdigitated plate Li₂S₆ batteries

<table>
<thead>
<tr>
<th></th>
<th>Nominal Capacity</th>
<th>Li₂S₆ Concentration</th>
<th>Catholyte Volume</th>
<th>Lithium Mass</th>
<th>Lithium Film Thickness</th>
<th>Lithium–Molybdenum Separation</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>5 mA·h·cm⁻²</td>
<td>0.89M</td>
<td>70 µL</td>
<td>1.3 mg</td>
<td>~1.3 µm</td>
<td>~34 µm</td>
</tr>
<tr>
<td>β</td>
<td>8.2 mA·h·cm⁻²</td>
<td>1.5M</td>
<td>68 µL</td>
<td>2.1 mg</td>
<td>~2.1 µm</td>
<td>~33 µm</td>
</tr>
</tbody>
</table>
References

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