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UNIVERSITY OF CALIFORNIA
RIVERSIDE

Synthesis of Lithium Sulfide Carbon Composites via Aerosol Spray Pyrolysis

A Dissertation submitted in partial satisfaction
of the requirements for the degree of

Doctor of Philosophy
in
Chemical and Environmental Engineering
by
Noam Hart

June 2017

Dissertation Committee:

Dr. Juchen Guo, Chairperson

Dr. Phillip Christopher

Dr. Lorenzo Mangolini

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Noam Hart

2017

The Dissertation of Noam Hart is Approved:

Committee Chairperson

University of California, Riverside

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Dedication

This dissertation is dedicated to my mother, Valerie; the real doctah here.

She read that paper already. She's just testing to see if I have.

ABSTRACT OF THE DISSERTATION

Synthesis of Lithium Sulfide Carbon Composites via Aerosol Spray Pyrolysis

by

Noam Hart

Doctor of Philosophy, Graduate Program in Chemical and Environmental Engineering

University of California, Riverside, June 2017

Dr. Juchen Guo, Chairperson

This work is an investigation of lithium sulfide carbon ($\text{Li}_2\text{S}@C$) composites synthesis via Aerosol Spray Pyrolysis (ASP). These composites comprise the active portion of a cathode for a Li- Li_2S battery, designed to outperform state of the art Li-ion cells in specific capacity (mAh/g). Producing these composites with ASP taps into the flexibility, product homogeneity and scalability of the system. This project hopes to bridge the gap between promising laboratory scale demonstrations and a commercially viable product.

The key concept of this project is the rationally designed $\text{Li}_2\text{S}@C$ composite microstructure, which consists of nano-scale Li_2S particles uniformly encapsulated in a carbon matrix. We propose ASP as the synthesis method due to its unique operational mechanism: reactant precursors are atomized as aerosol so that each reactant particle is an individual micro-reactor. Operation in micro-reactor scale offers negligible heat and mass transport lags, dramatically improving kinetics and microstructure control.

Three different Li_2S precursors are investigated; lithium nitrate, lithium carbonate and lithium acetate, respectively with sucrose as the carbon precursor. Effective $\text{Li}_2\text{S}-C$ cathodes

have been produced from these three systems and each system delivers subtle microstructure and compositional differences, performing differently as a result. Lithium nitrate and sucrose derived particles appear to perform better in C/5 charging, with a specific capacity of 424 mAh/g after 40 cycles, with a capacity degradation of 0.00156. Whereas lithium carbonate and sucrose derived particles perform better in C/10 charging, with a specific capacity of 438 after 40 cycles, with a capacity degradation of 0.000612. Suggesting differences in architecture, such as porosity, particle size and particle size distribution play a role in affecting performance at different charge rates.

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UNITS

Potential, V

Specific Capacity, $\frac{\text{mAh}}{\text{g}}$

Specific Energy, $\frac{\text{Wh}}{\text{kg}}$

1 INTRODUCTION

1.1 IMPORTANCE AND SCOPE

1.1.1 Energy storage as a technology enabler

The leap from flip-phones to smartphones, with touch screens, pocket-friendly form-factors and wifi connectivity were enabled by the rollout of lithium-ion cells. The previous standard, NiMH (Nickel Metal Hydride), were bulkier and ran at a lower nominal voltage. By transitioning to higher capacity li-ion cells, which ran at 3.6V, a single cell could power the device; whereas NiMH, with a 1.2V nominal output, required two or three cells in series to overcome the resistances in the device. By cutting down to a single cell, the non-capacity components of the cell; casing, governor circuit, terminals; could be minimized. Between less space spent on non-capacity components and the inherently higher capacities of the chemistry, li-ion enabled devices with significantly greater energy requirements. A device

could now run multiple apps simultaneously on a full color backlit touch screen. The charge could be topped up at any point in the day, since li-ion did not suffer from the memory effect plaguing NiMH. Without li-ion, The iPhone would not have been possible. (1)

In a parallel sense, Ni-MH has brought electric drive hybrid vehicles to mass market appeal, in Toyota's iconic Prius and Honda's Insight. Nearly a decade behind the smartphone market, Toyota has recently decided to reconsider li-ion for its cars, having eschewed it for years over safety concerns. While a failed cell per million may be a reasonable bet for a phone that holds just one cell, these odds become significantly less appealing in a car that requires hundreds or thousands of cells. If a single li-ion cell suffers catastrophic failure, the entire pack may go up in flames. The original Prius pack held 240 cells¹, The Tesla Roadster held 6,800². Moreover, a car battery is expected to offer ten years of service, whereas a phone can be expected to be replaced, along with its cell, after two years. The odds of a catastrophic failure, and tens of thousands of dollars in a total loss, are quite high.

While safety is the greatest concern for both automotive and electronics applications, form factor takes close second in electronics. In automotive applications, mass is the next greatest concern. Whereas a few extra grams will not make a difference in already light cell phones, a battery pack sufficient to drive a car four hundred miles would weigh in at close to five metric tons. Chevrolet's announced deal for the Bolt, from supplier LG Chem, pegs the cost at 145 \$/kWh. Even at that cut rate price, a four hundred mile pack will cost nearly \$18,000³ for the cells alone.

¹ <http://toyotapriusbattery.com>

² <http://large.stanford.edu/publications/coal/references/docs/tesla.pdf>

³ Assumes 3.3 miles/kWh, 265 kWh/kg.

A safer, lighter, cheaper cell is necessary to enable the next generation of electric drive vehicles. The promise of a higher capacity, made of cheaper materials with fewer failure modes has made the lithium-sulfur chemistry an attractive research option for years; the following reviews address general progress in the field, discuss challenges and note opportunities for improvement (2) (3) (4) (5) (6) (7) (8). While some notable differences exist between li-ion and lithium-sulfur cells, they both rely on the same general mechanism of action and are subject to similar performance bottlenecks.

1.2 FUNDAMENTALS OF 'ROCKING CHAIR' ELECTROCHEMISTRY

1.2.1 Steady-state mechanism (assumes no degradation mechanisms)

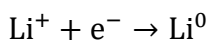
In a Rocking Chair cell, electric energy is converted to chemical energy, via redox reactions. During discharge, an oxidation reaction occurs at the anode,



The electron travels through an external circuit, delivering power to the device, and

reunites with lithium at the cathode, reversing the reaction. During charge, reduction of lithium at the cathode draws

the electron out into the circuit, forcing the lithium to return to the anode, to complete the reaction (9),



In a sense, the lithium rocks back and forth, hence the term, Rocking Chair.

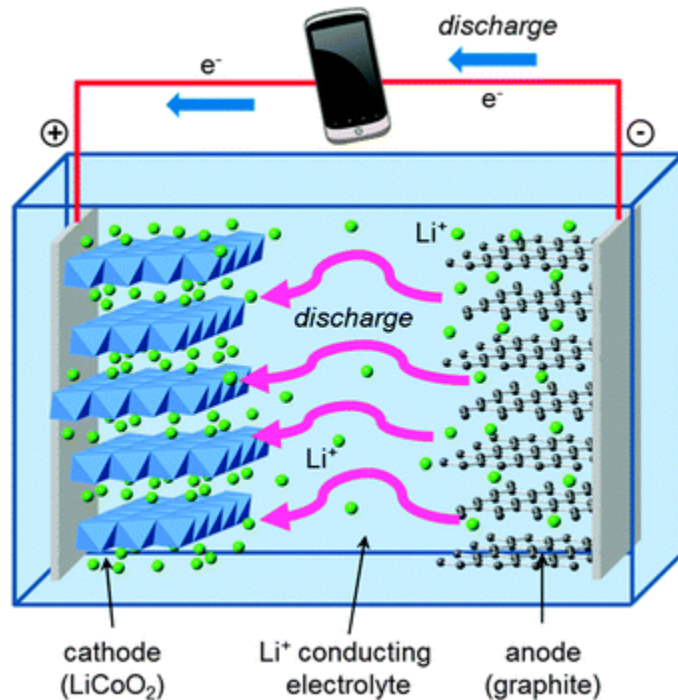
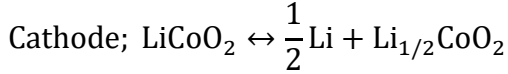
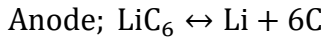


Figure 1 - Diagram of the internal function of a lithium ion cell during discharge. (158)

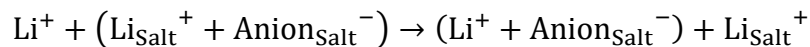
1.2.2 Role of the components

The anode and cathode serve as storage units for the cycling lithium. In the case of li-ion cells, the traditional anode is graphite, while the cathode is a lithium metal oxide, commonly LiCoO_2 . These electrodes are crystalline hosts, that the lithium travels in and out of, without changing the fundamental structure or chemical properties. This type of electrode is called an Intercalation Electrode. The overall capacity of the cell depends on the amount of lithium which can be reversibly inserted and removed from within these electrodes. For every six atoms of carbon in graphite, a single lithium can be stored. For every unit of LiCoO_2 , half a unit of lithium can be safely extracted,



If these two electrodes were to come into contact, a short circuit is formed, whereby the path of electronic least resistance is the cell itself. To prevent direct contact of the two electrodes, a thin polymer separator is used (10). This separator must be conductive of the ions that flow through it, but sufficiently insulating of electrons to cause them to flow through the external circuit.

To facilitating the movement of the ions, an organic liquid electrolyte wets the separator and electrodes. The electrolyte is composed of a liquid organic solvent, lithium salts and additives. The solvent dissolves the ions of the salt, which participate in a relay of the lithium ions,



In this way, it is not necessary for a lithium ion to travel across the cell, from one electrode to another, to meet the electron at the other side.

Owing to the electronic insulation across the cell, electrons are forced outside of the cell to move from one electrode to the other. This is facilitated by metal foils backing the electrodes; aluminum at the cathode and copper at the anode; so selected for their stabilities at high and low voltages, respectively.

1.3 ISSUES WITH THE STATE OF THE ART – LI-ION

1.3.1 Theoretical Capacity Limitations

The current an electrode can store is proportional to the lithium it can store; for each Li^+ ion that moves from one electrode to the other, a single electron will travel through the circuit.

The capacity of a single electrode is calculated as follows,

$$\frac{n \text{ electrons} * \text{Faraday constant}}{\text{Molar mass of electrode material}} = \text{Specific capacity of electrode material}$$

One ideal high capacity arrangement would be a silicon (Si) anode across a lithium sulfide (Li_2S) cathode. In the case of a lithium sulfide cathode, the calculation proceeds as follows,

$$\frac{2 e^{-} * \frac{96,485 \text{ As}}{\text{mol } e^{-}} * \frac{1 \text{ hr}}{3600 \text{ s}} * \frac{1000 \text{ mA}}{\text{A}}}{\left(\frac{45.95 \text{ g}}{\text{mol}}\right)} = 1166 \frac{\text{mAh}}{\text{g}} \text{Li}_2\text{S}$$

In the case of a silicon anode, the calculation proceeds as follows,

$$\frac{3.6 \text{ e}^- * \frac{96,485 \text{ As}}{\text{mol e}^-} * \frac{1 \text{ hr}}{3600 \text{ s}} * \frac{1000 \text{ mA}}{\text{A}}}{\left(\frac{28.085 \text{ g}}{\text{mol}}\right)} = 3435 \frac{\text{mAh}}{\text{g}} \text{ Si}$$

These contrast with the traditional, mass market li-ion cell, with a graphite anode across a lithium cobalt oxide (LiCoO₂) cathode. In the case of lithium cobalt oxide, the calculation proceeds as follows,

$$\frac{\frac{1}{2} \text{ e}^- * \frac{96,485 \text{ A s}}{\text{mol e}^-} * \frac{1 \text{ hr}}{3600 \text{ s}} * \frac{1000 \text{ mA}}{\text{A}}}{\left(\frac{97.87 \text{ g}}{\text{mol}}\right)} = 137 \frac{\text{mAh}}{\text{g}} \text{ LiCoO}_2$$

In the case of graphite, the calculation proceeds as follows,

$$\frac{\frac{1}{6} \text{ e}^- * \frac{96,485 \text{ A s}}{\text{mol e}^-} * \frac{1 \text{ hr}}{3600 \text{ s}} * \frac{1000 \text{ mA}}{\text{A}}}{\left(\frac{12.011 \text{ g}}{\text{mol}}\right)} = 372 \frac{\text{mAh}}{\text{g}} \text{ Graphite}$$

Due to the low utilization of lithium in a traditional intercalation electrode, 1/2 lithium per unit LiCoO₂ and 1/6 lithium per unit graphite, the specific capacity of a combination of intercalation electrodes is meaningfully lower than for a combination of conversion electrodes.

These specific capacities, at the electrode level, translate to theoretical capacities at the cell level as follows,

$$\frac{1}{\left(\left(\frac{1}{\text{Anode}_{\text{Sp. Cap.}}}\right) + \left(\frac{1}{\text{Cathode}_{\text{Sp. Cap.}}}\right)\right)} = \text{Cell}_{\text{Sp. Cap.}}$$

In the case of Si-Li₂S, the theoretical capacity of the cell is,

$$\frac{1}{\left(\left(\frac{1}{3435 \text{ mAh/g}}\right) + \left(\frac{1}{1166 \text{ mAh/g}}\right)\right)} = 870 \text{ mAh/g}$$

In the case of a graphite-LiCoO₂, the theoretical capacity of the cell is,

$$\frac{1}{\left(\left(\frac{1}{372 \text{ mAh/g}}\right) + \left(\frac{1}{137 \text{ mAh/g}}\right)\right)} = 100 \text{ mAh/g}$$

All of the above will translate to energy density terms, mWh/g, by multiplying the capacity by the potential; mAh/g * V = mWh/g. For a Si-Li₂S combination, the cell potential is 1.7V; for a graphite-LiCoO₂ the cell potential is 3.8V, offering 1480mWh/g and 370mWh/g theoretical energy density, respectively.

These theoretical calculations do not take into account non-capacity components. An actual graphite-LiCoO₂ cell may offer 243 mWh/g, which represents 70% of its theoretical energy density. Since many of the advances that brought li-ion to 70% of realization of the theoretical capacity would translate to a Si-Li₂S cell, we can suppose that a well developed Si-Li₂S technology may at some point reach such percentages, offering above 1,000 mWh/g.

1.3.2 Structural Limitations

In the case of intercalation cathodes, reversibility can be affected by the integrity of the crystal structure (11) (12) (13) (14). In the highest capacity intercalation cathodes, this integrity depends on a limited stoichiometric change in lithium (15) (16) (17). If too much lithium leaves the cathode during charge, the crystal structure may collapse to fill the void, or destabilize the charge distribution of the lattice sufficiently to ‘throw oxygen’ into the electrolyte, resulting in thermal runaway, rupture due to the evolution of gaseous products

and eventually a visible fire. This in turn leads to a ceiling on a practical cell energy of 265Wh/kg⁴. For applications that favor high capacity, low weight and low cost, this renders intercalation cathode cells unattractive; as multiple cells, with a heavy overall weight and significant cost, render a battery powered product less competitive with alternatively powered devices.

1.4 ALTERNATIVES

1.4.1 Alloying electrodes

One attractive alternative to lithium ion cells is the replacement of the intercalation electrodes with higher capacity electrodes. This can be achieved by using lithium alloying materials, which interact with significantly greater stoichiometric amounts of lithium, at a fraction of the weight of an intercalation electrode (18) (19) (20) (21) (22) (23). Tin and silicon will alloy with lithium to a theoretical stoichiometric amount of $\text{Li}_{4.4}\text{Sn}$ and $\text{Li}_{4.4}\text{Si}$, respectively. This offers a theoretical ceiling of 994 and 4,200 mAh/g (21), respectively, comparing favorably to graphite's 372 mAh/g. These greater capacities may translate to fewer cells, lower mass, lower cell volume, or some combination of the above. All of which result in, for various reasons, reduced costs, improved application performance and the enabling of new applications.

By definition however, this means more lithium will enter and leave the electrode upon cycling, than in intercalation electrodes. This leads to a particular challenge, that of mechanical damage and fracture of the electrodes. While graphite anodes are known to

⁴ In the case of Panasonic's NCR20700.

expand and contract by 10% of their initial volume (24), tin and silicon have been shown to experience 260% (25) and 300% (26) volume shifts, respectively. These changes in volume cause two problems, both of which result in lost capacity over cycling.

First, the dramatic change in volume disrupts the integrity of the SEI (Solid-Electrolyte-Interphase), a layer of electrolyte decomposition products that forms on the surface of the electrodes. The SEI will thicken, spending electrolyte and lithium, until sufficient potential resistance renders the interface with electrolyte harmless. Covering an electrode that experiences dramatic volume change however, the SEI will crack and re-expose electrode surface to fresh electrolyte,

which will then react to fill these cracks, as presented in the adjoining figure. This leads to a

loss of lithium, the ions directly proportional to the current a

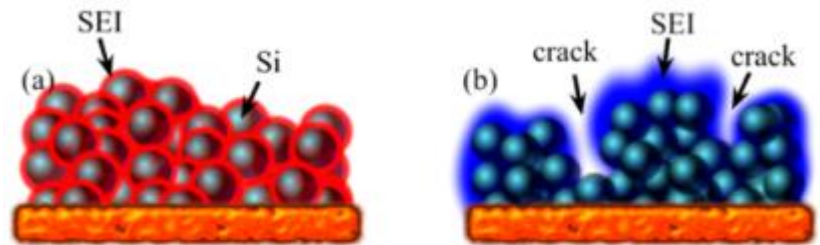


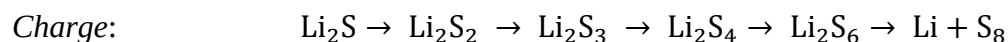
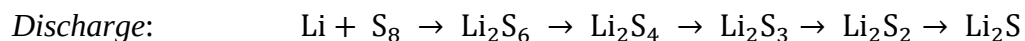
Figure 2 - Schematic of long cycled silicon anode. (a) electrolyte mix with crack preventing additive, (b) standard electrolyte mix, without crack preventing additive. (159)

cell can store, as well as a spending of the electrolyte, the medium which facilitates ion transport. Sufficient loss thereof will hinder ionic diffusion, rendering the cell dead.

Second, the processes of expansion and contraction yield alternating tensile and compressive stresses within the electrode. While compressive stress has been suggested to be beneficial, tensile stresses have been shown to fracture the electrode material, leading to cracks within the electrode, which fill with new SEI, leading to loss of electrical contact from the current collector. Electrode material which loses electrical contact requires a higher voltage to chemically engage, which renders it lost during cycling.

1.4.2 Sulfur electrodes and their challenges

Another class of high capacity electrodes react with the carrier ion to form liquid phase intermediates. Sulfur reacts with lithium in a solid-liquid-solid sequence. The fully lithiated state (a discharged cell) sees sulfur as lithium-sulfide (Li_2S). The fully charged state sees sulfur as elemental sulfur (S_8 rings). A sequence of intermediate molecules, known as polysulfides, of the form Li_2S_x , are soluble in liquid electrolyte (27). Due to the electrode's transition into liquid phase during both charge and discharge, the challenge of tensile stresses fracturing the electrode are irrelevant. Instead, this electrode dissolves into the electrolyte solution and redeposits upon formation of insoluble species.



The various phases of sulfur are electronically insulating⁵. This has lead the research community to explore different host structures which serve as conductive aids to the electrode. Recent work has focused on encasing sulfur in carbon. Carbon can be deployed as single-wall nanotubes (28) (29), rubber covalently bonded to sulfur (30), multiwall nanotubes, amorphous carbon, graphene or graphite. A carbon host may take a variety of shapes, depending on precursors and production methods used. Carbon is electronically and ionically conductive (31) and less dense than sulfur. These aspects are all beneficial in the application of carbon as a host material for a sulfur electrode. If properly arranged, the carbon host structure may even serve to trap polysulfides. Entrapment of polysulfides is

⁵ Sulfur is electronically insulating, at $5 \cdot 10^{-30}$ S/cm at 25°C, (155)

crucial for the cycle life of the cell. If the polysulfides are allowed to leave the cathode, which they will by simple diffusion gradient, the sulfur content they represent is lost and cell capacity degrades.

Much of this research utilized the low melting point of sulfur (32) (33) (34) (35) (36) (37) to introduce a molten elemental sulfur into preexisting carbon hosts. This solution is relatively simple, allowing for handling in atmosphere and a wide selection of cathode binders; since sulfur is unreactive and insoluble in solvents (Water, NMP) appropriate for the introduction of binder polymers (PEO, PVDF, CMC, brown alginate). Since neither sulfur nor carbon are reactive to atmosphere at room temperature, much of the processing after the introduction of the melt can be done without need of containment, on a lab bench.

Unfortunately, because these methods rely on a carbon host that can accept sulfur in molten state, it invariably means that it can also relinquish polysulfides as they drift in the electrolyte. The performance of these cells has been lacking, as the following reviews present (38) (7) (6) (2).

1.4.3 Lithium Sulfide as a Cathode

1.4.3.1 State of the art

In an effort to address the poor performance of sulfur cathodes, the fully lithiated phase of sulfur, Li_2S , has been explored (39). By starting with a lithiated cathode, the choice of anode is now open to non-lithium options, such as the aforementioned silicon, tin and germanium.

Various methods exist for the formation of a Li_2S cathode, encapsulated in a host matrix.

1.4.3.1.1 Direct mechanical introduction

In (40) Fu et al introduce Li_2S as powder onto a CNT substrate or directly onto the walls of a coin cell via spatula.

1.4.3.1.2 THF Dissolution

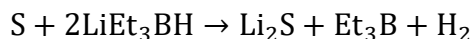
In (41), Wang et al introduce Li_2S via injection into the cell from a $\text{LiClO}_4 - \text{THF}$ solution.

1.4.3.1.3 Precipitation from an ethanol solution

In (42) Wu et al exploit the solubility of Li_2S in ethanol. Here Li_2S is either precipitated out of ethanol on its own, or MWCNT (multiwalled carbon nano tubes) are introduced prior to solvent evaporation, offering a nucleation substrate for Li_2S . In (43), Han et al go a step further, introducing Li_2S , PVP as a carbon source and $\text{Li}_6\text{PS}_5\text{Cl}$, via ethanol, vacuuming the mix and calcining in argon.

1.4.3.1.4 Reaction of Sulfur in solution

In (44), Yoon et al, formed carbon coated Li_2S particles by dissolving sulfur in toluene, mixed with graphene oxide (GO) dispersed in tetrahydrofuran (THF). Lithium triethylborohydride (LiEt_3BH) is added, to lithiate the sulfur as follows,



The Li_2S forms in a sphere around the GO. The solution is heated to remove the THF.

Chemical vapor deposition is used to form an amorphous carbon coating around the $\text{Li}_2\text{S}/\text{GO}$ particles. The weight ratio of $\text{Li}_2\text{S}:\text{GO}:\text{Carbon}$ is 85:2:13. CVD was performed in a turning furnace that generated an even coating over the entire particle population. Results showed a meaningful improvement in capacity retention with a uniform CVD generated

carbon coating. While results were promising, this system requires the use of organic solvents and early on formation of Li_2S . This combination leads to significant volumes of organic solvents evaporated in a glovebox, leading to high maintenance costs. Moreover, such start to finish reliance on a glovebox environment suggests limited scalability, due to the cost of such work spaces.

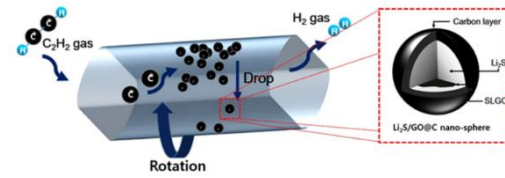


Figure 3 - Rotating furnace CVD environment and schematic

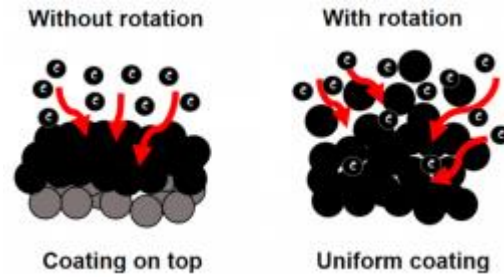


Figure 4 – Comparison of rotated and unrotated particles during CVD coating.

1.4.3.1.5 Ball Milling

In Lin et al, (45), employs mixing of Li_2S and carbon black via ball milling. The addition of Pyrrole as a carbon source to coat the particles yields an N-doped carbon after calcination. In (46), Nagao et al deploy high energy ball milling to mix Li_2S , acetylene black and $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ solid state electrolyte, which was pressed to form a compact disc, bonded to more of the solid state electrolyte. In (47) Cai et al employ high energy ball milling to create strong bonds with a carbon additive. They attribute the dry milling technique to higher utilization of Li_2S than wet milling, due to smaller particle size an better association of the Li_2S with C. In (48) Takeuchi et al introduce Li_2S to acetylene black in a ball milling environment, which is followed up by spark plasma sintering, to form the final $\text{Li}_2\text{S}@C$ composite.

In (49), Shaw introduces Li_2S either by ball milling, synthesized from bubbling an H_2S feed through LiCl solution, or the reduction of sulfur with LiEt_3BH . These are then followed up by coating with a $\text{Li}_4\text{T}_{15}\text{O}_{12}$ host. While this method suggests flexibility in the generation of

the original Li_2S active material, the prospect of coating with $\text{Li}_4\text{Ti}_5\text{O}_{12}$, itself an intercalation material in the anode voltage range, compromises the high specific capacity promised by a Li-S cell, as this shell itself will dramatically increase the mass of the cathode. Alternately, this patent offers a carbon coating formed via solvothermal reaction of pyrrole around the existing Li_2S particle. While this offers a lower weight support structure, even this composite falls into the trap of handling Li_2S prior to the preparation of a cathode. Every step in which the material handled is sensitive to the environment means an increased need for glovebox use, and as such greater costs.

1.4.3.1.6 Introduction as polysulfide

In (50), Han et al introduce the sulfur content as Li_2S_6 , which calcines down to Li_2S in the carbon host. In (51) and (52) Fu et al introduce sulfur content as Li_2S_6 onto a various carbon substrates and use it as is. In (53), Guo et al reacted Li_2S and S to form polysulfides, which were later treated to revert back to Li_2S .

1.4.3.1.7 Introduction as Li_2SO_4

In (54) Li et al exploit Li_2SO_4 's insolubility in ethanol, to induce migration of Li_2SO_4 in solution toward graphene oxide (GO) platelets. Once dried, the carbon content of the GO is used to reduce Li_2SO_4 to Li_2S in a flow of argon. Remaining GO offers a conductive matrix.

1.4.3.1.8 Polymerization of carbon host around Li_2S

In (55), Seh et al introduce micron sized Li_2S to pyrrole, which was allowed to polymerize overnight around the primary Li_2S particles. This polymer was left Unsintered, as the Li-N interactions it offered provide suitable performance.

1.4.3.1.9 Considerations

In all of the above systems, a batch-wise approach to the manufacture of the Li_2S composites suggests expensive operation upon scale-up. Many of these systems require the use of organic solvents in the production of the particle, extending the danger of solvents handling to the earliest steps. Moreover, by beginning with Li_2S , the materials must be maintained in containment early on, lest they react with moisture to form LiOH , or Li_2SO_x species as a result of exposure to oxygen. This would have the effect of increasing storage and production costs dramatically. Laboratory experience and consultation with Dr Gleb Yushin suggest that even in a regulated argon environment of a glovebox, the shelf life of high performance Li_2S particles is limited to a couple weeks at most, and the glovebox must be regenerated frequently to maintain a pristine enough environment.

These batch approaches to electrode production might prove worth it, were the specific energy and cycle stability compelling. Unfortunately, the body of literature on the subject has not yet produced a scalable method for the production of a Li_2S cathode that delivers both high areal loading of sulfur, with high sulfur utilization and commercially relevant cycle stability.

This work hinged on retaining a scalable production technique for the composite architecture, deploying ASP as a production method. The introduction of a batch process later on was justified by considering that later iterations of the design could combine both systems into one, whereby the final product of ASP is a finished $\text{Li}_2\text{S}@C$ composite. The challenge then, was to produce a composite that performed well.

1.4.3.2 Un-lithiated anode unlocked

A fully lithiated sulfur cathode, Li_2S , need not be coupled with a lithiated anode. Si- Li_2S systems have been demonstrated (56) (57) (58) (59), with the promise of a theoretical specific energy of 1550 Wh/kg. Such an anode could operate at a sufficiently high voltage to preclude the formation of lithium dendrite, at reasonable charge densities (60) (61). This would dramatically improve cell safety, deminishing a failure mode that leads to immediate and irreversible loss of a cell, at best, or catastrophic thermal runaway at the worst. Improvements in cell safety, coupled with high theoretical specific energy, suggest application in aerospace and automotive products, where safety, light weight and high energy requirements are prevalent.

1.4.3.3 High voltage requirement upon first charge

Unlike Sulfur cathodes, which are assembled in the fully charged state, Li_2S must be charged at first. Li_2S however is considered electrochemically inactive, requiring a high voltage to initiate and complete the first charge (62). This is a complicating factor, in terms of appropriate components and cell life. In order to tap into all Li_2S in the cathode, first charge voltages are driven near 4V vs Li. Around these potentials, an irreversible plateau appears, likely an indication of the reaction of LiTFSI with the aluminum of the current collector (63). At this point, the function of the current collector is compromised, offering poor

conductivity or having lost contact with the cathode. As such, completing utilization of Li_2S is not guaranteed, within safe potentials.

In an effort to mitigate these high potentials, lower charge rates may be used in the first charge. This has been shown to reduce initiation potential, as articulated in the following figure.

1.4.3.4 Fully discharged state means long rest period prior to formation of polysulfides is available

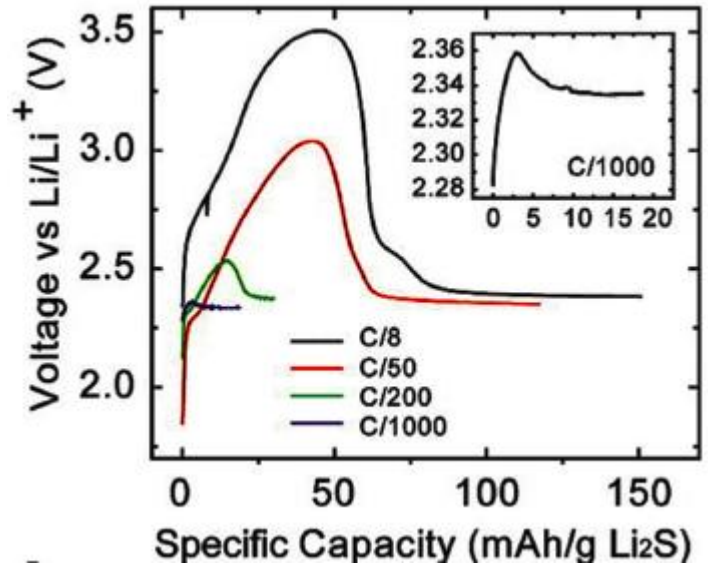


Figure 5 - Initiation voltage of Li_2S cathode as a function of charge rate. (164)

While Li_2S cathodes belong in the Li-S cell class, they are distinct in several key ways. A Li_2S cathode yields a cell assembled at a state of full discharge. As such, it is not only feasible to let an assembled cell rest for an extended period, it is in fact advisable. In (52) Fu et al show the benefits of rest on an in-situ formed Li_2S cathode, reducing first charge voltage.

Because self discharge will not occur at a state of full discharge, no polysulfides will form as a result of rest prior to the first charge. This offers an initial electrolyte environment free of polysulfides. In (64), Xiong et al show that the presence of polysulfides in solution prior to initial cycling affects the resistivity of the cell and future performance.

1.4.4 Economic Comparison

The relevance of this work is ultimately in its application. If a Li_2S cathode is going to be commercialized, it must outperform the state of the art at least in terms of specific energy (Wh/kg). A teardown of Panasonic's 18650b (65) reveals the masses of individual components of a commercial energy (designed for high capacity) cell. By assuming similar mass for non capacity components, such as the windings, cap, steel casing, etc. a benchmark can be set for hypothetical $\text{Li-Li}_2\text{S}$ and $\text{Si-Li}_2\text{S}$ cells. Assuming a 1,000 mAh/g accessible capacity of the $\text{Li}_2\text{S@C}$ composite material, varying areal loading (mg/cm^2) of Li_2S and various electrolyte volume to

	NCR18650B	Li-Li₂S 18650
Packaging foil	0.31 g	0.31 g
Steel can	3.65 g	3.65 g
Insulator discs	0.13 g	0.13 g
Positive pole	1.56 g	1.56 g
Negative pole	0.69 g	0.69 g
Anode current collector	3.0 g	0 g
Cathode current collector	2.6 g	2.6 g
Separator	1.5 g	1.5 g
Ni mandrels	0.56 g	0.56 g
Inert mass	14.0 g	11.0 g
Anode mass	11.4 g	100% excess
Cathode mass	17.4 g	Variable
Electrolyte	4.3 g	Variable
Cell mass	47.1 g	?
Cathode	LiNiCoAlO₂	Li₂S@C
Area (cm^2)	372.1	372.1
Active weight fraction	0.95	0.9
Active material capacity	200 mAh/g	850 mAh/g
Nominal Voltage	3.7 V	2.1 V
Anode	Graphite	Li metal
Area (cm^2)	334.3	334.3
Active weight fraction	0.95	0.9
Active material capacity	300 mAh/g	3862 mAh/g
Nominal Voltage	0.1 V	0 V

Table 1 - Comparison of benchmark product, NCR18650B, and $\text{Li-Li}_2\text{S}$ cell with the proposed $\text{Li}_2\text{S@C}$ cathode.

sulfur mass (E/S) ratios, the following projections for an 18650 format cell are offered,

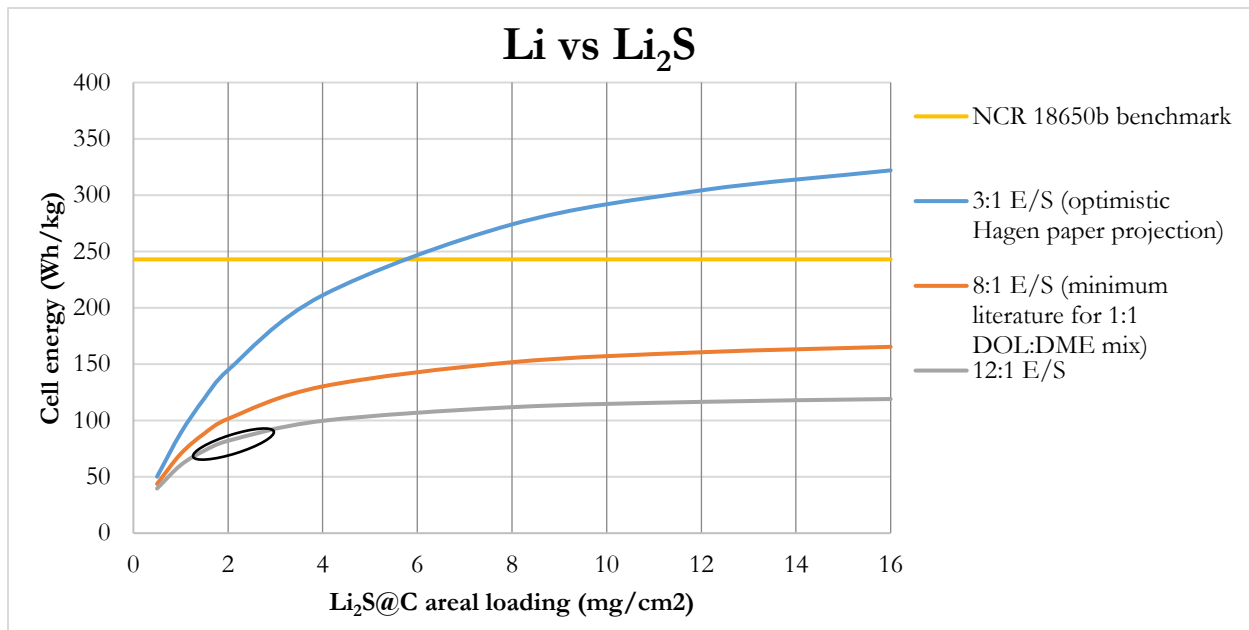
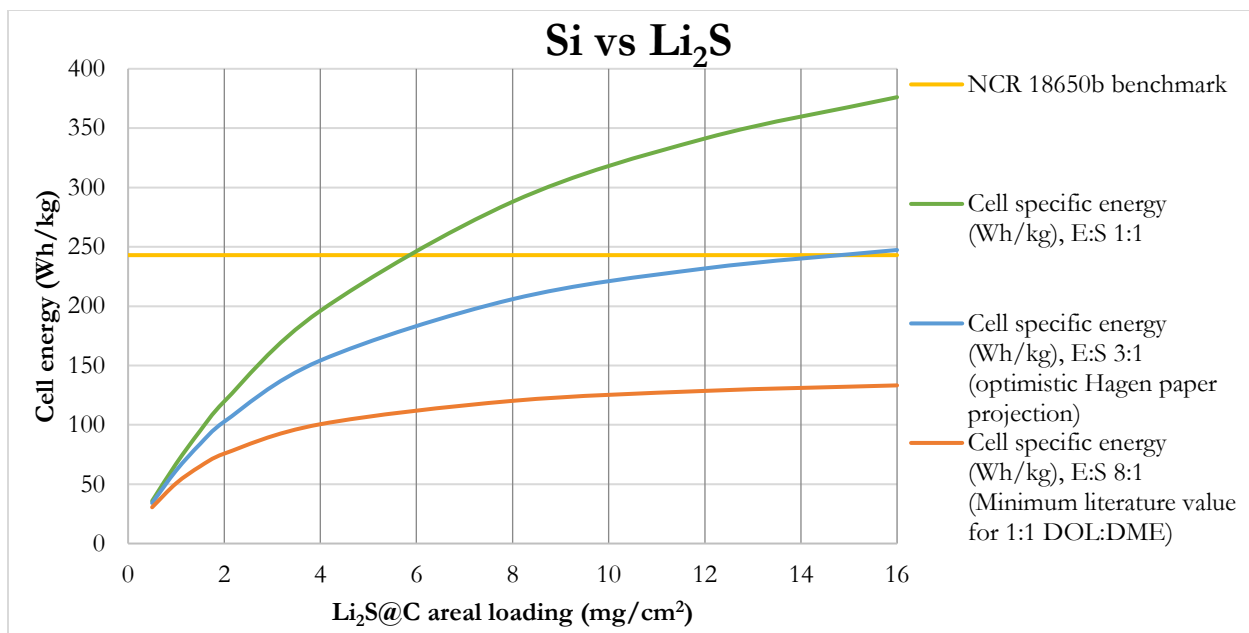


Figure 6 - Li vs Li₂S 18650 configuration cell specific energy projection. Three scenarios are considered, varying in E/S ratios.

Due to limitations which are described later on, this work was able to produce functioning cells whose specific energy lay within the black circle. Improvements in electrolyte chemistry are necessary to realize shifting to lower E/S scenarios (orange and blue curves), while optimization of electrode pasting methodology are required to advance the results to the right within the same scenario. This project suggests an areal loading of 6 mg/cm² Li₂S would be necessary to overtake the NCR18650b. Such loadings exist in the literature, for sulfur cathodes and are not wholly unreasonable. The requirement that an E/S ratio of 3:1 be accomplished, however, is a different proposition altogether.

The Li-Li₂S system enjoys a higher voltage than an equivalent Si-Li₂S configuration. As such, the following projection describes the requirement for an Si-Li₂S cell to be competitive with the NCR18650b.



With Si-Li₂S, it is evident an even more ambitious E/S ratio must be devised to overtake the NCR18650b, in terms of specific energy.

2 METHODS

2.1 ASP SYNTHESIS APPARATUS

The ASP system developed in this project is illustrated in adjacent figure. Aqueous reactants solution is aspirated from a reservoir into a Collision type atomizer (TSI Corp, Model 3076) where an argon carrier stream shears the feed into droplets. A sharp bend upward eliminates droplets larger than $2\mu\text{m}$, as these high inertia particles strike the wall and return to the reservoir via the reflux line. The aerosol proceeds upward through a diffusion drier, where dessicant extracts the solvent (H_2O). Upon drying, both lithium salt (Li_2S precursor) and carbon precursor co-precipitate into a hierarchal structure (66), defining the ultimate dispersal of Li_2S in the carbon. The solvent-poor particles are carried into a tube furnace where drying is complete and the themally driven reactions take place, at a temperature setting of 850°C . The pyrolyzed particles are finally collected with a stainless steel mesh (McMaster Carr, 200 by 1400 mesh, 304SS) with a $10\mu\text{m}$ pore size.

Temperature conditions in the reaction zone were ascertained by 30cm K-type thermocouple, during argon flow simulating that of a production run. The temperture profile experienced by a typical paticle in flight along the reactor is approxiamted by the following calibration curve, with set points of 800 , 850 and 900°C ,

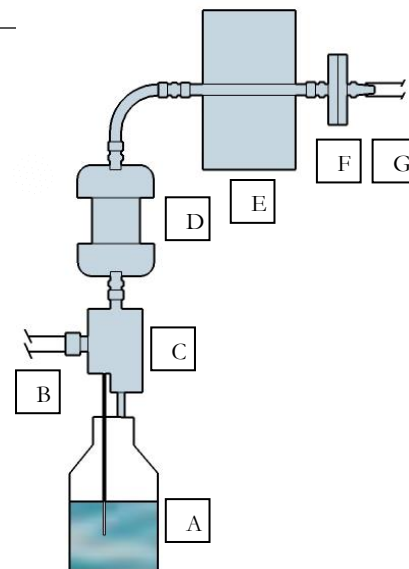


Figure 7 - Schematic of the ASP system.
A: reservoir, B: carrier gas, C: atomizer, D: diffusion drier, E: furnace, F: filter, and G: exhaust.

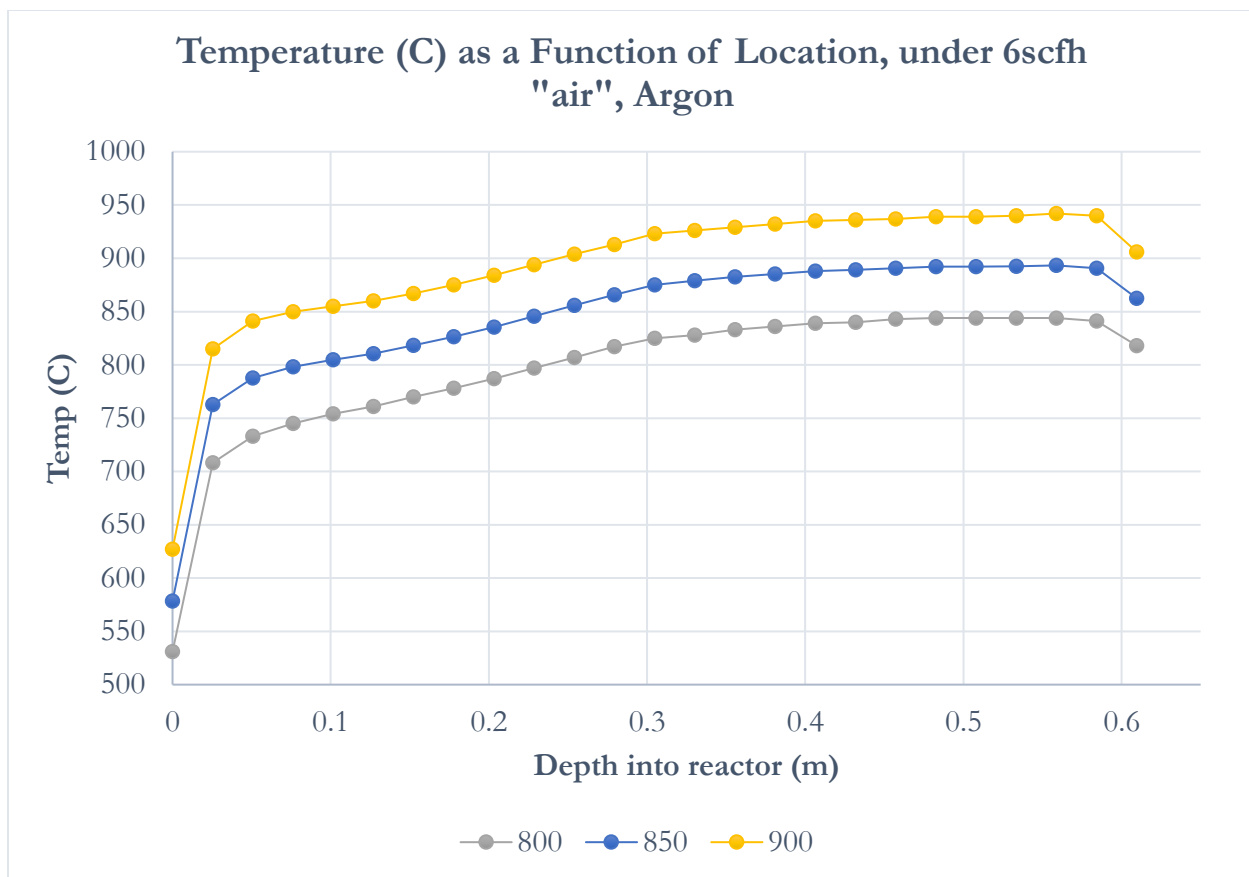


Figure 8 - Temperature calibration of the ASP reaction zone.

2.1.1 Design comments for the ASP apparatus

This system went through numerous adjustments to improve mass yield (mass-collected/mass-fed). These adjustments included a vertical rather than horizontal pathway during drying. During travel through the dryer the aerosol is still solvent-rich and considerably more massive. Solvent content in solution ranges 92-98% by mass. These more massive particles are more prone to ballistic impaction and since they are wet and will not bounce off the walls, the aerosol will suffer significant wall losses. To prevent further wall losses, the entire system could be adjusted to a vertical position. The use of a a steel mesh filter in a steel housing allows for relatively high temperature collection. This allows collection closer to the heated

zone, and prevention of losses due to thermophoresis, whereby a relatively cool tube wall causes the stream to bend outward. While a downward path is ideal for wall loss prevention overall, this would require a different type of atomizer, as the 3076 must remain upright to operate properly. An upward path is thereby a reasonable compromise.

Different tubes were considered for the heated zone. Stainless steel tubing was robust and offered a reliable seal, but required a long cooldown under argon flow to prevent corrosion from exposure to air at high temperatures. Quartz tubing, while chemically inert and robust, suffers from regular breakage and a need for replacement. A 2" diameter quartz tube was attempted, in lieu of the 1/2" tube, to increase residence time in the reaction zone, and offer more complete carbonization of the carbon precursor, by the following logic,

$$Q = VA$$

If A, the cross sectional area of the tube is increased by a factor of four, so too did V, the velocity decrease by the same factor, under the same flow, Q, as controlled by the pressure at the argon tank. Unfortunately, the increased residence time lead to increased wall losses due to ballistic impaction. In essence, the aerosol stayed in the heated zone long enough to fall onto the tube wall. Arguably, a vertical arrangement of the heated zone may alleviate this concern, allowing for greater residence times and or lower reaction temperatures. Moreover, during testing with a larger tube diameter, significant losses were incurred in the final restriction to the 1/2" outlet to the filter housing. A larger filter outlet may alleviate these losses.

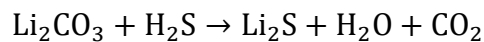
The filter and filter housing originally deployed were a 0.2 μ m pore plastic filter in a plastic housing (both, Millipore). This system is designed for entrapment of particles in a liquid

stream, at lower temperatures. At sufficiently high filter temperatures, this plastic filter will melt to the housing. This means the filter must be kept far enough away for the stream temperature to drop below 100°C. While this lower temperature protects the plastic filter, offering superior entrapment due to finer pores, it also means that solvent may recondense in the sample. Lithium carbonate hydrate is stable above 100°C, and the hydration of the primary particle may result in expansion and damage to the secondary host material. The use of steel mesh, with larger pores may lead to greater losses and as such lower yields, but it does not sacrifice on particle quality.

Finally, replacement of the diffusion dryer with an auxiliary gas stream, diluting the aerosol, may prove a superior choice for aerosol drying. The diffusion dryer is the most labor intensive aspect of the system, and its drying capacity (40ml of solvent) represented a production bottleneck. Moreover, the capacity of the dryer to remove solvent is not steady state throughout the production. As the dryer saturates solvent is removed more slowly, which affects the architecture of the final particle. The use of an alternative, steady state system is beneficial for quality control purposes.

2.2 ASP POST TREATMENT APPARATUS

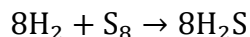
The $\text{Li}_2\text{CO}_3@\text{C}$ composite particles from ASP are subsequently reacted with H_2S gas in a tubular furnace to produce $\text{Li}_2\text{S}@\text{C}$ composite according to the following sulfidation reaction at a set point of 725°C.



H₂S gas is introduced as a mix, H₂S / Ar (5%/95%). Exhaust bearing H₂S must be remediated before venting. A bubbler with 40g NaOH dissolved into 500ml of ultrapure DI water is used to react the reaction zone flue stream. The remediated stream is vented into a fume hood. The vented stream was assessed for H₂S concentration and found to range from 0.00ppm and 4.00ppm; sufficiently remediated for venting, but still potentially detectable to members of the lab.

2.2.1 Design comments for the Post treatment apparatus

The original method deployed here was an H₂/Ar (5%/95%) passed over an upstream boat of molten elemental sulfur. The reaction proceeds as follows, to deliver H₂S,



This system offered a lower concentration of H₂S, which is safer, in the advent of leaks, but also less dependable in terms of completing the conversion of Li₂CO₃ to Li₂S.

Moreover, the presence of elemental sulfur vapor in the reaction environment lead to sulfur deposition on the Li₂S@C particles, during the cooling of the reactor, when the sample temperature dips below the melting point of sulfur. This external deposition of sulfur lead to poor performance, due to active material external to the carbon host.

As yet unpublished work suggests that a 100% H₂S stream can convert lithium hydroxide to Li₂S at temperatures tolerable to the binder in an electrode (<120°C). This could make for significantly easier, and as such cheaper, electrode production; as the air and moisture sensitive Li₂S is introduced after the electrode is fully prepared. This does however require a

dangerously high concentration of H_2S and is as such unattractive. Ideally, a method that avoids the use of H_2S is preferable.

Due to the flow conditions inside the heat treatment chamber, the temperature environment across the position of the boat are as follows,

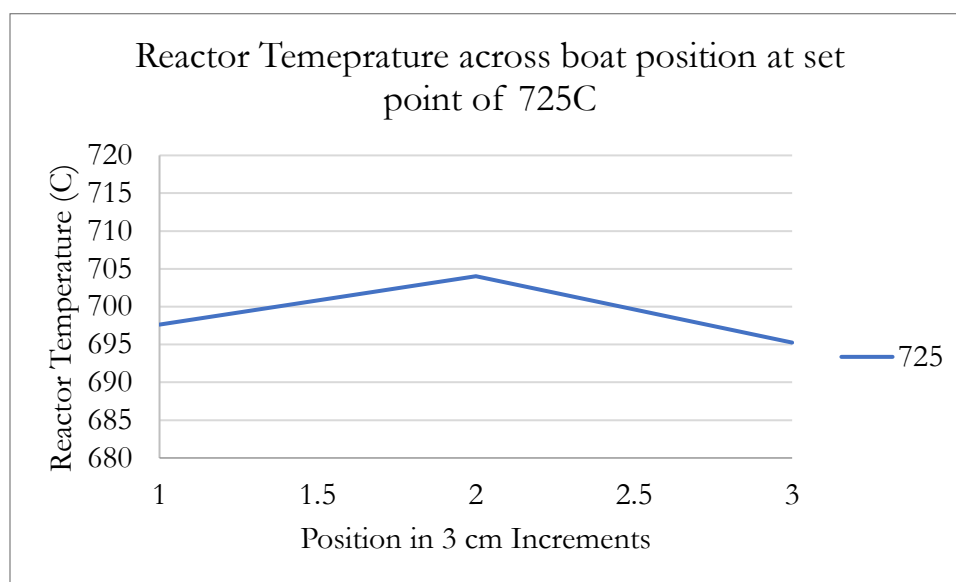


Figure 9 - Temperature calibration of the post treatment furnace.

The above assertion is based on a calibration done from 500°C to 900°C in 100°C increments, seen here.

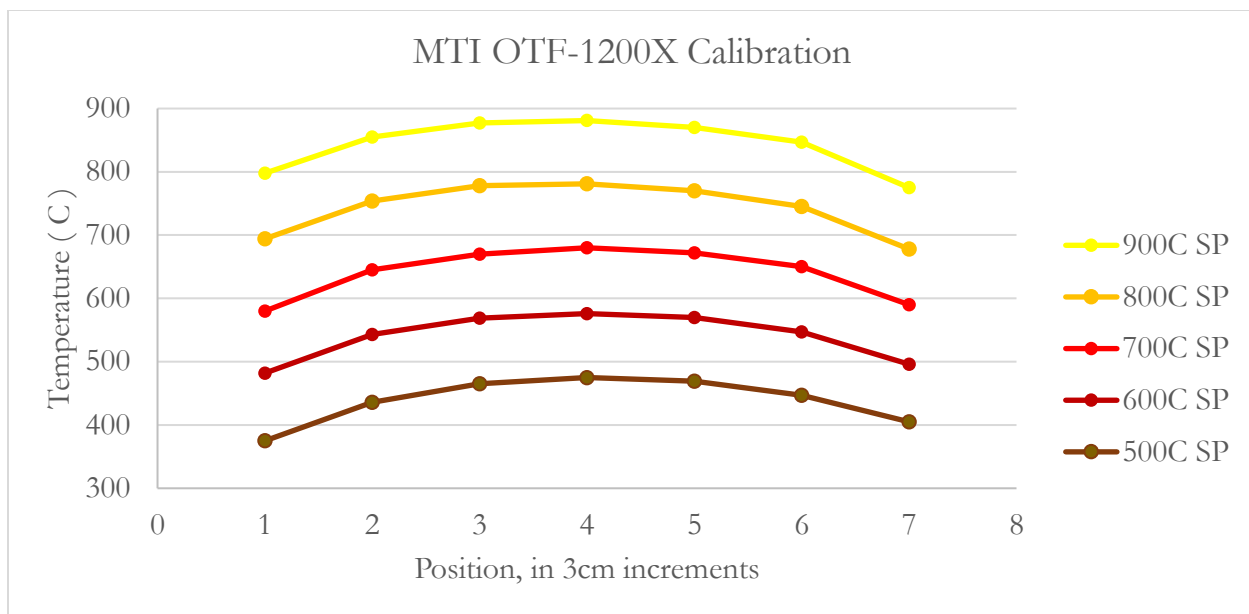
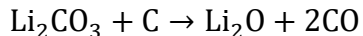


Figure 4 - Temperature calibration of the post treatment furnace. Boat position in treatment is from position 3 to 5.

Maintaining a consistent temperature environment for the entire $\text{Li}_2\text{CO}_3@\text{C}$ sample, while offering easy exposure to the gas stream, means spreading a thin layer of sample over a small region in the tube. This limits treatment runs to no more than 150mg of $\text{Li}_2\text{CO}_3@\text{C}$. This limits electrode production to a single batch per H_2S treatment, reducing repeatability.

Due to the promotion of the Boudouard reaction by Li_2CO_3 (67), and the resulting depressed decomposition temperature for static Li_2CO_3 in the presence of carbon (68), which follows this mechanism,



The H_2S feed is switched on, from the initial UHP argon, below 500°C . Otherwise, the host structure may be damaged during the temperature ramp. It is suspected that this depressed thermal decomposition temperature of Li_2CO_3 confers the added benefit of beginning the

conversion to Li_2S at lower temperatures, forming a Li_2S shell around the Li_2CO_3 . This would help prevent the losses of Li_2CO_3 due to melting (M.P. 723°C) or vaporization. Experimental observation (3.8.2017, experimental notes) of the reactor at (set point) 725°C under argon flow presented with a black smoke and burnt smell, confirming reaction in the absence of H_2S , likely that of the consumption of carbon by carbothermic decomposition of Li_2CO_3 .

2.3 CHARACTERIZATION

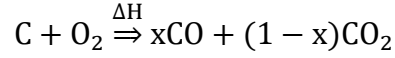
2.3.1 TGA

Thermo-Gravimetric Analysis (TGA) observation was performed in lab on a TA Instruments Q-50 on alumina pans with platinum bails suspended by a platinum hang down wire.

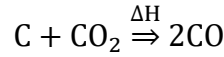
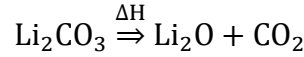
TGA utilizes a temperature programmable furnace sleeve and a gas flow feed, to affect physical and chemical changes on a sample. The gas feed utilized in this work is either dry air, or argon, offering oxidative and inert condition, respectively. In this work, TGA is utilized to assess the ratio of carbon to lithium species; either Li_2CO_3 or Li_2S , depending on the stage of the process the sample is collected. The use of dry air as a gas feed allows for the oxidation of carbon beginning around 350°C (depending on the quality of the carbon), at a heating ramp of $10^\circ\text{C}/\text{min}$. The remaining mass, depending on the methods of preparation and TGA programming, may be Li_2O , Li_2CO_3 , Li_2SO_4 or traces of Li_2S .

In the case of $\text{Li}_2\text{CO}_3@\text{C}$ particles, the ratio of carbon to Li_2CO_3 is ascertained via a flow of dry air. Heating under a flow of dry air will yield mass loss during the oxidation of carbon,

due to the following reaction, where x increases, non-linearly, with the temperature of the reaction.



Complicating the measurement is the matter of carbothermal decomposition of Li_2CO_3 , as a participant in the Boudouard Reaction, whereby the thermal decomposition temperature of Li_2CO_3 in the presence of carbon is depressed, due to the following two reactions,



The oxidation of carbon by CO_2 drives down the activation energy of the decomposition of Li_2CO_3 , expediting reaction at lower temperatures (68). As such a more conclusive TGA run reaches the decomposition of Li_2CO_3 to Li_2O , where the identity of the lithium specie can be certain, rather than a combination of Li_2CO_3 and Li_2O , at an unknown ratio. This leads to increased wear on the TGA thermocouple, by exposure to oxidizing gas.

For $\text{Li}_2\text{CO}_3@\text{C}$

$$\frac{\left(\text{Li}_2\text{O mass} * \frac{\text{Li}_2\text{S molar mass}}{\text{Li}_2\text{O molar mass}} \right)}{\left(\text{Carbon} + \left(\text{Li}_2\text{O mass} * \frac{\text{Li}_2\text{S molar mass}}{\text{Li}_2\text{O molar mass}} \right) \right) \text{ mass}} * 1166 \text{ mAh/g}$$

$$= \text{Powder theoretical capacity mAh/g}$$

This assessment is instructive about the available lithium content of a composite, but is not a precise predictor of the final product's capacity due to two reasons. First, carbon mass has

been shown to alter during post treatment; which leads the above method to overestimate carbon content and as such underestimate capacity. Second, complete conversion of Li_2CO_3 to Li_2S is not guaranteed; which leads to an overestimation of capacity.

2.3.1.1 TGA methods development

A TGA program was devised with the express purpose of analyzing the Li_2S content in an $\text{Li}_2\text{S}@C$ composite. This program overcomes the reactivity of Li_2S to atmospheric oxygen and moisture, by pretreating with HCl , yielding a sample that results in a single temperature stable lithium species, Li_2O . This allows for an unambiguous analysis of Li_2S content in the original composite. This method is appropriate for the analysis of lithium content in $\text{Li}_2\text{CO}_3@C$ (such as this work), $\text{LiOH}@C$ composites (69), $\text{Li}_2\text{SO}_4@C$ (54), which may be used as $\text{Li}_2\text{S}@C$ precursors.

The program includes temperature plateaus at 120°C, 500°C, 550°C, 650°C and 800°C. The program operates under a flow of argon until ten minutes into the plateau at 550°C, when the gas feed is switched to dry air, switching from an inert to an oxidizing environment. This program was designed to parse out the various physical and chemical reactions with as great a resolution as can be expected in TGA. A final analysis of the species present at any moment in the sample pan would benefit from GC-MS sampling of the exhaust gases. This is however outside the scope of this work. Best estimates of sample speciation, based on literature and XRD, will be offered.

A pristine sample of Li_2CO_3 treated to the TGA program produced the following result.

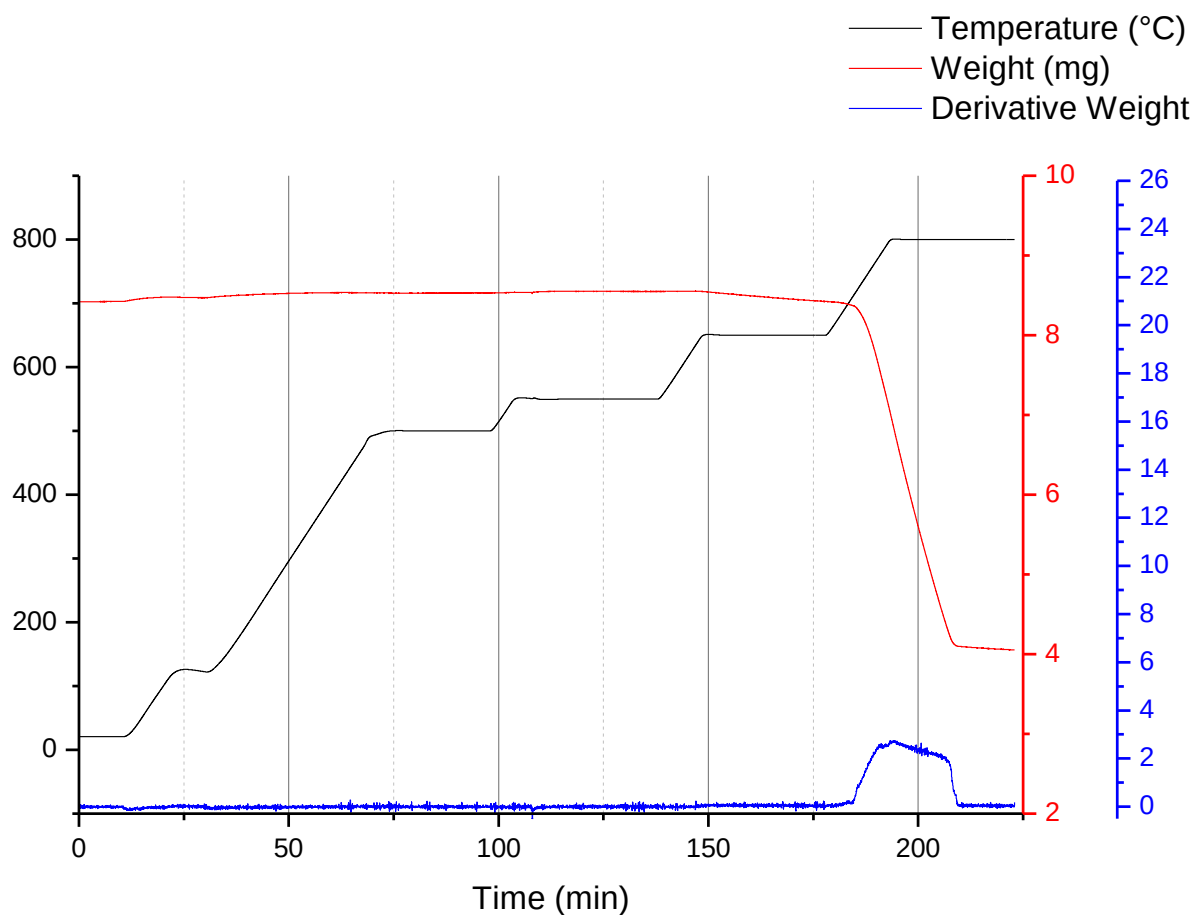
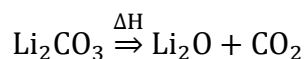


Figure 10 - TGA run of pristine Li_2CO_3

The slight increases in mass prior to the onset of mass loss, accounting for mass increase prior to 150 minutes may be attributed to error as a result of buoyancy. As the gas stream becomes hotter and less dense, the pan enjoys less buoyancy, as it displaces a lighter gas, reading as a slight mass increase. The TGA is designed to correct for these fluctuations, limiting the effect to that observed above. As such while calculation are not adjusted to these changes (which amount to fractions of a percent), they are noteworthy in a discussion of error.

Above 675°C Li_2CO_3 experiences thermal decomposition, yielding Li_2O and some Li_2O_2 .

Below 725°C the Boudouard reaction favors CO_2 , yielding, mostly, solid Li_2O ,



Above 725°C, however, the Boudouard reaction tends to favor CO , which is more thermodynamically stable at these higher temperatures, as articulated in the following figure,

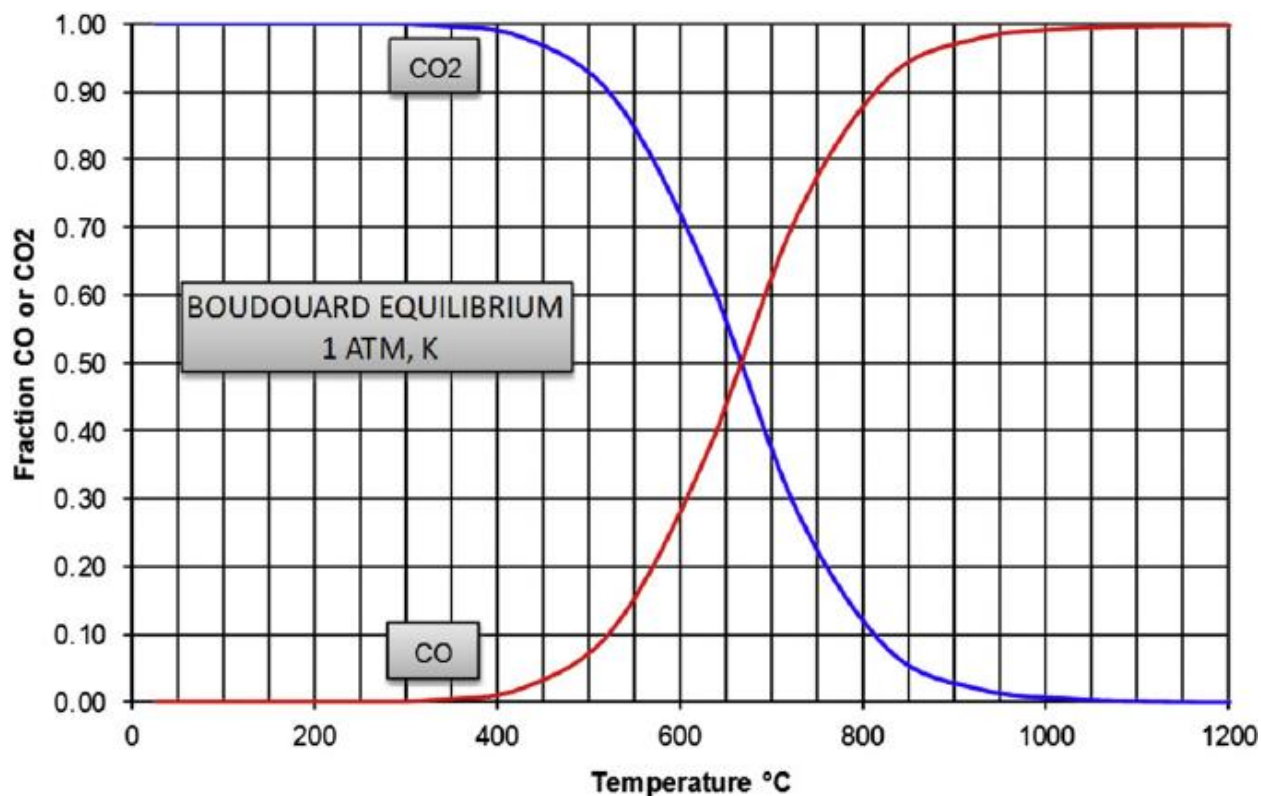
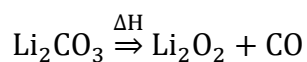
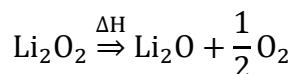


Figure 11 - Boudouard's Reaction Equilibrium vs Temperature at 1 atm. (70)

As a result, thermal decomposition occurring above 725°C may see the emergence of the following reaction,



Continuing exposure to heat will eventually decompose lithium peroxide to lithium oxide, in the following way,



The formation of Li_2O exclusively would suggest a loss of nearly 59.6% mass of the sample, while the formation of Li_2O_2 exclusively would suggest a roughly 38.1% mass loss. The mass loss in the above is 51.5%, suggesting a mix of both Li_2O and Li_2O_2 . The shallow downward slope that follows represents continuing decomposition toward Li_2O .

Observing Derivative Weight serves as a fingerprint of the particular reaction. The position, along the X axis, and character (sharp for high kinetics, truncated for slow kinetics or transport limited) of the Derivative Weight plot allows some measure of identification of the reactions on going, and as such the identity of reactants and products. As such, in comparing one sample to another, the Derivative Weight plot is set to a similar minimum and maximum, in this case: -0.5 to 26. Since the TGA will adjust the program backward or forward based on temperature during ramps, observing X position based on the time coordinate is incomplete, while observing temperature only may be less instructive during temperature plateaus. For the majority of the decomposition of Li_2CO_3 then, the Derivative Weight signature resides at (713, 800)°C and (185, 209)min. These points were taken as the outer limits where the Derivative Weight registers as 0.3, a value that signal a departure from the noise, and the clear initiation or winding down of mass loss.

By contrast, a $\text{Li}_2\text{CO}_3@\text{C}$ sample shows a more complex path of decomposition, as follows,

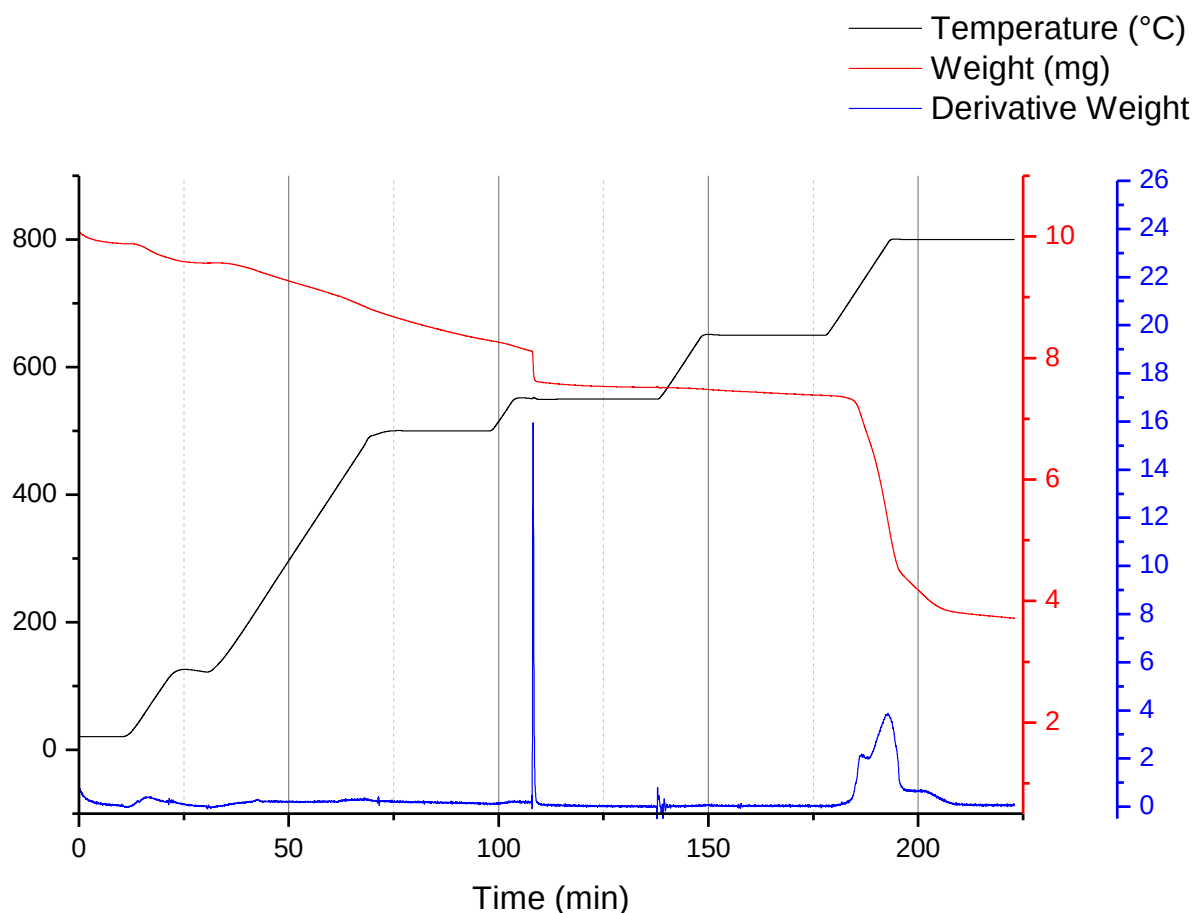


Figure 12 - TGA run of $\text{Li}_2\text{CO}_3@\text{C}$. Sample generated from the 3N2S composition.

In the TGA run of $\text{Li}_2\text{CO}_3@\text{C}$ we can observe mass loss for both Li_2CO_3 decomposition, observable at (707, 800)°C (184, 206)min, and carbon mass loss to oxidation occurring most prominently at (551, 551)°C (108, 109)min. The oxidation of carbon occurs at the switch from argon to oxygen, at a sufficiently high temperature to initiate a vigorous reaction to oxygen. Mass losses from room temperature to 120°C represent the loss of hydration, either from moisture deposited on the surface of the composite, or from waters of hydration in $\text{Li}_2\text{CO}_3 \cdot \text{H}_2\text{O}$. As evidenced by the following TGA run, of high surface area activated carbon,

mass losses across 120-550°C can be ascribed to the decomposition of carbon, even when already highly decomposed.

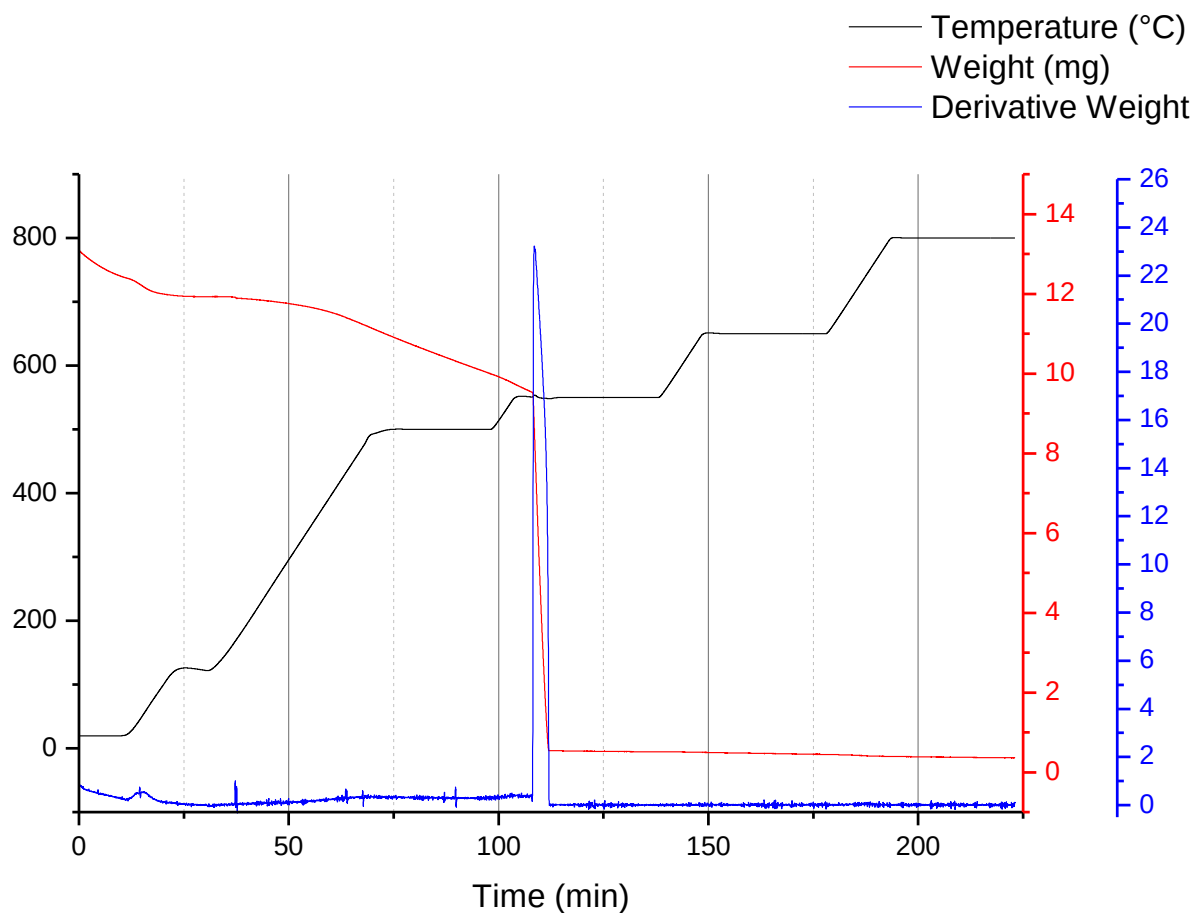


Figure 13 - TGA run of high surface area activated carbon, made of coconut.

Continuing mass loss beyond that point is beyond the margin of error, and can be ascribed merely to early onset of Li_2CO_3 decomposition, since pristine Li_2CO_3 does not decompose this early in the program. Remaining carbon, possibly trapped within the composite may be contributing to a carbothermal decomposition of Li_2CO_3 . To illustrate this assertion, an argon only, earlier method, shows an overlap for the decomposition of Li_2CO_3 and carbon.

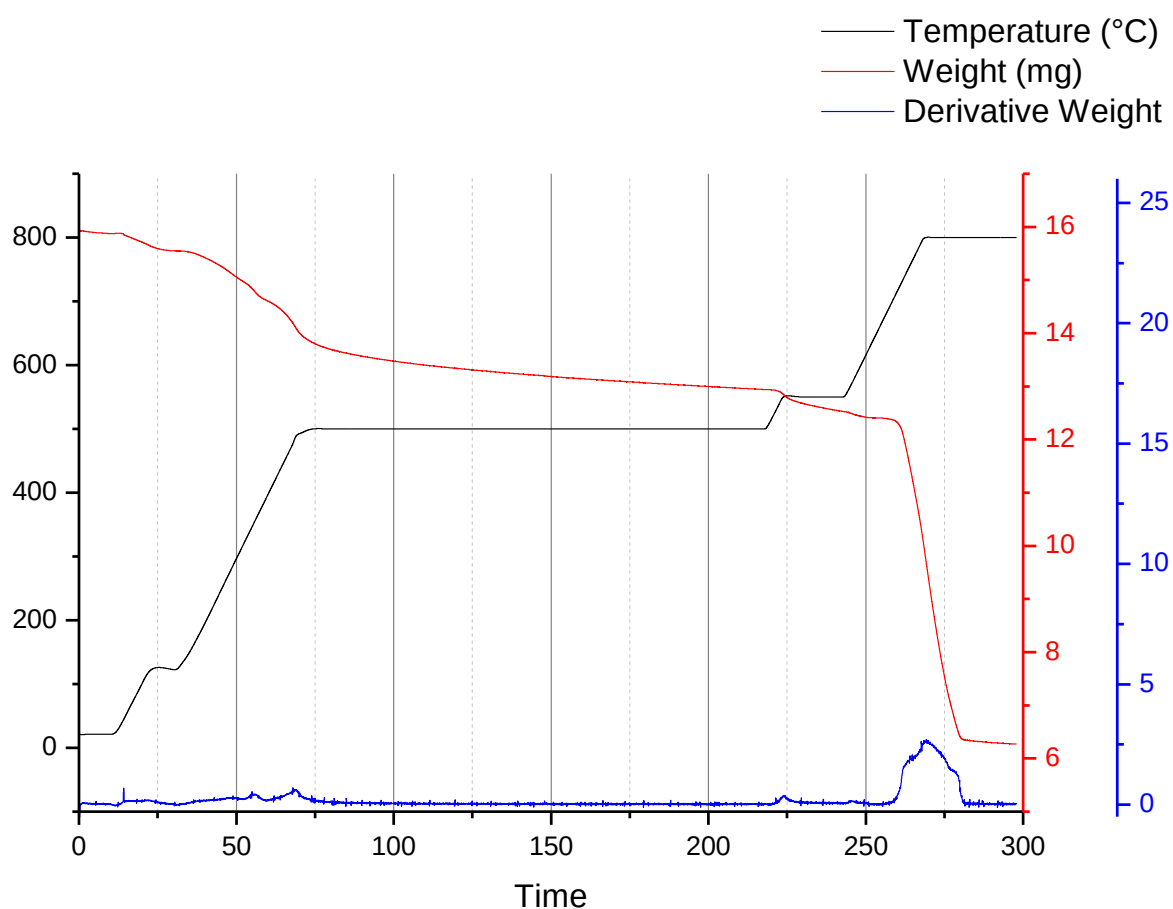


Figure 14 - Argon only TGA method, showing the reactions of $\text{Li}_2\text{CO}_3@\text{C}$ under a temperature program.

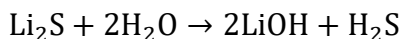
Here a mass loss of 48.9% during the characteristic mass loss for Li_2CO_3 decomposition evidences neither a complete decomposition to Li_2O , as illustrated by the continuing, slower mass loss nor a clean agreement with the decomposition of pristine Li_2CO_3 , which presented with a more aggressive 51.5% mass loss. Moreover, the continuing slow mass loss leading up to the decomposition of Li_2CO_3 suggests that carbon decomposition was still on going. The presence of carbon would explain the greater mass loss, both as loss attributable to the loss of carbon to the oxygen of the process stream, and possibly in carbothermal decomposition

of Li_2CO_3 . An argon only TGA program would have been preferable, as it more accurately reflects the process environment of the H_2S treatment. The overlap of C and Li_2CO_3 related mass losses makes it less precise, requiring the use of an oxidizing stream during the program.

2.3.1.2 Application of TGA method

The assessment of $\text{Li}_2\text{CO}_3@\text{C}$ composition is used largely to drive particle design, rationally selecting for a reasonable carbon mass for the purposes of mechanical entrapment and conductivity, while maintain a relevant active material loading. It assumes that no carbon mass is lost during the final H_2S treatment step, which does not bear out of the data. Indeed, some mass loss is observed after H_2S treatment, likely due to the carbothermal decomposition of Li_2CO_3 during treatment. Discussion of evidence of this carbon loss will follow later on.

Finding the final composition is a problematic proposition. $\text{Li}_2\text{S}@\text{C}$ particles are subject to fast, though incomplete reaction, with ambient moisture, in the following reaction,



This reaction does not run to completion, leaving some Li_2S behind, possibly protected within a shell of LiOH , which resists the infiltration of reactant H_2O and the evacuation of product H_2S . Even complete immersion in DI water and sonication leaves some Li_2S behind, as evidenced by XRD.

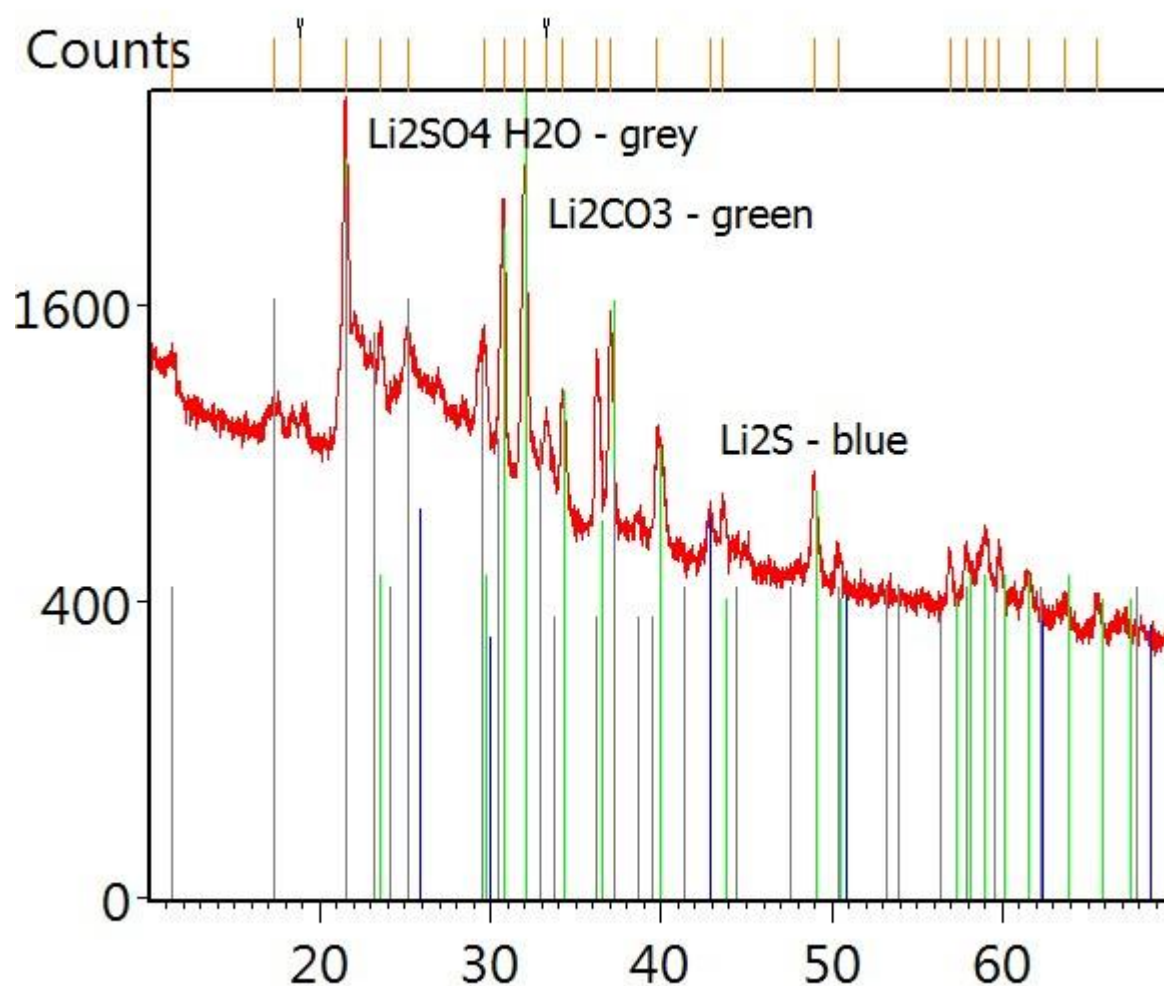
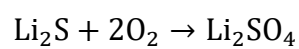


Figure 15 - XRD scan of Li_2SO_4 derived $\text{Li}_2\text{S}@C$ particle, after H_2O wash.

Relying on TGA to parse out the composition of $\text{Li}_2\text{S}@C$ is tricky. Oxidation of $\text{Li}_2\text{S}@C$ should result in mass loss due to carbon oxidation and mass gain due to Li_2S oxidation, as such,



In theory the final weight should represent bare Li_2SO_4 . However, the conversion of an unknown fraction of Li_2S into LiOH makes this analysis impossible. Since the mass loss due to carbon oxidation and mass gain due to Li_2S oxidation overlap, their respective contributions to the final mass can not be parsed out. The final mass then is a combination of unknown fractions of Li_2SO_4 , LiOH , Li_2O_2 and Li_2O , or at higher temperatures, Li_2SO_4 and Li_2O . The combination of Li_2O and Li_2SO_4 at unknown ratios makes this technique inappropriate for ascertaining the value of Li_2S in the composite.

In response to this challenge, it is assumed, as a conservative estimate, that the entirety of the composite $\text{Li}_2\text{S}@C$ is Li_2S . This informs the theoretical capacity calculation and the electrolyte to sulfur ratio. The latter represents an important variable, which bears heavily on the feasibility of the composite as a commercial product; both in terms of affecting high sulfur utilization to achieve high capacity, and in terms of maintaining high cycle stability.

2.3.1.3 Sample pretreatment for TGA method

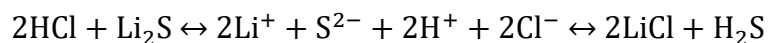
An attempt to resolve this issue involves the pretreatment of $\text{Li}_2\text{S}@C$. Immersing $\text{Li}_2\text{S}@C$ in water and sonicating, proved to incompletely react the material to $\text{LiOH}@C$, as mass gains due to remaining Li_2S , oxidizing to Li_2SO_4 , obscured the loss due to carbon oxidation. Some mixture of Li_2SO_4 and Li_2O (the thermal decomposition product of LiOH) of unknown composition remains, yielding inconclusive results. The anion reactant replacing S^{2-} in Li_2S would ideally have a significantly higher K_a value than H_2S , promoting the ionization of the replacing anion, yielding a recombination of the S^{2-} anion as H_2S , evolving as gas as the water is evaporated off. K_a is formulated as follows, with values in the proceeding table,

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Table 2 - K_a values of relevant acids. Values extracted from University of Washington publication, (71)

K_a	Acid		Base conjugate	
	Name	Formula	Formula	Name
1.3×10^6	Hydrochloric acid	HCl	Cl^-	Chloride ion
1.0×10^3	Sulfuric acid	H_2SO_4	HSO_4^-	Hydrogen sulfate ion
2.4×10^1	Nitric acid	HNO_3	NO_3^-	Nitrate ion
1.0×10^{-2}	Hydrogen Sulfate ion	HSO_4^-	SO_4^{2-}	Sulfate ion
4.4×10^{-7}	Carbonic Acid	H_2CO_3	HCO_3^-	Hydrogen carbonate ion
1.1×10^{-7}	Hydrosulfuric acid	H_2S	HS^-	Hydrogen sulfide ion
1.3×10^{-13}	Hydrogen sulfide ion	HS^-	S^{2-}	Sulfide ion
1×10^{-14}	Water	H_2O	OH^-	Hydroxide ion

Considering hydrochloric acid (HCl) and Hydrogen Sulfide (H_2S) we see that the high K_a value of HCl and low values for H_2S and HS^- , drive the equilibrium toward ionized Cl^- and dissolved H_2S .



In this case, chloride ions remain in solution, available for recombination with lithium ions upon solvent evaporation, whereas the H_2S and any excess HCl may evolve as gas. As such,

acids such as HCl and HNO₃ (which likewise has a much higher K_a than H₂S and HS⁻) would be appropriate. XRD testing of the pretreated sample with HNO₃ yielded a complex speciation including ammonium related species of lithium sulfate. Since the goal of this pretreatment is to simplify the sample to offer easily read TGA findings, HNO₃ was deemed inappropriate as a pretreatment option.

Moreover, due to HNO₃'s lower K_a value relative to H₂SO₄, an HNO₃ treatment would not be appropriate for a Li₂SO₄ sourced material.

It was hypothesized that merely wetting Li₂S@C was insufficient, since the product of this reaction is poorly soluble in water, leading to local saturation in the fine pores of the composite, preventing further conversion to LiOH. A more soluble reaction product is desirable. Lithium Chloride (LiCl) is meaningfully more soluble than LiOH at room temperature, as can be seen in the following figure,

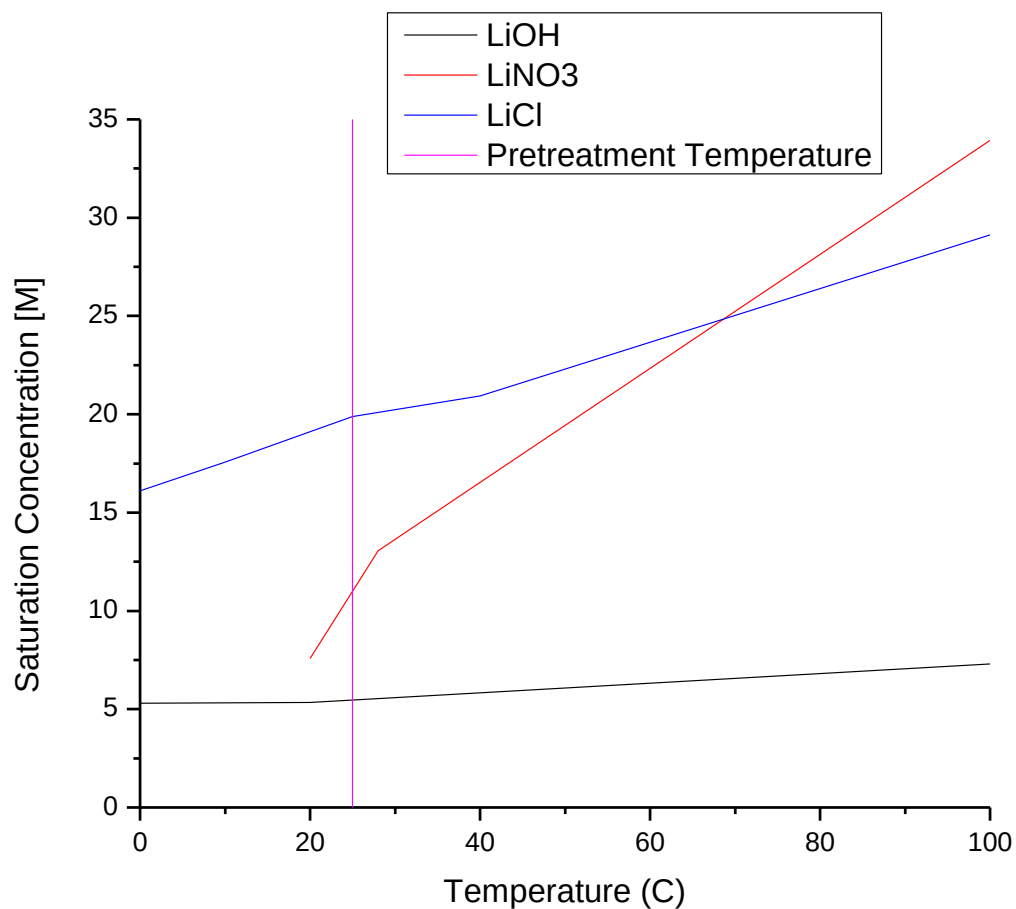
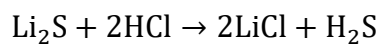
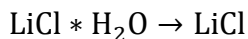


Figure 16 - Solubility of pretreatment relevant lithium salts in aqueous solution.

Conversion to LiCl can be achieved by sonication of $\text{Li}_2\text{S}@C$ in a highly concentrated HCl solution, yielding the following reaction,



The mixture is allowed to evaporate at room temperature in a hood. Due to the formation of LiCl hydrates, this followed by a finishing in an oven at 120°C, to promote the following decomposition,



Excess HCl, as well as dissolved H₂S, will leave as a gas. The resulting dry powder would be a mix of LiCl, remaining LiOH and carbon. The choice of LiCl as a TGA analyte is advantageous as well due to its stability in oxygen. LiCl shows a stable loss of mass starting at 650°C, when exposed to a 10°C/min ramp, due to evaporation. After isolating mass loss due to carbon, and precluding other reactions that may affect mass, the mass of sample right before characteristic losses due to LiCl evaporation, is taken as LiCl. Mass loss related to LiCl can be seen in the following TGA run of pristine LiCl.

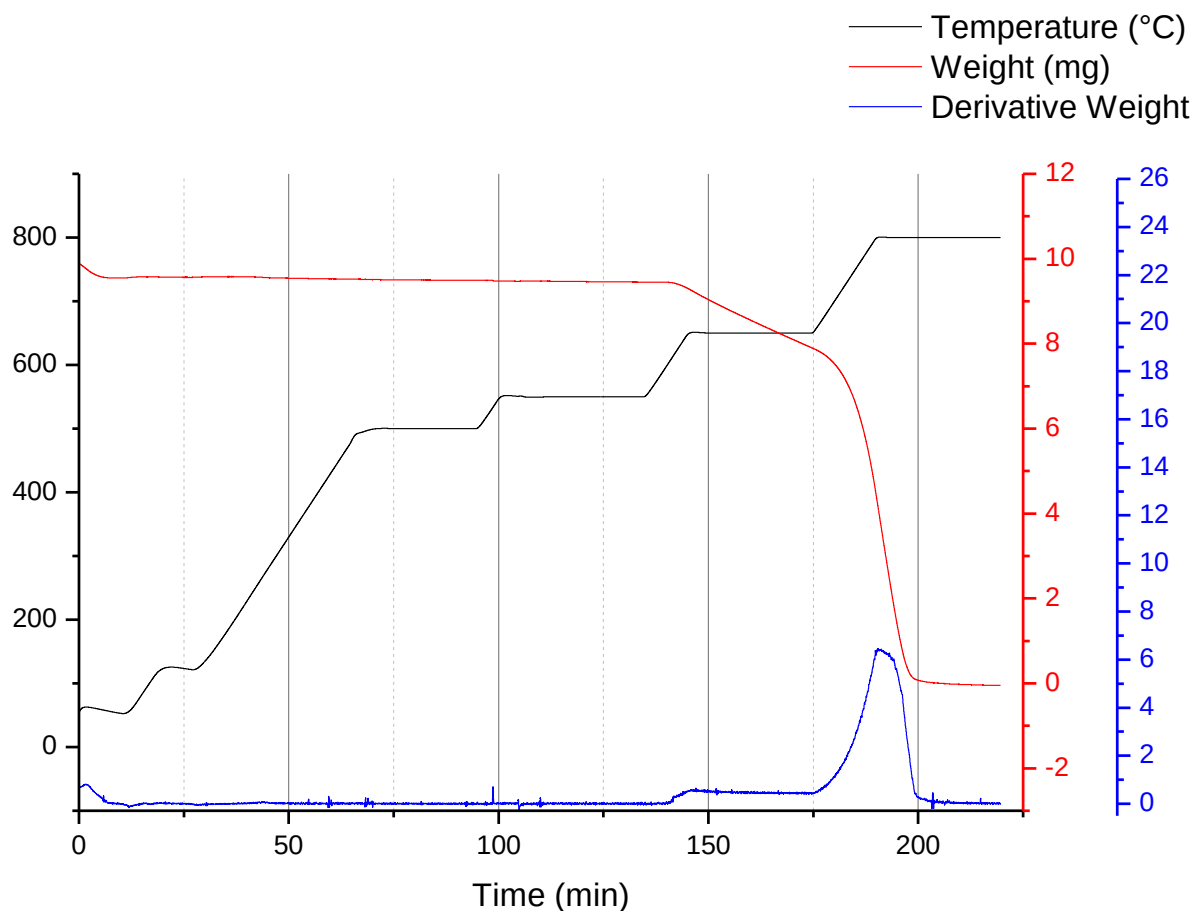


Figure 17 - TGA run of pristine Lithium Chloride (LiCl).

The absence of change at the moment of the switch from argon to dry air is the central strength of the selection of LiCl. Mass loss for LiCl occurs in two phases, with a distinct rate during the plateau at 650°C (with a derivative weight that rises to 0.54 and stabilizes at 0.44) and an increase in rate during the ramp to 800°C. The complete loss of mass by the end of the ramp shows that LiCl does not decompose to a temperature stable specie, such as Li_2O in the presence of oxygen.

Changes in mass for a sample of LiOH can be seen in the following plot,

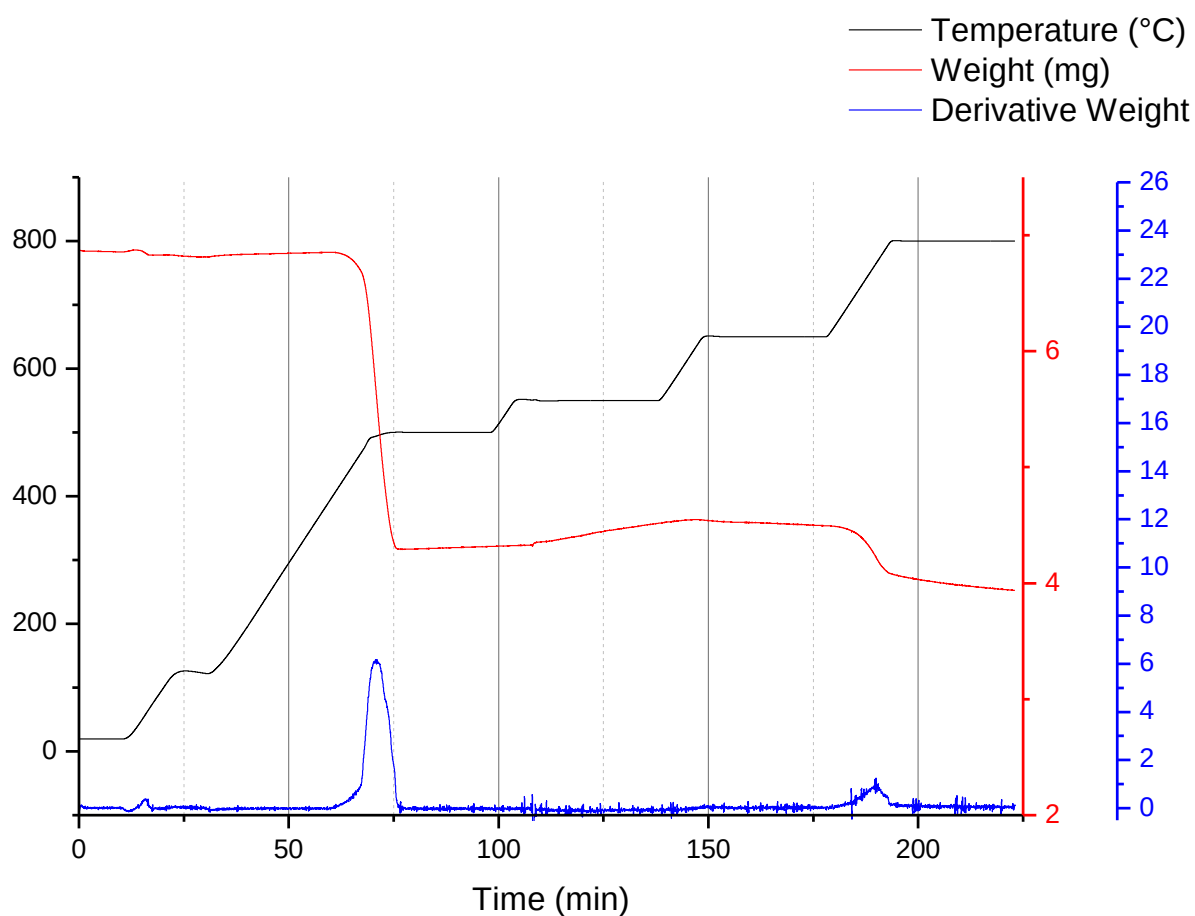
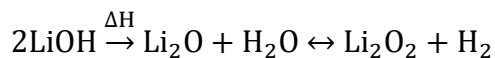
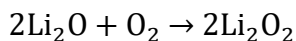


Figure 18 - TGA run of pristine lithium hydroxide (LiOH)

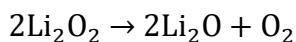
The first mass loss peaks at 71 minutes, occurring across (434, 500)°C, (64,76)min, representing the following reactions,



Complete decomposition to Li_2O would present with a mass loss of roughly 27%, whereas here a mass loss of 17.2% occurs, suggesting some content of Li_2O_2 is formed; which is confirmed later on upon mass loss. Upon switching to oxygen during the 550°C plateau an acceleration in mass increase is observed. Here some lithium oxide is oxidized to lithium peroxide, by the following action,



Lithium peroxide is known to decompose from as low a temperature as 450°C (72). This run however shows that formation of Li_2O_2 continues until roughly 575°C, and mass loss initiates beyond 650°C where rapid decomposition occurs, back to lithium oxide, reversing the above reaction,



This reaction continues until Li_2O_2 content is exhausted by the 800°C plateau, whereupon Li_2O begins to evaporate. As such the lithium content attributable to oxides is taken as the mass at the end of the sharp decline leading into the 800°C plateau.

2.3.1.4 Pretreated sample analysis

This analysis can then be performed on an HCl pretreated sample,

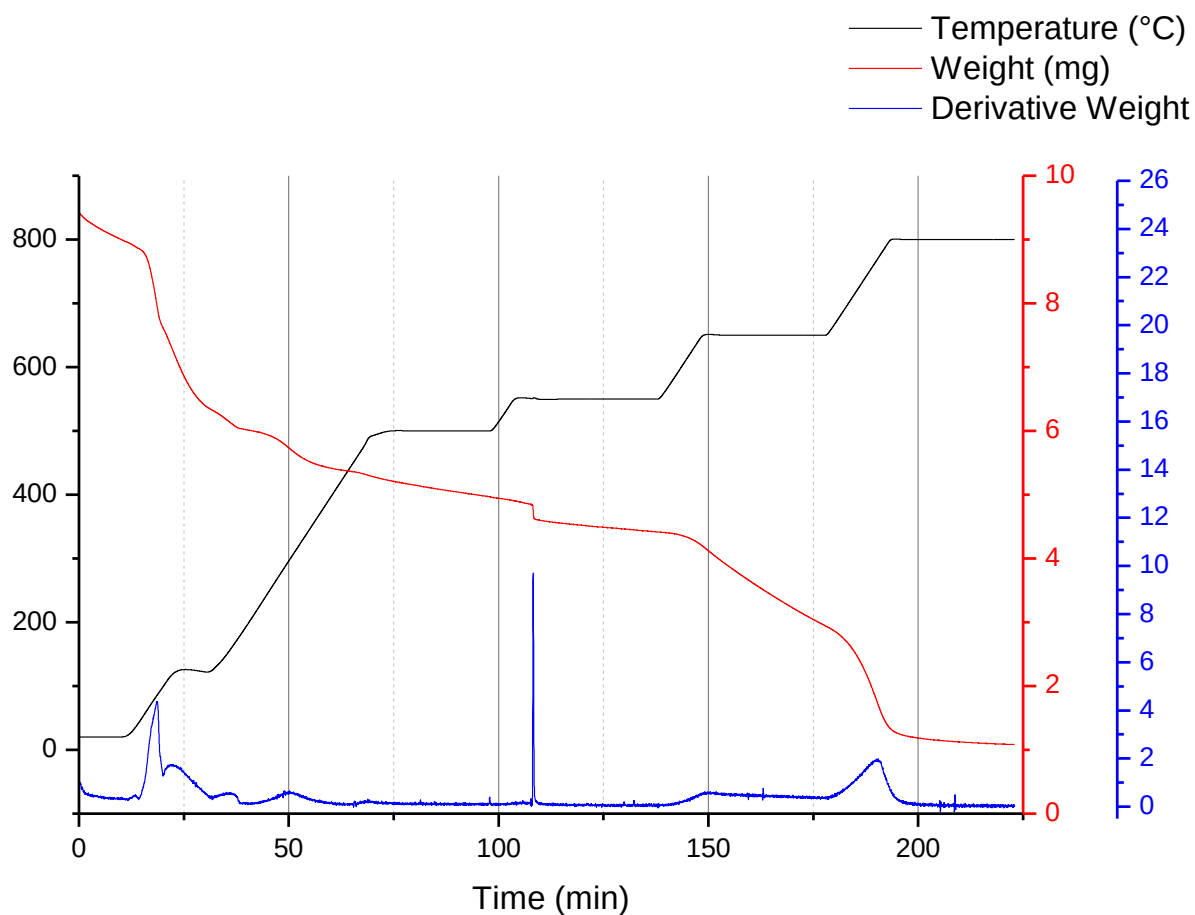


Figure 19- TGA run of an HCl pretreated sample of 3N2S derived $\text{Li}_2\text{S}@C$; This is specific to batch #8, which features in the results of this thesis.

The presence of mass at the end of the ramp to 800°C suggests some Li_2O content, and as such incomplete conversion by HCl. This content is taken as Li_2O , and the lithium content it represents is as follows,

$$1.256 \text{ mg Li}_2\text{O} * \frac{1 \text{ mmol Li}_2\text{O}}{29.88 \text{ mg Li}_2\text{O}} * \frac{1 \text{ mmol Li}_2\text{S}}{1 \text{ mmol Li}_2\text{O}} * \frac{45.95 \text{ mg Li}_2\text{S}}{1 \text{ mmol Li}_2\text{S}} = 1.932 \text{ mg Li}_2\text{S}$$

Mass loss bearing the signature of LiCl evaporation appears at the 650°C plateau. Mass loss associated with final Li₂O content is subtracted from the mass at the beginning of the LiCl related mass loss.

$$4.313 \text{ mg (LiCl + Li}_2\text{O)} - 1.932 \text{ mg Li}_2\text{O} = 2.381 \text{ mg LiCl}$$

This yields to the following content of Li₂S, attributable to LiCl,

$$2.381 \text{ mg LiCl} * \frac{1 \text{ mmol LiCl}}{42.394 \text{ mg LiCl}} * \frac{1 \text{ mmol Li}_2\text{S}}{2 \text{ mmol LiCl}} * \frac{45.95 \text{ mg Li}_2\text{S}}{1 \text{ mmol Li}_2\text{S}} = 1.290 \text{ mg Li}_2\text{S}$$

The mass of dry sample is taken at the point of lowest Derivative Weight, which is 6.022mg. Beyond this point decomposition of carbon is certainly occurring, but before it mass loss from the dehydration of LiCl*H₂O is ongoing.

$$6.022 \text{ mg (LiCl + Li}_2\text{O + C)} - 4.313 \text{ mg (LiCl + Li}_2\text{O)} = 1.709 \text{ mg C}$$

The Li₂S content of the Li₂S@C composite is calculated as follows,

$$\begin{aligned} & \frac{1.932 \text{ mg Li}_2\text{S}_{\text{attributable to Li}_2\text{O}} + 1.290 \text{ mg Li}_2\text{S}_{\text{attributable to LiCl}}}{1.709 \text{ mg C} + 1.932 \text{ mg Li}_2\text{S}_{\text{attributable to Li}_2\text{O}} + 1.290 \text{ mg Li}_2\text{S}_{\text{attributable to LiCl}}} \\ &= \frac{3.222 \text{ mg Li}_2\text{S}}{4.922 \text{ mg Composite powder}} = 0.6546 \text{ Li}_2\text{S content} \end{aligned}$$

The theoretical capacity of this composite is then,

$$0.6546 \text{ Li}_2\text{S} * 1166 \text{ mAh/g} = 763.28 \text{ mAh/g}$$

2.3.2 Cycler

Battery cycling was done on ARBIN, Neware and MTI cyclers, in lab. Charge and discharge in this work is pursued as a function of calculated cathode theoretical capacity. The mass of

$\text{Li}_2\text{S}@C$ is calculated from cathode mass and charging rates, in milli-amperes (mA) are set as a function of this mass. Charge and discharge rates are set as a fraction of theoretical capacity, in C-rate, where '1/n' is the rate at which the cell will be fully charged in 'n' hours, such that 1/50 C will charge a cell in 50 hours. This method was selected in accordance with literature, where it is widely recognized that C rate affects performance (73), (74).

An alternative and common method is to charge relative to cathode area, in units mA/cm^2 . Due to the variation in electrode loading within the same batch, as evidenced by the following histogram, this method is inappropriate, as it will lead to significant variation in performance within the same batch, making it more difficult to access the quality of the material.

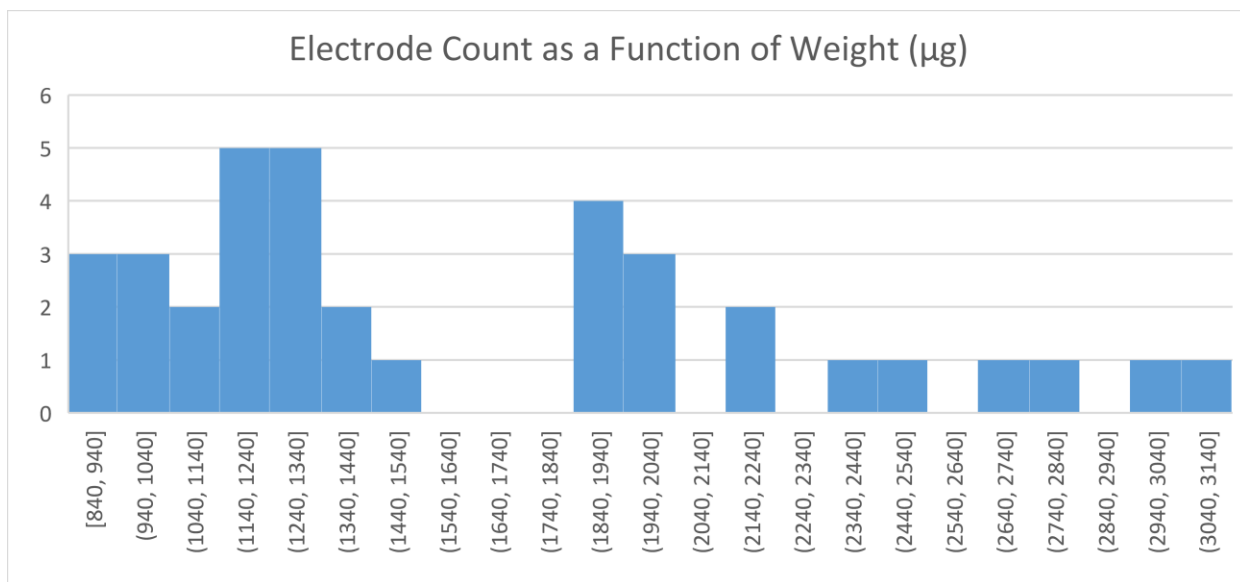


Figure 20 - Weight distribution histogram for cathodes punched from 3N2S batch #6. As separated in 100μg bins.

The following sequence was used as a cycling protocol where the first four steps account for the cell's first cycle and subsequent cycles follow programming in steps 5 through 10.

Step	Type	Value	Voltage cutoff	Go To
1	Rest (min)	300	-	Step 2
2	Charge (C rate)	1/20	3.4	Step 3
3	Rest (min)	10	-	Step 4
4	Discharge (C rate)	1/10 or 1/5	1.8	Step 5
5	Rest (min)	10	-	Step 6
6	Charge (C rate)	1/10 or 1/5	2.6	Step 7
7	Rest (min)	10	-	Step 8
8	Discharge (C rate)	1/10 or 1/5	1.8	Step 9
9	Rest (min)	10	-	Step 10
10	End	Cycle back	-	Step 5

2.3.2.1 Rate selection

Selection of the appropriate rate is a compromise. Faster rates mean less capacity is utilized, but slower rates mean more time for the dissolution of polysulfides, leading to capacity fade in subsequent cycles.

First cycle rate are especially slow, owing to the resistive nature of bare Li_2S , prior to the presence of polysulfides in solution. While subsequent charges occur in the presence of dissolved polysulfides, the first charge does not have such an advantage. This leads to

dramatically higher overpotential, with Li_2S activating above 2.7V, and full capacity reached well above 3.3V. At normal charge and discharge rates, of 1/10 and 1/5 C, these overpotentials are exacerbated, leading to even higher voltages necessary to see reaction. Such high potentials activate unwanted reactions, such as the corrosion of the steel casing by the LiTFSI electrolyte salt, above 3.9V. The selection of lower rates for the first charge and discharge were made in order to fully access the capacity of the cathode. It is recognized however, that these slow charge rates allow for significant capacity loss, which bears out in the drop of capacity seen in subsequent cycles.

2.3.3 Cyclic Voltammetry

2.3.4 XRD

X-ray Diffraction observation was performed at the University of California, Riverside's PANalytical Empyrean, operating between 10 and 70 degrees, using the standard $\frac{1}{2}$, 10 and 8 masks. For $\text{Li}_2\text{CO}_3@\text{C}$ samples, preparation was done by packing powder onto a stainless steel substrate, when sufficient powder was available to cover it entirely. When low sample mass was available, a zero diffraction silicon or silica substrate was used (MTIXTL inc.). Scans lasting ten minutes were deemed sufficient to characterize these samples. For $\text{Li}_2\text{S}@\text{C}$ samples, a zero diffraction silicon or silica substrate (MTIXTL inc.) was introduced into an argon filled glovebox. Sample is loaded onto the center of the substrate, leaving a wide margin of clean substrate. Kapton tape is applied to seal the sample off from the environment, utilizing the clean edges of the substrate to ensure a good seal. Poor sealing will lead to reaction, detectable by the evolution of H_2S , the potent, unmistakable scent of rotten eggs. Due to obstruction by the kapton tape, obscuring the peaks as a large carbon

signal, scans of either ten or twenty eight minutes were employed. Once fully sealed by the Kapton tape, these samples are loaded either into a spring loaded holder, or onto a pressed putty. To facilitate a flat positioning of the substrate on the putty, press the substrate into the putty with two glass microscope slides, one on each side of the substrate, until the slides are flush with the outside of the holder and can press down no further.

2.3.5 TEM

Transmission Electron Microscopy observation was performed at the University of California, Riverside's Central Facility for Advanced Microscopy and Microanalysis (CFAMM), on an FEI Tecnai12, operating at 120kV. Sample preparation was done by dispersing $\text{Li}_2\text{CO}_3@\text{C}$ particles, or HCl acid washed $\text{Li}_2\text{S}@\text{C}$ particles, in ethanol. The dispersion was dropped onto a lacey carbon Cu grid (300 mesh), suspended by negative action, anti-capillary tweezers.

2.3.6 SEM

Scanning Electron Microscopy observation was performed at the University of California, Riverside's Nova NanoSEM 450. Sample preparation was done by dropping dry powder onto a sticky carbon tape substrate, then blowing off loose particles.

3 ASP

3.1 APPLICATION OF SPRAY PYROLYSIS

ASP is a scalable powder production system used in the pigment, advanced ceramics and catalyst industries (66) (75) (76). In general, ASP involves aerosolizing a reactant solution followed by a pyrolysis step under an inert or reactive environment. The ASP process is distinctive in that each reactant solution droplet acts as a micro-reactor. Selection of a micro-reactor scale enables this project to harness low thermal transport limitations which affords fast reaction kinetics. Moreover, by drawing from a well mixed solution, ASP generates droplets of uniform solution concentrations. Both of these factors come together to deliver a homogenous product from the start of production to finish, with results that are arguably independent of scale.

ASP has been investigated for the production of electrode materials including LiCoO_2 (77) (78) (79) (80) (81) (82)), $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ (83), LiMn_2O_4 (84) (85) (86) (87) (88), LiMMnO_4 ($\text{M}=\text{Ni}, \text{Co}, \text{Fe}, \text{Mg}, \text{Al}$) (89) (90) (91) (92) (93), LiFePO_4 , (94) (95) (96) (97) (98) (99), LiNiCoAlO_2 (100). Interest in ASP is due to the flexibility of the method. ASP offers a wide range of variables to control the outcomes of production volume, particle size distribution, composition and morphology. The aerosol can be generated by a variety of means, including ultra-sonication, an electric field or high velocity gas followed by tube furnace heating, plasma, flame or heating at the collection surface⁽⁵⁶⁾. This project utilizes high velocity gas as the atomizing method, followed by simple furnace heating. This method is the simplest, and least flexible option to deliver both atomization and a heat treatment. As

such, success with this system is a powerful proof of concept. As this project was conceived to be a drop-in solution with existing technologies for electrochemical storage manufacturing, ASP was selected to leverage an existing skillset in the energy storage work force.

3.2 FUNDAMENTALS

This project relies on aerosol spray pyrolysis as shape and size setting mechanism for the production of precursor powder. The term ‘aerosol’ refers to a population of non-gas objects sufficiently small as to be suspended in a gas stream. In this case, a population of solution droplets that evolve into dry particles across a heated reaction path. The solution involves a carrier solvent, which is evolved off, and precursor solutes, which precipitate within the droplet as the solvent is removed, and solute concentration increases past the concentration of saturation for that solute in this solvent.

In this system the carrier solvent is water, carrying water soluble Li_2S and carbon precursors. Lithium salts were used as Li_2S precursors and sucrose was used as carbon precursor. The goal of the spray pyrolysis step is to produce hierarchal particles where a lithium salt is encased by a carbonized material. The carbon precursor need not be fully carbonized (becoming pure amorphous carbon), but it must be sufficiently carbonized that during subsequent heat treatment, where the powder sits in an immobilized boat, the powder will not melt, fuse or agglomerate, or fail to contain its lithium salt content.

Water is used as a carrier solvent for several reasons. As a solvent, it can dissolve a variety of sufficiently ionic solutes, covering a variety of salts and carbohydrates, which are suitable as

Li_2S and carbon precursors, respectively. With an eye toward scale-up, the choice of water as a solvent meant cheaper feed costs than organic solvents. And lastly, the relatively low viscosity of water, when compared to organic solvents, means collisions between droplets will result in a spherical shape. The use of more viscous solvents may lead to slower relaxation of the surface tensions and the occurrence of peanut shaped particles, if only two collided, up to massive agglomerates, for multiple collisions (101).

3.2.1 Micro-reactor system

Aerosol spray pyrolysis delivers a mist of particles through a heated region, as carried by a gas stream. In this design, every particle is a micro-reactor, as the reactions carried out in the system occur while the particle remains suspended in the gas stream, essentially independent of neighboring particles. Heat transport through the droplet is significantly higher than that of the gas stream, as can be observed in the proceeding plot. As such, the temperature inside the particle can be assumed to be in equilibrium with the temperature of the gas stream.

By deploying such an aerosol, the temperature of the reacting matter is determined less so by the position within the particle, but the particle's position within the reactor. This design obviates the detrimental effects of temperature gradients in reactor environments, delivering a predictable and consistent treatment to the feed material.

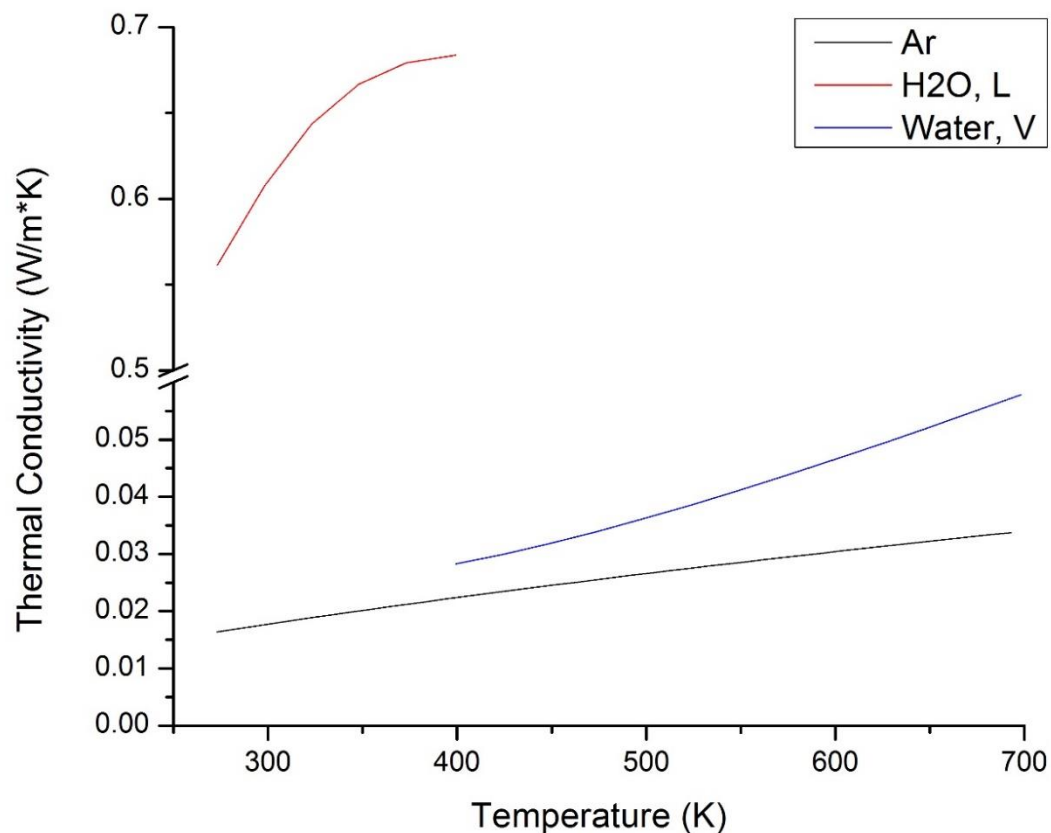
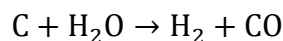


Figure 21 - Isobaric thermal conductivity of major aerosol components, for a wet particle.

<http://webbook.nist.gov/chemistry/fluid/>. Conductivity for the carbonized content of a particle may range from 7 to 50 W/mK, depending on level of carbonization and particle structure. Details vs temperature were not available, as the precise identity of the dry particle, per its heat transport, is hard to define. Suffice it to say that it meaningfully exceeds the heat transport of the gas stream.

3.2.1.1 Solvent loss

Given the composition of the pyrolyzed particle, namely of some lithium specie encased in carbon, it is critical that the stream not consume or otherwise react with the particle. The presence of moisture in the stream, at elevated temperatures represents such a risk.



The water gas reaction, as seen above, is an endothermic reaction ($\Delta H = + 131 \text{ kJ/mol}$). As such the elevated temperatures of the reactor (600-900°C), necessary to carbonize the carbon precursor, would drive the reaction toward the products, consuming the carbon host. To accommodate a removal of the solvent, a diffusion dryer is employed between the atomizer and the heated zone.

The diffusion dryer consists of a 1/2" diameter steel sheath through which the aerosol travels, surrounded by a cylinder filled with silica gel beads. The silica gel serves as a condensation surface for water vapor. Condensation of the water vapor draws moisture out of the stream, which in turn draws moisture out of the aerosol droplets, out to the stream. This drying technique offers a relatively slow solvent loss, which is beneficial for the formation of dense particles.

3.2.1.2 Relative diffusion of solutes, solvent and impact on architecture

Slow solvent loss allows for the randomly dispersed solutes to re-equilibrate across a shrinking droplet. In a shrinking droplet, the mean concentration of solutes can be described as such,

$$C_m = C_o \left(\frac{R_o}{R} \right)^3$$

Where C denotes concentration, R is radius, subscript m is the mean and subscript o is the initial condition. As the droplet loses solvent the concentration increases by a cubed factor (101). As the concentration at a radius r within the droplet exceeds the saturation

concentration, solutes begin to precipitate. If the concentration across the droplet exceeds saturation more or less at the same time across the entire droplet, solutes will precipitate across the entire volume, in what is termed volume precipitation, delivering a dense particle.

Alternatively, If the solvent loss is too rapid, the solutes near the outside of the droplet have little time to diffuse, via concentration gradient, deeper into the particle. This condition leads to surface precipitation, where a highly concentrated solute, at the outer edge of the drying particle, forms a shell. This shell is then subject to rupture, if further solvent cannot diffuse through the shell. Since a coherent hierarchical structure is desired, and rupture represents poor protection of the internal, active material, a shell structure is not desirable.

The following figure articulates the architectural results of different reactor conditions for an aerosol particle. The top row shows a particle where solutes precipitated more or less at the same time across the particle, leading to volume precipitation, yielding a dense particle. The subsequent row details surface precipitation, where solvent loss rate exceeded the diffusion rate of solutes. This leads to a shell forming around the droplet, where solvent remains to evaporate. If the shell permeability is too low for solvent escape, pressure from the evaporation of solvent will lead to a rupture. If shell permeability is sufficiently high, solvent vapor may escape, leaving an intact shell. Due to the materials selected in this work, odd structures resulting from melting are not an issue. Particles produced in this work are almost entirely spherical.

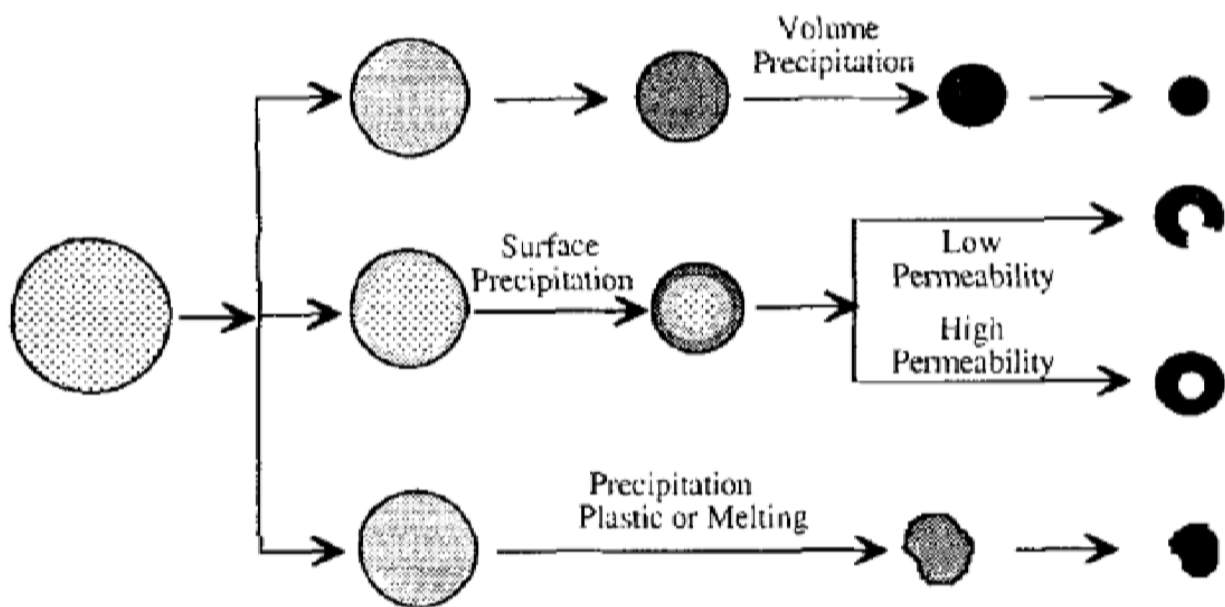


Figure 5 - Aerosol particle morphology as a function of reactor conditions (101)

This behavior can be described by the relationship of two concepts, the characteristic time of evaporation t_e , and the characteristic time of diffusion, t_d . If $t_e/t_d \gg 1$, the particle will be dense. If $t_e/t_d \ll 1$, the particle will be hollow. In this work, the relationship of t_e and t_d is affected by choice of solute, choice of solvent, reactor temperature or the control of solvent vapor pressure in reactor. The following figure shows the morphology of a particle comprised of 45nm SiO_2 beads. On the left, suspension in methanol lead to a $t_e/t_d = 0.5$ and a hollow particle. On the right the same beads are suspended in water, with a much lower vapor pressure than methanol, as such a greater characteristic time of evaporation. Here $t_e/t_d = 2.1$, yielding a dense particle.

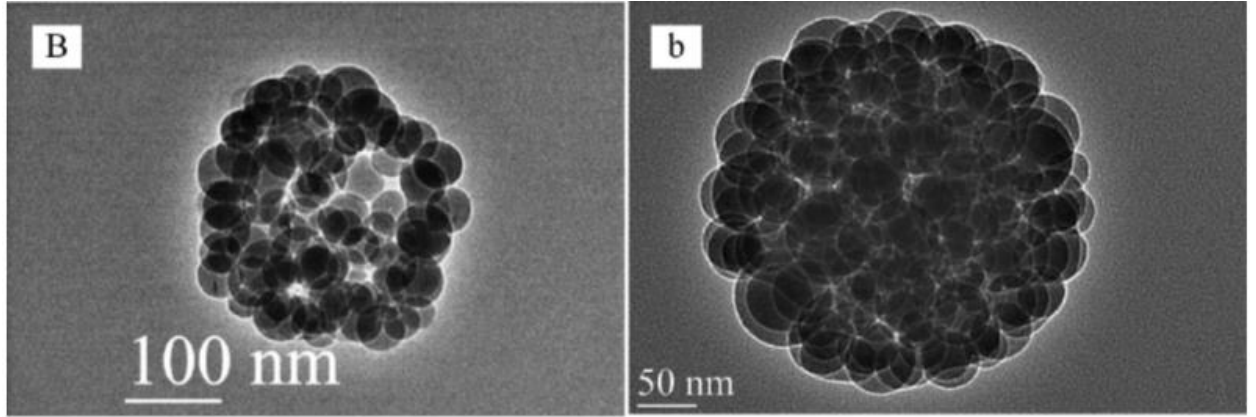


Figure 6 – Morphological effects for the relation of t_e/t_d for a particle comprised of silica nanoparticles suspended in methanol (left) and water (right) (102)

3.2.2 Path design

3.2.2.1 Residence time

Aided by the catalytic action of the lithium salts chosen as precursors, carbonization does not require a high residence time. For a flow system comprised of a series of tubes, it is sufficient to consider the following relation when considering the system,

$$Q = VA$$

Where Q is aerosol flow, in units $\text{cm}^3/\text{second}$, V is velocity along the axial direction of the tube, in units cm/second and A is the cross sectional area of the tube, in units cm^2 .

While the rest of the system had been comprised of 1/2" fittings from the beginning, early adjustments to the design considered modification of the 1/2" pyrolysis zone to 2" and 3" tubes. No particular improvement was noted in particle quality, as a cathode composite, but yield losses were significant. Since the area of a circle is a function of r^2 , adjusting the pyrolysis reactor to 2" resulted in a fourfold increase in residence time, while the 3" tube

resulted in a nine fold increase in residence time. These increases in residence time yielded a streak of black deposition at the bottom of the pyrolysis tube, toward the outlet. Suggesting ballistic losses of the powder prior to reaching the collection filter. Moreover, Brownian motion may have played a role in deposition losses as well, for the finer particles, as the tubing darkened along its entire diameter, near the tube outlet.

Were greater residence time deemed meaningfully helpful for some reason, such as in combining the pyrolysis step with a post treatment step, the pyrolysis chamber should be aligned such that flow from entrance to exit moved toward gravity. In this way, ballistic action would merely accelerate the particles toward collection, rather than lead to wall losses.

3.2.2.2 Heating regime

A preheater situated between the atomizer and diffusion dryer was considered as a means of removing solvent more effectively from the aerosol stream, to enable the use of Li_2SO_4 as the nucleating salt. At minimum, the formation of Maillardized (exhibiting some level of carbonization) particles with substantial carbon content ($>50\%$) are necessary, when using Li_2SO_4 as a lithium salt.

The preheater consisted of 1/2" copper tubing with three full loops, wrapped in three heating tapes, encased in an insulating box. Preheater temperature was measured by placing a K-type thermocouple at the outlet. Temperatures of 75°C to 350°C were attempted with sucrose, glucose and cellobiose as carbon sources, and lithium sulfate as a nucleator.

Operation at 75°C at the preheater and 400°C pyrolysis lead to a collection filter soaked in aqueous aerosol product. This is incompatible with powder production, as any hierarchical architecture generated will lead to redissolution of lithium salts. Operation at 200°C of the

preheater, with no pyrolysis generated lightly Maillardized particles with a carbon content of 79%, per TGA assessment. Light Maillardation results in light brown particles, subject to melting at higher temperatures in post processing. Despite the high carbon content, thought to help in encasing the lithium salt, this product was insufficiently Maillardized to be an effective encasement in post treatment.

Operation at 200°C with pyrolysis reaction at 600°C generated well Maillardized particles with a carbon content of 4.2%, per TGA assessment. This carbon content was deemed too low to be useful. Operation at 350°C yielded highly agglomerated particles, which may lead yield loss due to ballistic deposition down stream in pyrolysis chamber and uneven downstream processing. It was determined, due to this variability in results, none of which beneficial, that a preheater was not necessarily helpful.

A practical issue with the preheater was the formation of high concentration plugs in the heating coil. This plug lead to increasing material losses, as the aerosol struck the growing obstruction, until the plug sealed the system enough to create a buildup of pressure that destroyed the quartz atomizer.

The system runs at a rate of 2-4 ml of solution drawn per hour, where solvent represents 70-98% by weight of the solution. Variability in solution draw is attributable to increasing pressure drop over the course of a run, as filter deposition increases, as well as solution viscosity at varying levels of solute concentration. 25psig setting results in a flow of 8.6 SCFH argon at room temperature, as measured down stream of the pyrolysis section, which converts to roughly 244 liters per hour (LPH). At 20°C the partial pressure of water is 0.34 psi. At 75°C, the partial pressure of water is 5.6 psi. This translates to a saturation of the

solvent in the aerosol stream at 0.8% and 14% respectively, across unheated and minimally heated entrances to the diffusion dryer. At a rate of 4 ml per hour, water vapor represents, at most 100 ml of vapor per hour in a stream of 244 LPH, or 0.04% at room temperature. Argon and steam volume per hour would scale together linearly at higher temperatures. The preheater concept was abandoned ultimately, having shown no beneficial effects, due to the conceptual understanding that a heated stream has a higher carrying capacity of steam and as such would not benefit the diffusion drying process.

3.2.3 Concentration vs particle size

In ASP, final particle sizing is proportional to initial droplet sizing, as articulated in the following plot, whereby the ratio of initial concentration, C_o , over saturation concentration, C_s , determines the unpyrolyzed particle size. The ratio of total solute concentration (C_o) to their saturation concentration (C_s) in NitS at the low end and CarS at the high end, are roughly 0.1 and 0.6 respectively. The atomizer employed in this study selects for aerosol droplets of maximum diameter of $2\mu\text{m}$. Given these ratios, maximum particles yielded from both would result in a maximum particle size below $2\mu\text{m}$, as described in the following plot.

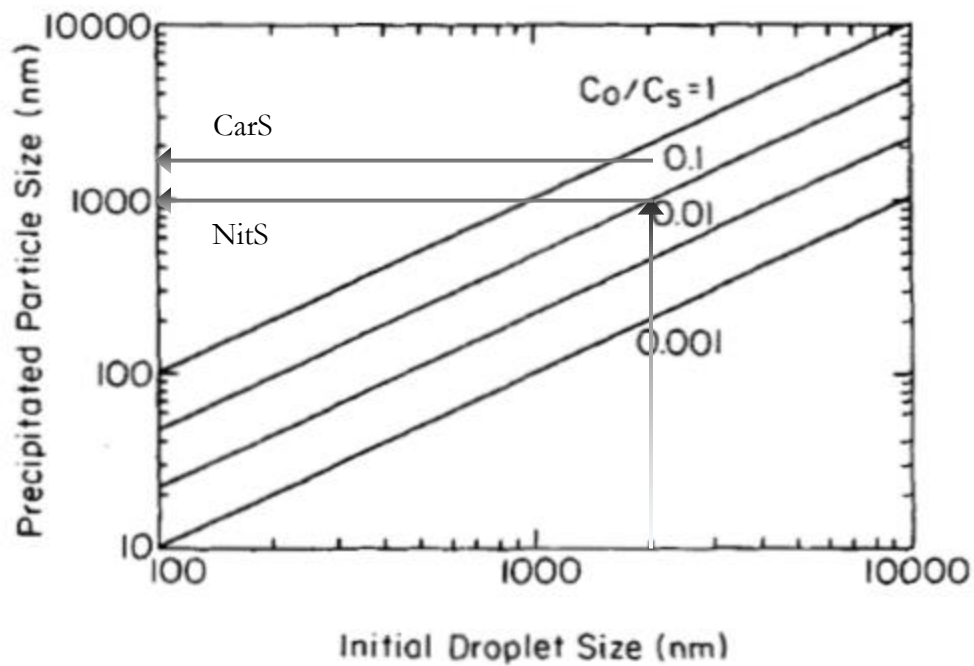


Figure 22 - Precipitate particle size as a function of solution concentration and droplet size before calcination. (101)

SEM evidence, however, shows much larger maximum size of the final particles. This suggests that the off-gassing of decomposition products during pyrolysis expand the particles as they form. The following image shows NitS particles, some of which exceed $10\mu\text{m}$.

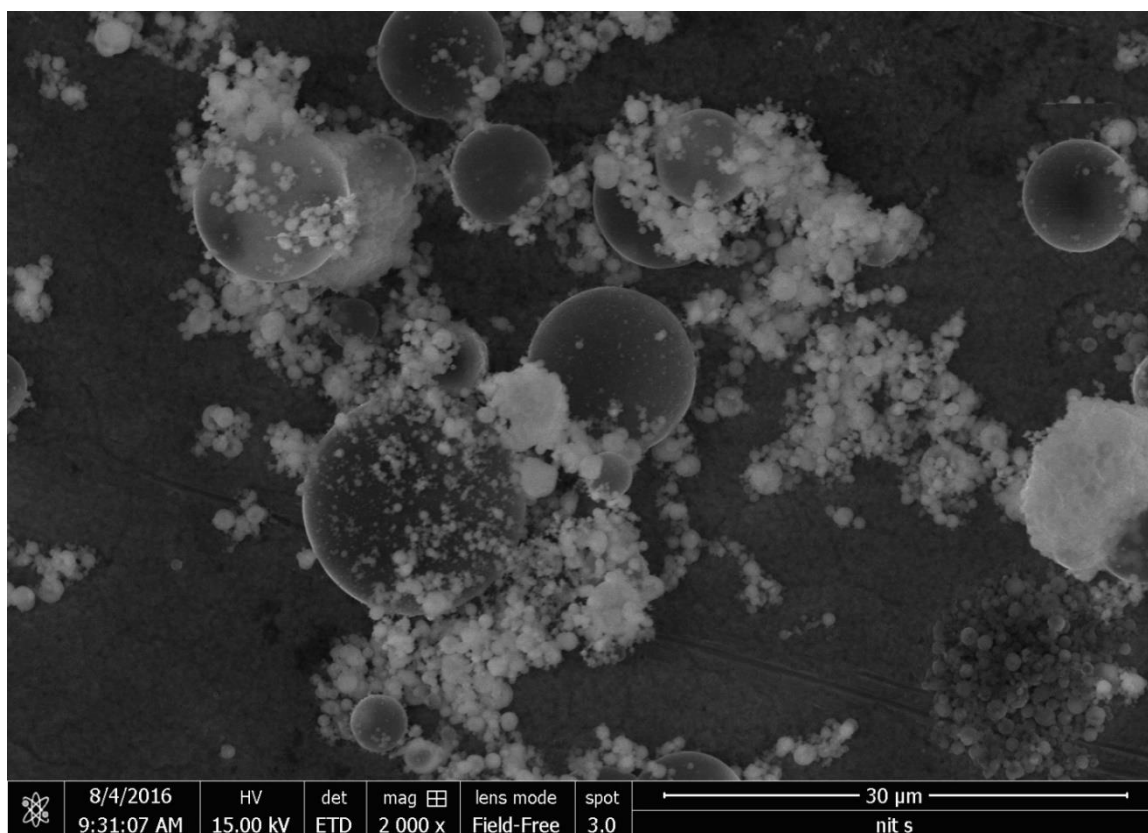


Figure 23 - SEM image of $\text{Li}_2\text{CO}_3@\text{C}$ NitS particles.

This off-gassing of decomposition products can also be seen to affect the architecture of larger particles. The following TEM image of the same NitS type particles shows large particles ruptured by off-gassing.

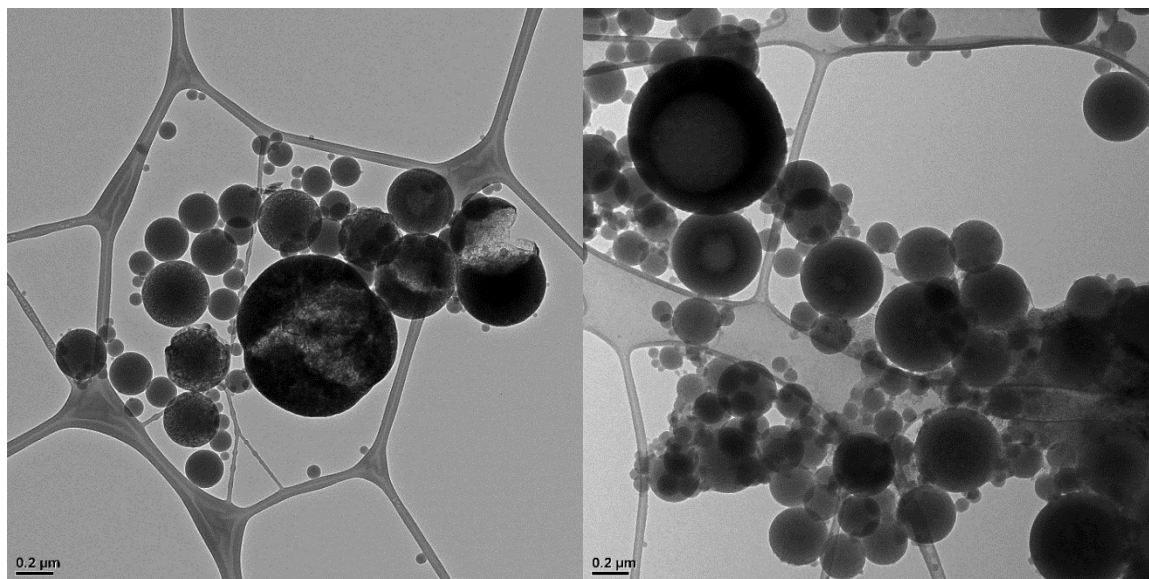


Figure 24 - TEM image of $\text{Li}_2\text{CO}_3@\text{C}$ NitS (left, 0011, 8.3.2016, HSU) and AceS (right, 505, 1_6.5K, 6.8.2016) particles.

This TEM shows a representative sample of NitS particles. All of which are more or less spherical, but the larger of the population are burst open or dramatically expanded. This behavior occurs only above $0.1\mu\text{m}$ in formulations where the lithium salt generates gaseous decomposition product, such as NitS and AceS. Li_2CO_3 is sufficiently stable in the reaction severity of the pyrolysis chamber not to off-gas during formation. As such this behavior is not observed in CarS particles. While not prone to off-gassing, CarS particles will generally take on a non-spherical shape, suggestive of melt as noted in (101).

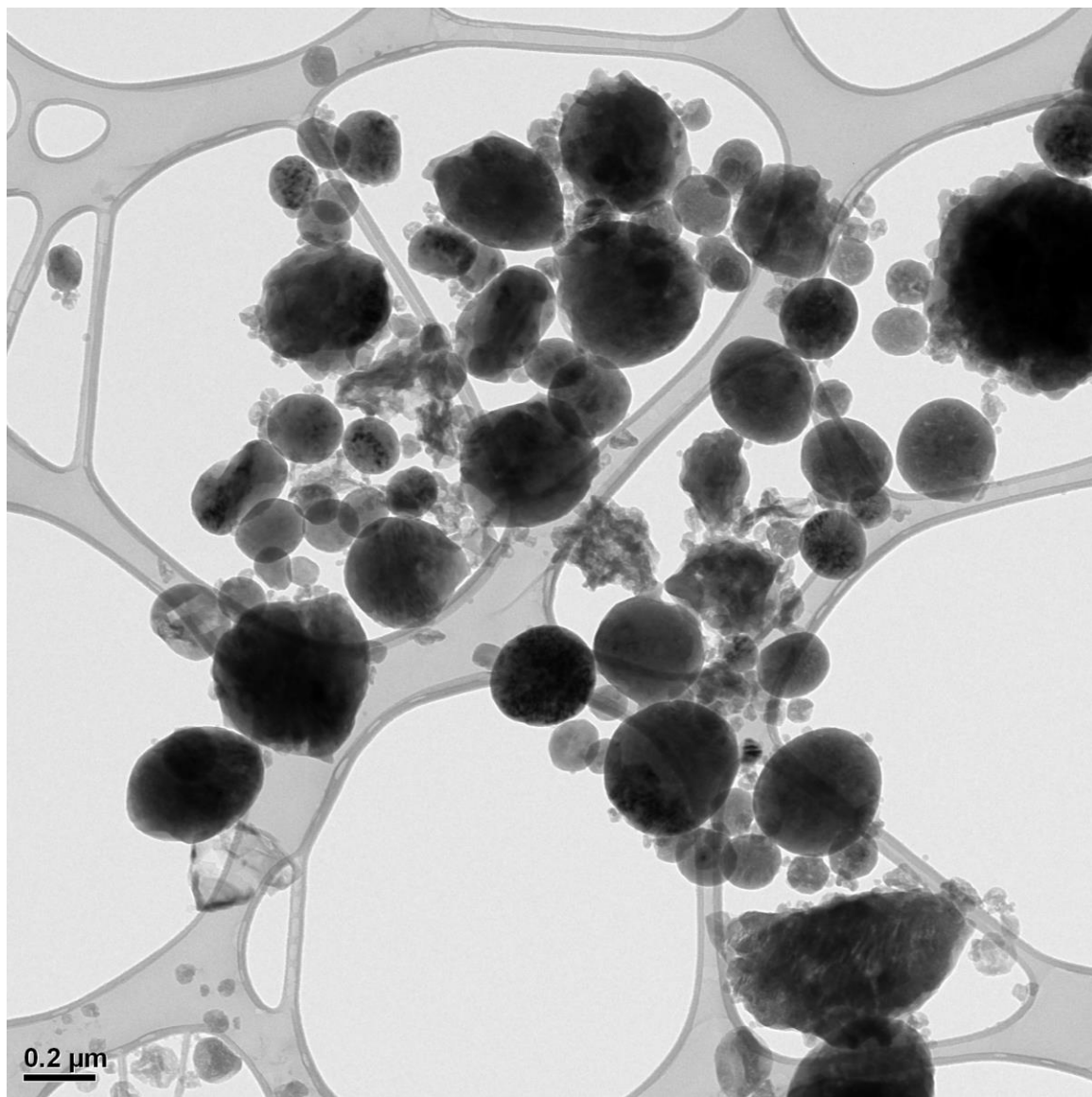


Figure 25 - TEM image of $\text{Li}_2\text{CO}_3@\text{C}$ CarS particles (421, 1_6.5K, 12.9.2015)

3.2.3.1 Diffusion dryer

3.2.3.1.1 Limitations of Lab Setup

Deemed the most practical means of aerosol solvent dilution, the diffusion dryer is an effective tool for the removal of sufficient solvent for the purposes of ASP. Due to the design, which employs a steel mesh tube, significant turbulence can be expected. This is thought to have contributed to the relatively low mass yields, hovering around 3-5%. While not all solute mass is expected to translate to powder mass, given the decomposition of the various precursors, 3-5% was almost unworkably low at times. This mass yield acted as an additional specification setter regarding solute concentration, driving the practical concentration of solutes upwards. Since the diffusion dryer appeared to maintain charge until roughly 40ml of solution passed through it, greater solute concentrations were needed to translate that 40ml of solution to a meaningful batch. This limitation is particularly poignant in the CarS formulation, where Li_2CO_3 saturation, at 0.17M, severely limited mass collected from CarS production to between 0.035 to 0.083g in the final formulation, 1C085S (0.1M Li_2CO_3 , 0.085M sucrose). AceS by comparison, yielded 0.043 to 0.127g, for the 3A015S formulation (0.3M lithium acetate, 0.015M sucrose). NitS yielded 0.139 to 0.257g, for 3N2S (0.3M lithium nitrate, 0.2M sucrose). As a result of this disparity, NitS was often used as the test bed for other variables, such as pyrolysis temperature, post treatment duration and temperature and eventually the electrolyte study. This lead to choices made that optimized the performance of 3N2S product, rather than optimal configurations for all three precursor sets.

The diffusion dryer, moreover, is not a steady state component of the system. As the run proceeds, the beads closest to the flow will saturate; this leads to a shallower gradient, and a weaker draw on moisture. As such, powder produced early on in a production run will experience a dryer pyrolysis environment, leading to faster heating in pyrolysis, and less carbon loss. The former may affect the architecture by way of tending toward surface precipitation, while the latter may result in better carbon coverage. As the run proceeds, a wetter aerosol stream leads to slower H₂O loss in pyrolysis (both from remaining moisture and from the dehydration of lithium salt hydrates), promoting less complete carbonization as well as the consumption of the outer most carbon in the matrix. At the end of a run, all powder is collected together, as there is no separation by production timing. This yields a mix of particles, with varying architectures and coverage, potentially yielding meaningful variation in composite quality as a cathode. This is an inherent source of non-reproducibility in this system, which would be absent in a steady state system.

3.2.3.1.2 Opportunity in Scale Up

The diffusion dryer facilitates sufficient dilution of aerosol solvent so as to reduce interaction later on in the heated zone. In this case H₂O acts as an oxidizer, consuming carbon and reducing damaging carbon coverage, as this attack will inherently arrive from the outside, consuming the outer most aspects of the carbon host; which are arguably the most important region of the carbon matrix.

Alternatively, sufficient solvent dilution can be accomplished by means of inert gas mixing, post atomization. A secondary gas flow may be introduced, dramatically lowering aerosol

concentration, possibly sufficiently to dry the stream for the purposes of reaction at elevated temperatures (600-900°C).

This method was considered impractical for laboratory scale, given the high flow of gas needed to achieve it. Industrial applications may benefit from a recycling system, able to capture the process gas and recirculate it into the ASP system.

A added benefit may be available in collecting waste heat from the ASP and introducing it via the secondary gas flow. Since this gas stream is introduced after atomization it will not effect the atomization action itself, but may offer a slower solvent drying rate than that available by the pyrolysis chamber alone. This may lead to better volume precipitation (101), densification of particles by staged pyrolysis segments (such as waste attempted with the preheater) and an overall increase in process efficiency due to the collection of waste heat.

3.3 ARCHITECTURE

3.3.1 Reference success of Sn@C architecture

This work is based on the previous success of ASP as a method or the encapsulation of tin in a carbon matrix, Sn@C. In (103) Guo et al showed that ASP can be deployed to template a spherical carbon host matrix around an active material. In this case, SnCl_2 was used as a Sn source, and sucrose as the carbon matrix precursor. This system benefitted from one shot production, where the formation of Sn metal and the carbon host occurred simultaneously in the 700°C environment.

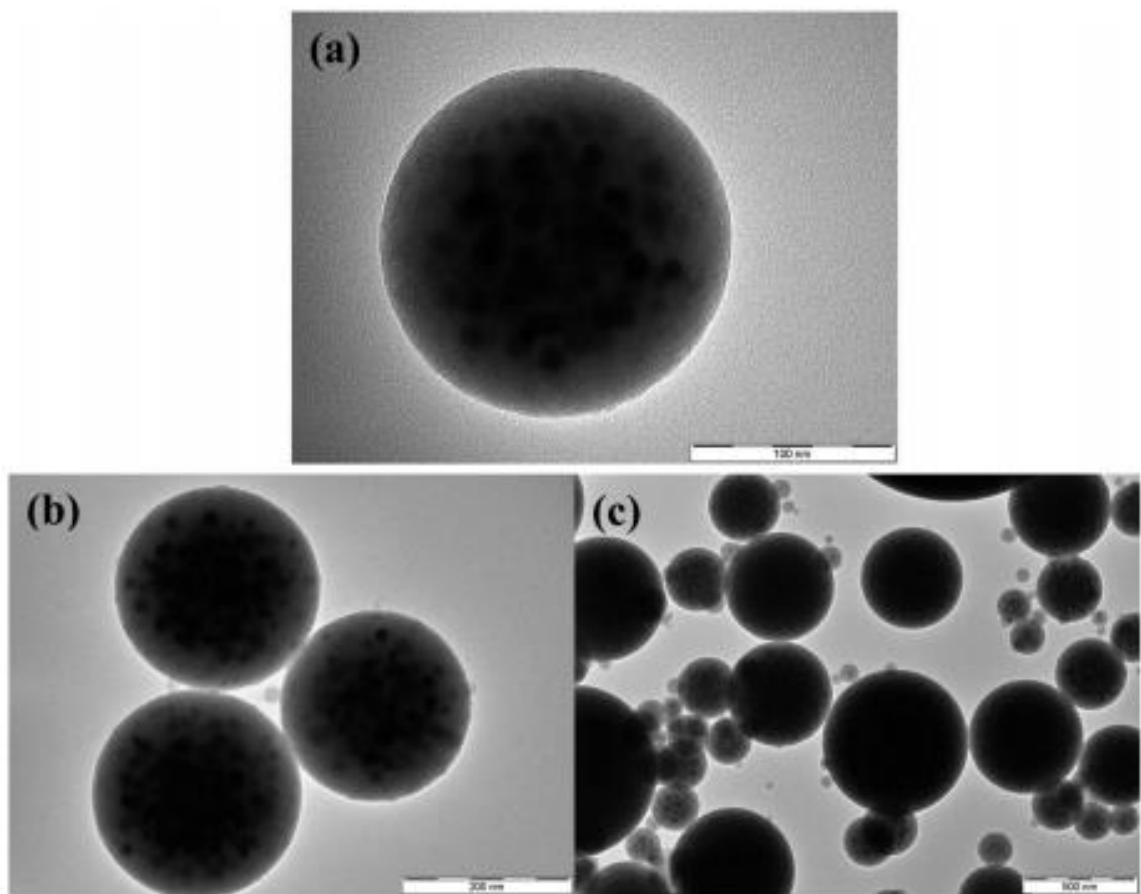


Figure 26 - TEM image of Sn@C composite. (103)

The use of a shape directing agent, Pluronic F127, is deployed to minimize the sizing of the carbon matrix, shortening the path of lithium ion travel through the particle, improving performance.

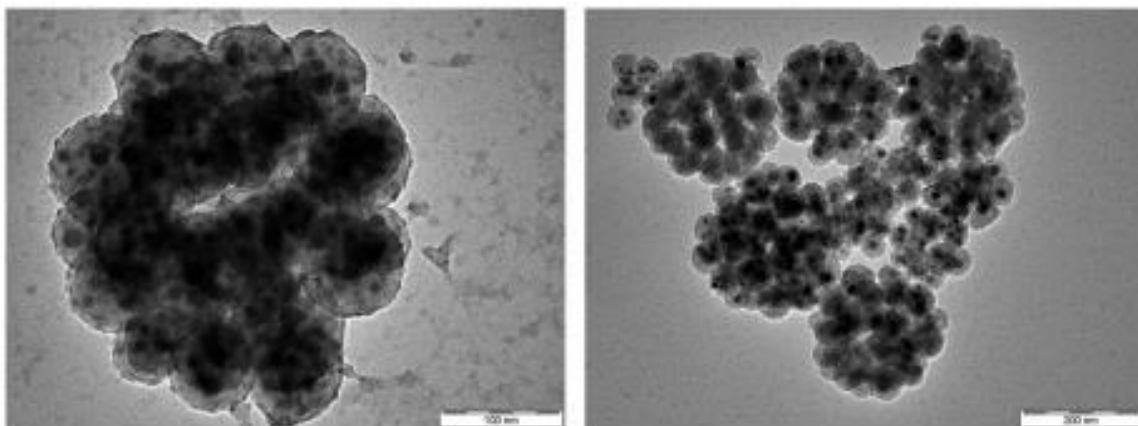


Figure 27 - Pluronic modified Sn@C particle. (103)

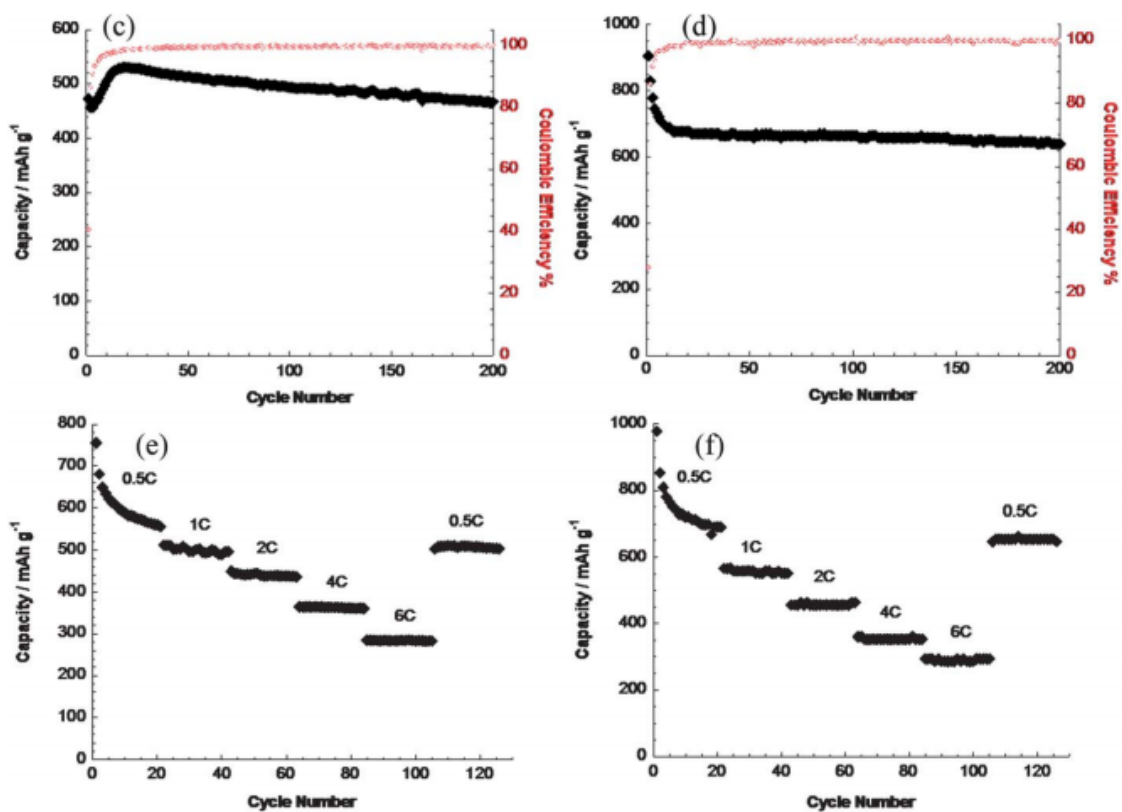
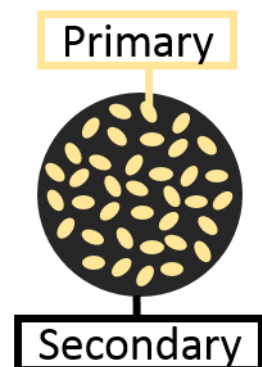


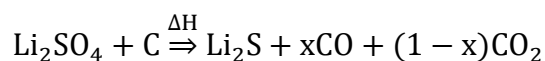
Figure 28 - Performance of the Sn@C composite (c & e) and F127 modified product (d & f) (103)

Shape modification was shown to meaningfully improve capacity as well as capacity retention. This work showed that architecture, particle sizing and size distribution influence performance. The goal of this work had been to first replicate this architecture, with sulfur species as the primary particle, in place of tin. Then to improve on performance via shape modification agents, such as F127.



3.3.2 $\text{Li}_2\text{SO}_4/\text{Suc}$

Known as an effective carbon precursor (104) (105) (106) (107) (108) (109) (110) (111), sucrose was selected to form the host primary particle around the active material. The initial plan was to form a carbon host around lithium sulfate (Li_2SO_4), which under sufficient heating will oxidize the carbon in the following reaction, yielding Li_2S encapsulated in remaining carbon,



While this scheme works well enough with static reactants, as placed in a boat under a flowing argon environment, it does not work in a spray pyrolysis setup. Early attempts to carbonize sucrose from a solution of Li_2SO_4 and sucrose yielded no powder whatsoever, as the carbon precursor decomposed completely at reactor temperatures and the lithium salt was carried off by moisture at the filter.

Magnesium nitrate and iron (III) nitrate were deployed as magnesium oxide and iron oxide precursors. The former can be seen in the proceeding figure. While both seed materials worked well enough in carbonizing sucrose, their mass in the final product was high, which

represents an unacceptable level of electrochemical dead weight. Washing these seeds out would mean washing out the Li_2SO_4 as well, defeating the purpose of the project.

Reintroducing sulfur or Li_2SO_4 later would not represent a novel approach, nor would the carbon host be reliable as an affective trap for sulfur species later on. If sulfur can be introduced from the outside, the thinking went, it could dissolve out during cycling.

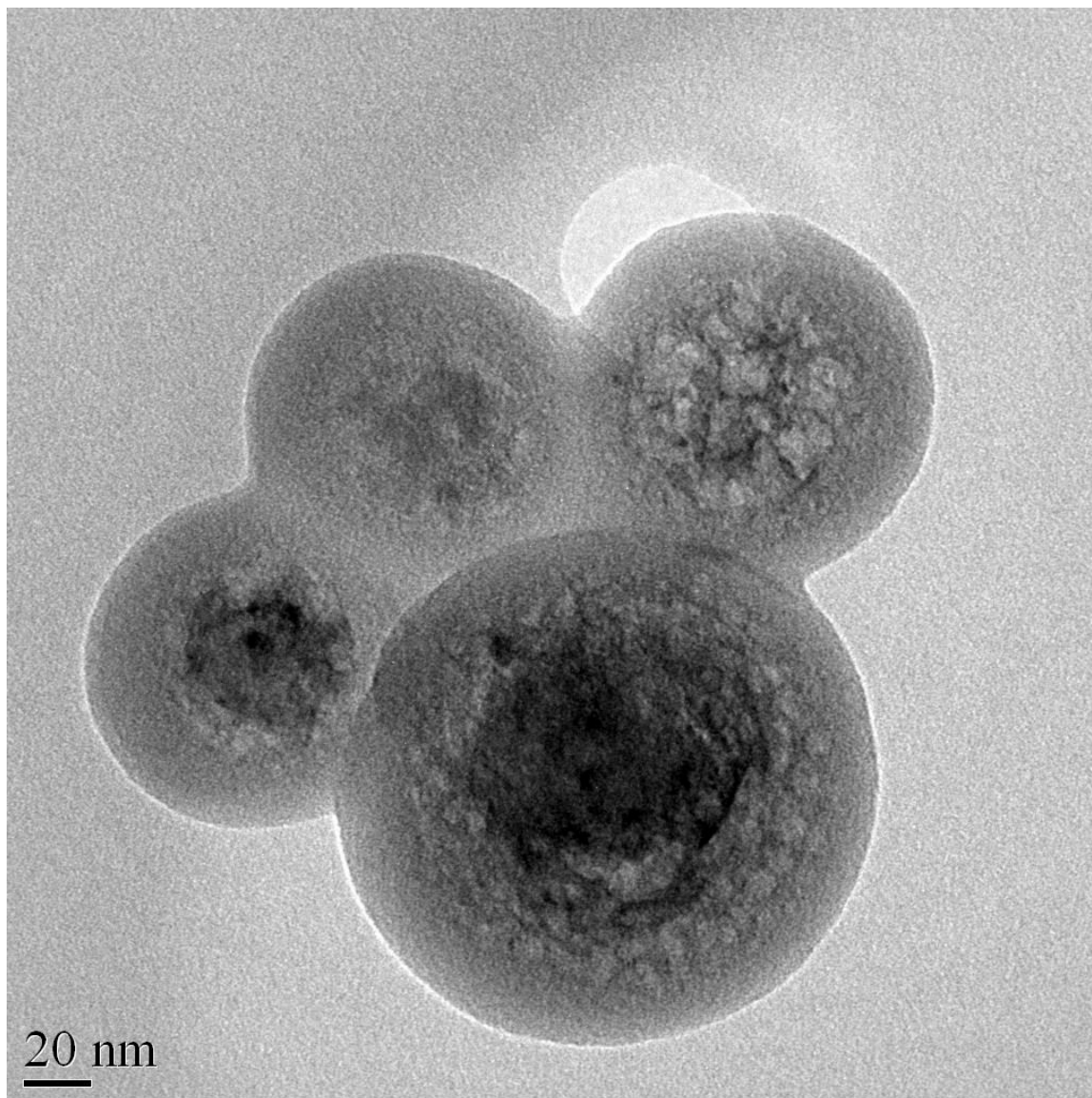


Figure 29 - TEM image of carbonized pyrolysis particles produced from a mix of Li_2SO_4 , magnesium nitrate and sucrose. The dark regions inside the particles represent MgO crystals.

However, placed in a boat under a stream of argon, Li_2SO_4 and sucrose formed a well carbonized product. Here the residence time for the sucrose in the reaction environment was on the order of hours, rather than a fraction of a second, allowing for carbonization to take

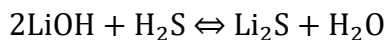
place. The challenge here was to ensure that the Li_2SO_4 remained inside the host as it carbonized.

Further development of this approach was attempted in conjunction with freeze drying as a means of templating the Li_2SO_4 into small domains, reducing crystal sizing and providing for small Li_2S particle sizing in the final product. Ultimately, this method yielded inconsistent performance and low capacities. As a result of the escape of oxidizing species, upward out of the sample, the upper region of the boat held sample would often yield a lighter color than the rest of the sample. This suggests exposure of the underlying primary material, be it converted Li_2S or the unconverted Li_2SO_4 precursor, both of which are white in color.

3.3.3 Alternate lithium salts

3.3.3.1 LiOH

An alternative approach, of introducing lithium independent of sulfur, then converting it to Li_2S later on was attempted. Lithium hydroxide, known to convert to Li_2S by the following reaction, was attempted.



Carbonization with LiOH was unimpressive. While some carbonized material formed, evident by a grey tint in the powder, the product was mostly very large crystals of LiOH , as can be seen in the proceeding TEM images.

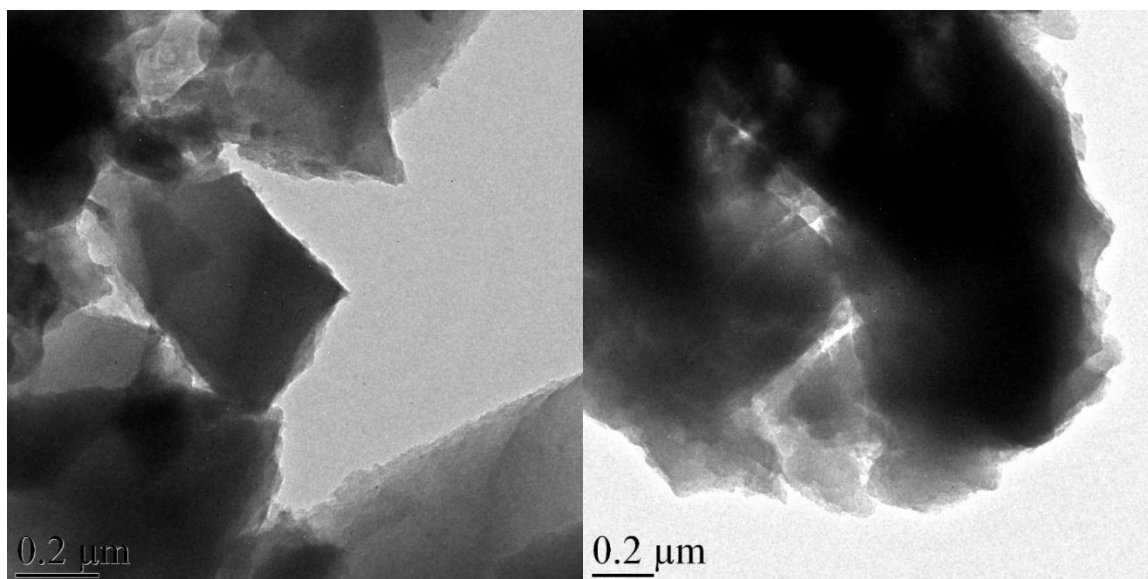
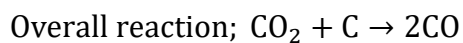
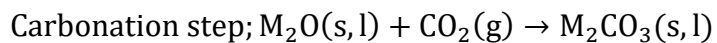
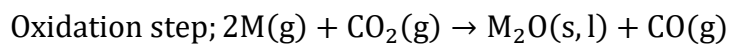
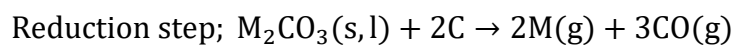


Figure 30 - TEM image of LiOH and sucrose pyrolysis product. Note the large LiOH cubic crystals.

While LiOH remains a promising Li_2S precursor, as explored in (69), it is not an effective carbonization nucleator, and as such inappropriate in a spray pyrolysis context.

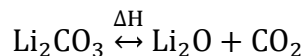
3.3.3.2 Li_2CO_3

Lithium carbonate is a known Boudouard Reaction catalyst. it has been suggested that alkali carbonates catalyze the Boudouard Reaction as intermediaries, as follows, where M represents the alkali atom (67),



Where the Reduction Step is considered to be the rate limiting step. This catalytic action appears to drive the rapid decomposition of carbohydrates to carbonaceous materials, a necessary step in the formation of carbon hosts in the short residence time of the pyrolysis reactor.

The presence of Li_2CO_3 appears to assist in the formation of pyrolytic carbon by acting as a local CO_2 sink, and limiting oxidizing nature of the pyrolysis environment. Thermal decomposition early on in the pyrolysis reactor releases CO_2 into the argon diluted reactor environment,



The remaining lithium may now act as a local CO_2 sink, driving the reaction toward reactants and preserving solid carbon around the lithium specie seed.

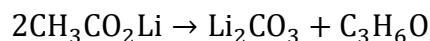
The knowledge base of alkali metal oxides as Boudouard catalysts has not specifically been studied a context where the alkali metal catalyst travels with the rest of the reaction participants, suggesting different results may arise from the presence of the alkali metal oxide. The actual mechanism by which carbon is formed in this chamber is outside the scope of this investigation, but whatever the mechanism in play, this action has driven the selection of the reaction precursors.

The use of other lithium salts other than Li_2CO_3 , which thermally decompose into Li_2CO_3 show the same action, though resulting in characteristically different architectures and carbon loading, as will be discussed next.

3.3.3.3 Acetate

3.3.3.3.1 Thermal decomp route

Lithium acetate ($\text{CH}_3\text{CO}_2\text{Li}$) is known to undergo thermal decomposition below 500°C in the following scheme (112),

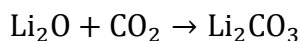
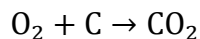
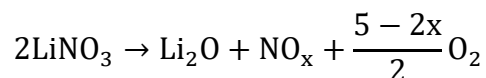


The acetate system displayed the lowest sucrose concentration needed to achieve a $\text{Li}_2\text{CO}_3@\text{C}$ with a 20-25% carbon weight, of 0.02M. This suggest that $\text{C}_3\text{H}_6\text{O}$ contributes to the carbon content of the particle.

3.3.3.4 Nitrate

3.3.3.4.1 Thermal decomp route

Lithium nitrate undergoes thermal decomposition in the following scheme,



This decomposition route suggests an inherent consumption of carbon adjacent to the decomposing LiNO_3 . This notion is corroborated by the relatively high concentration of sucrose necessary to generate a LiNO_3 based $\text{Li}_2\text{CO}_3@\text{C}$ particle with 20-25% carbon weight, of 0.25M.

3.3.4 Focus on comparing the architecture

3.3.4.1 TGA driven standardization, yields comparable though un-optimized composites

3.3.4.2 Carbonate vs Acetate vs Nitrate

3.4 CELL COMPONENT SELECTION AND RATIONALE

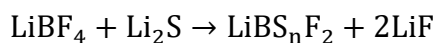
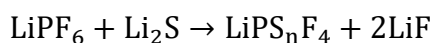
3.4.1 Electrolyte Selection

Identifying the appropriate electrolyte solution is a critical step in setting up this study.

Composed of solvent, lithium salt and additives, the electrolyte solution is a complex system which affects the performance and longevity of a cell. Traditional li-ion electrolyte components are inappropriate in a Li-S cell, due to reactivity with polysulfide (PS) intermediates.

3.4.1.1 Salt Selection

Li-ion appropriate salts include LiPF_6 (Lithium hexafluorophosphate), LiBF_4 (Lithium tetrafluoroborate), LiBOB (Lithium Bis(oxalato)borate) and $\text{LiBF}_2\text{C}_2\text{O}_4$ (Lithium oxalyldifluoroborate). These salts are reactive with Li_2S in the vein of following schemes (113),

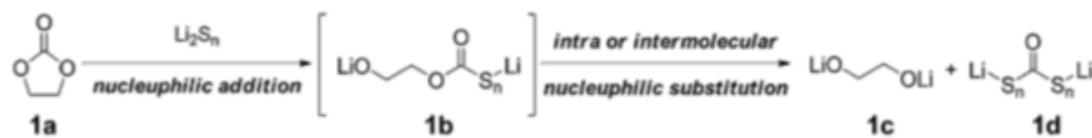


Moreover, the salts noted above are incompatible with some Li-S appropriate solvents, precluding them from application in Li-S cells (113). LiTFSI (Lithium Bis(trifluoromethane)sulfonimide) has been identified as an appropriate salt in Li-S cells, owing to high dissociation constant, high temperature stability and relatively high ion mobility in solution (114). Since this work was conceived of as a drop-in solution, compatible with existing Li-S components, LiTFSI was accepted as the lithium salt under investigation. Investigation of alternative salts, while ongoing in the literature (e.g. high concentrations of LiFSI as a protective coating promoter, (115), as well as LiDTI as a PS solubility reducer, (116)), is outside the scope of this work. If for no other reason than LiTFSI's reactivity to steel and aluminum, substrates common to commercial cells, LiTFSI has not been used in a commercial cell. As such, continuing research into alternative salts remains relevant to successful commercialization of Li-S cells.

3.4.1.2 Solvent Selection

Li-ion appropriate solvents consist of liquid carbonates, including EC (ethylene carbonate), EMC (ethylmethyl carbonate), DMC (dimethyl carbonate), DEC (diethyl carbonate), PC (Propylene carbonate). These compounds are known to react with PS in the following proposed schemes,

(a) EC decomposition



(b) EMC decomposition

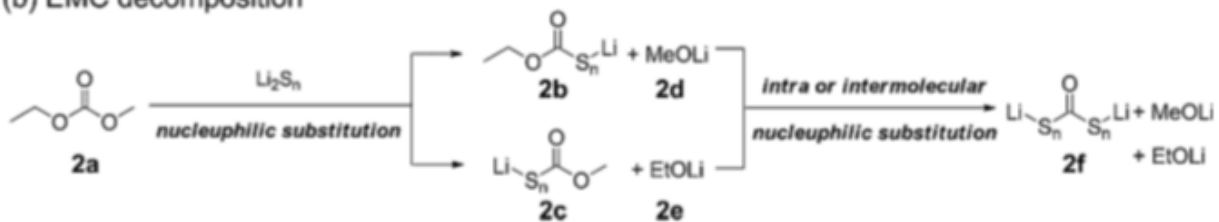


Figure 31 – Proposed reaction schemes for the consumption of PS by ring and linear carbonates. (117)

This set of irreversible reactions leads to a loss of accessible cathode sulfur mass, as well as a loss of lithium. Both result in a loss of capacity, as the following comparison articulates,

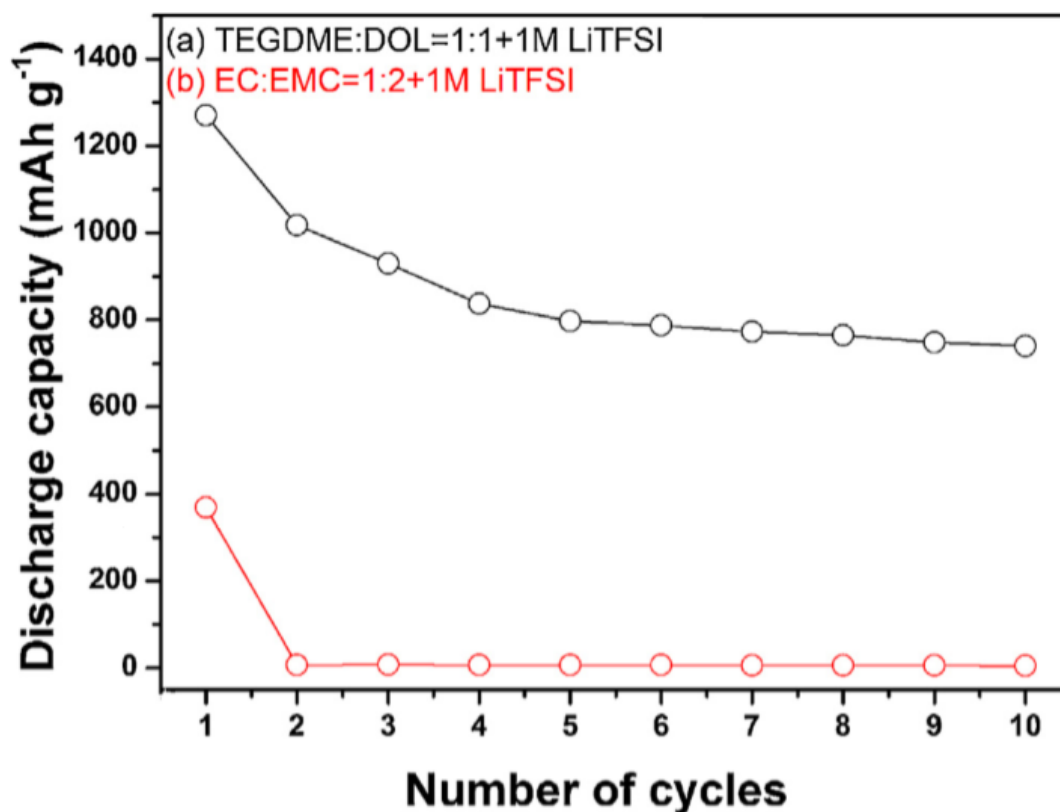


Figure 32 - Comparison of capacity retention for Li-S cell in carbonate (red) vs ether (black) electrolytes. Shows cycle performance of the Li-S cell at C/10 with (a) TEGDME:DOL = 1:1 with 1M LiTFSI and (b) EC:EMC = 1:2 with 1M LiTFSI. (117)

Appropriate solvents for Li-S cells have been identified. They include TEGDME (Tetraethylene glycol dimethyl ether), PEGDME (Poly(ethylene glycol) dimethyl ether), DOL (1,3-dioxolane), DME (Dimethoxyethane). These ether family solvents are known to dissolve PS and be minimally reactive to PS, making them appropriate for Li-S cells. The addition of room temperature ionic liquids, such as Pyr₁₄TFSI (1-Butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide)), an exotic new class of solvents, has garnered increasing interest as a cosolvent. These solvents present with very high viscosity however, which improves capacity retention by slowing PS migration, but leads to

sluggish kinetics, affecting rate capacity. Pyr₁₄TFSI has also been suggested to contribute to the formation of a beneficial SEI on lithium metal, improving cycle stability by preventing the interaction of PS with the anode surface (118) (119).

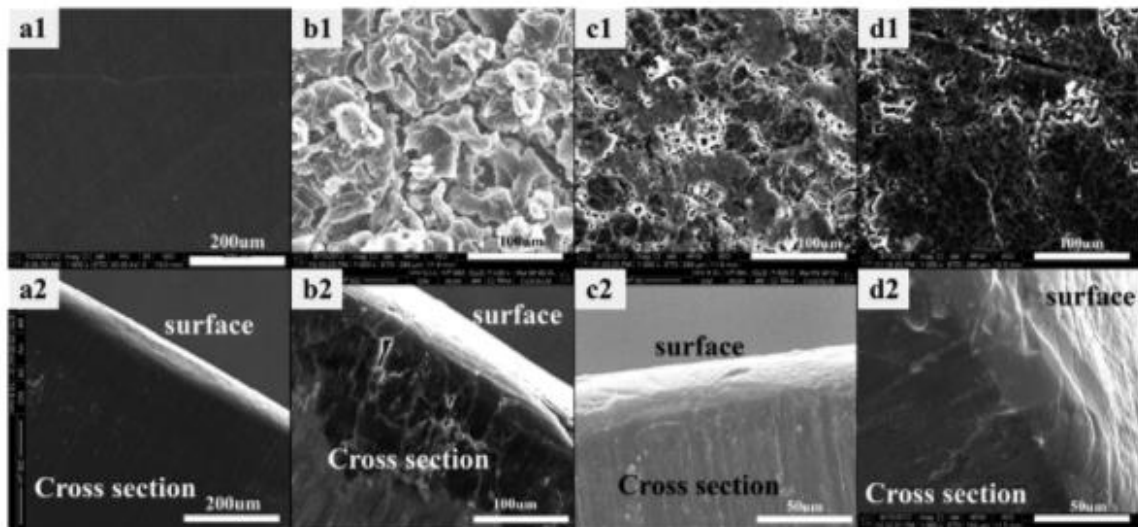


Figure 33 - SEM images of lithium metal anode surface and cross sections of (a1 and a2) fresh lithium metal and lithium metal cycled in (b1 and b2) the baseline electrolyte, (c1 and c2) 50% Pyr₁₄TFSI containing electrolyte, and (d1 and d2) 75% Pyr₁₄TFSI containing electrolyte for 100 cycles at C/5. (118)

A study was conducted with select composite formulations, to identify the most appropriate electrolyte mix for various charging rates. The electrolyte components must first excel in a slower charging/discharging regime (C/20), where resilience to PS dissolution will be most observable. The best performing mix will then be subjected to faster regimes (C/10 and C/5) where typical daily use and performance can be simulated.

A high carbon content composite (3N25S) was selected to consider the effect of various electrolyte solvents on performance. The high carbon content would arguably contribute to higher deposition surfaces for insoluble products, greater diffusion distances for PS and as

such a greater barrier for the action of the shuttle. Three electrolyte systems were considered, comprised of combinations of the following four solvents;

Table 3 - Solvents explored as electrolyte components

Colloquial name	Density (g/ml), ρ	Dynamic Viscosity (cP), μ	Kinematic Viscosity (cP), μ	Ionic conductivity (mS/cm), σ
TEGDME	0.986	3.26 ⁶	-	
DOL	1.06	0.57 ⁶	-	
DME	0.868	0.46 ⁶	-	
Pyr ₁₄ TFSI	1.41 ⁷	-	98 ⁷	6.0 ⁷ , 2 ⁸ & 2.2 ⁹

⁶ (5)

⁷ (156)

⁸ (161)

⁹ (162)

Table 4 - Solutions deployed as electrolytes, with calculated dynamic viscosity. All solutions included 1M LiTFSI and 1.5%wt LiNO₃.

Solvent components	Volume ratio	Est. dynamic viscosity (cP) of solvents	Measured viscosity (cP) of solution	Ionic conductivity of solution, σ , (mS/cm)
DOL:DME	1:1	0.52	1.56 ¹⁰	13.21 ¹⁰
TEGDME	1	3.26		
DOL:DME: Pyr ₁₄ TFSI	1.2:1.8:1	1.39	$\approx 3.07^{10}$	$\approx 13.82^{10}$
DOL:DME: Pyr ₁₄ TFSI	1:1:2	4.50	7.41 ¹⁰	10.40 ¹⁰

Estimation of the kinematic viscosities of mixtures was done using the mass based version of the Refutas Equation for the calculation of hydrocarbon fluid mix viscosities (120). The Refutas Equation calculates the kinematic viscosity, relevant to fluids in flow. In the context of a closed electrochemical cell, however, the electrolyte is essentially at rest, so the results are converted to dynamic viscosity. The method is as follows,

VBN_i , Viscosity Blending Number of solution component i

x_i , mass fraction of solution component i

¹⁰ (118), source uses a 1:1 ratio of DOL:DME and no LiNO₃, which will result in slightly smaller values than in this work. Values are offered for relative purposes, rather than asserting absolute values.

ν , kinematic viscosity

μ , dynamic viscosity

Values available for fluids in terms of dynamic viscosity are converted to kinematic viscosity by this relation,

$$\nu = \mu / \rho$$

Viscosity Blending Numbers are calculated, yielding the kinematic viscosity of the mix,

$$VBN_i = 14.534 * \ln(\ln(\nu_i + 0.8)) + 10.975$$

$$VBN_{mix} = \sum_{i=0}^n x_i * VBN_i$$

$$\nu_{mix} = \exp \left(\exp \left(\frac{VBN_{mix} - 10.975}{14.534} \right) \right) - 0.8$$

Returning a value of the dynamic viscosity of the mix, μ_{mix} , required parsing out the density contributions of each component, added linearly.

$$\rho_{mix} = x_1 \rho_1 + \dots + x_n \rho_n$$

$$\mu_{mix} = \nu_{mix} * \rho_{mix}$$

All cells presented were tested with an electrolyte volume (ml) to calculated sulfur mass(g) ratio of 30:1. This ratio has shown to be sufficiently low to improve cycle stability, but high enough to be able to wet the entire surface of the electrode. Cycling data show that within the first few cycles, cells loaded with electrolyte mix DOL:DME, the least viscous of the set,

showed dramatic PS shuttling. The shuttle can be observed by the long plateaus around 2.4V during charge.

This behavior occurred even in the presence of LiNO_3 as an additive, which has been shown to reduce shuttle behavior (121) (122). Contrasted with the cells where TEGDME was used as an electrolyte solvent, where higher viscosity allows for capacity to retain over a longer period. Here we see limited shuttling as evidenced by a stable, though albeit <0.8 coulombic efficiency. The use of an overall more viscous solvent mixture, with 1:1:2 DOL:DME:Pyr₁₄TFSI offers significantly lower shuttling, as evidenced by a coulombic efficiency approaching unity.

A comparison of the cycle stability of the three electrolyte varieties can be seen below,

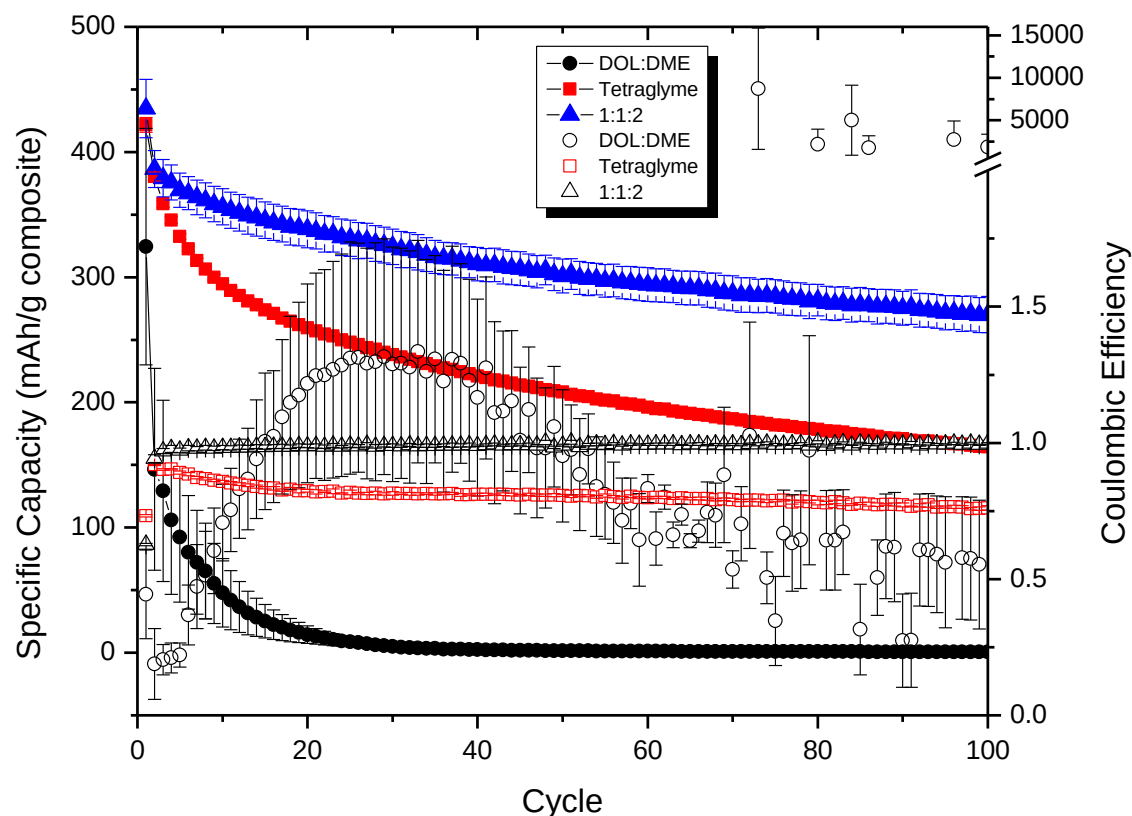


Figure 34 - Cycling stability plot of 1:1 DOL:DME (black), Tetraglyme (red) and 1:1:2 DOL:DME: Pyr₁₄TFSI (blue), in filled squares. Coulombic efficiencies for each are represented in empty squares.

A correlation may be made between coulombic efficiency (CE), a ratio of discharge over charge current, with the cycle stability of the cells. In the 1:1:2 mix, a CE close to unity suggests that very limited shuttling occurs, which correlates with the best cycle stability in this study. By comparison the tetraglyme set shows a CE of around 0.8 after about the 20th cycle, suggesting a robust shuttle effect, which may account for the relatively aggressive cycle

instability. The 1:1 DOL:DME set however, drops to effectively zero capacity by the 40th cycle. For this set, the CE is relatively meaningless, and indeed becomes rather erratic around the 60th cycle. For the 1:1 DOL:DME set it is suspected that due to very low viscosity, as well as high PS solubility, the sulfur (as elemental sulfur as well as PS) content of the cathode dissolves readily into the electrolyte, failing to redeposit at the cathode.

As discussed in (118), the addition of Pyr₁₄TFSI has a meaningful effect on the formation and stability of the SEI and the prevention of contact between polysulfides and the lithium anode, leading to a retarded parasitic reaction and better capacity retention. Addition of this high viscosity component however leads to reduced rate capacity, so full replacement of the electrolyte with Pyr₁₄TFSI is impractical (118).

3.4.1.3 Solvent Mix Optimization

Given the benefits derived from the presence of Pyr₁₄TFSI along with DOL:DME, further combinations of these cosolvents was explored. This study considered two variables, (a) the DOL:DME ratio and (b) Pyr₁₄TFSI content. Both of which were thought to affect performance both by affecting viscosity and by affecting the quality of the SEI.

Work by (123) showed that altering the DOL:DME ratio in a DOL:DME cosolvent system yields meaningful changes in performance. It was suggested in (Wang et al, 2010) that a minimum DOL content was needed to benefit SEI quality, that a low DOL:DME ratio (1:2 in the paper) was the highest performer, due to increased PS solubility from higher DME content. It was suggested that this higher PS solubility lead to higher sulfur utilization, leading to higher capacity. In this study, the DOL:DME ratios attempted were: 1:1, 1:1.5 and 1:3.

Pyr₁₄TFSI content was minimized to reduce viscosity, while maintaining a sufficient presence to impart a beneficial effect. Pyr₁₄TFSI content was explored at 1/4 and 1/8. The following table articulates the mixes attempted. All mixes included 1M LiTFSI and 1.5%wt LiNO₃.

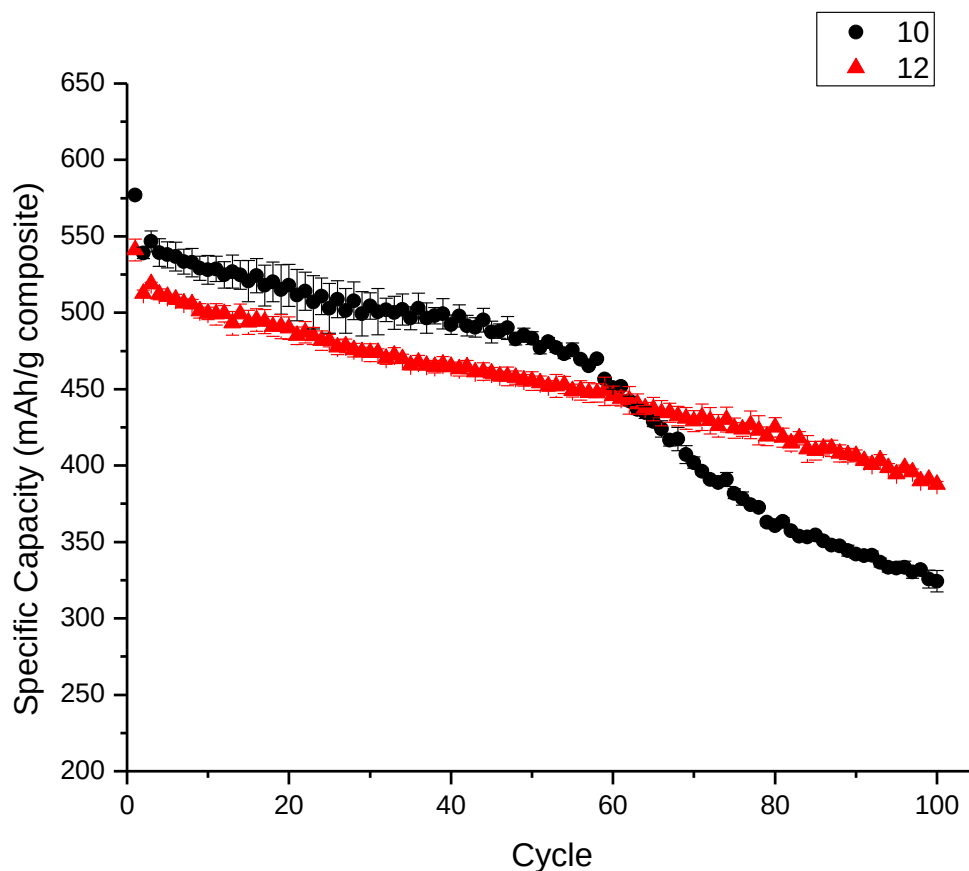
Table 5 - DOL:DME:Pyr₁₄TFSI mixes attempted.

Mix #	Volume ratios DOL:DME:Pyr ₁₄ TFSI	DOL:DME ratio	Pyr ₁₄ TFSI content	Est. dynamic viscosity (cP) of solvents	Pyr ₁₄ ⁺ /Li ⁺
1b	40:60:100	1:1.5	1/2	4.58	1.26
2	12:18:10	1:1.5	1/4	1.4	0.64
2b	12:18 (sans Pyr ₁₄)	1:1.5	-	0.51	-
3	28:42:10	1:1.5	1/8	0.82	0.32
4	75:225:100	1:3	1/4	1.4	0.65
5	175:525:100	1:3	1/8	0.81	0.33

3.4.1.3.1 E/S ratio optimization

Since this set of electrolytes offer lower viscosity mixes, heavier electrodes become possible, as the lower viscosity electrolyte is able to penetrate deeper into an electrode. Using heavier electrodes allows in turn for lower E/S ratios, as the higher sulfur content means that even minimized electrolyte volume will be sufficient to wet the surface of the cathode and provide sufficient ionic conductivity through the porous polymer separator (which saturates at around 10 μ l of electrolyte). The following results show two cells each for an E/S of 10 and 12.

Figure 35 - Low E/S electrolyte loading of mix #2 , cycling of 3N2S cells. Showing E/S of 10 in red triangles, and E/S of 12 in black circles.



As articulated by the error bars, the behavior of each pair of cells tracked very closely. Both 10 E/S cells began to show dramatic retention losses just prior to their 60th cycle. While a post mortem of these cells is outside the scope of this work, similar results appear in literature. (124) shows a comparison of E/S of 13.3, 10 and 6.5, using an electrolyte composed of 1:1wt ratio of DOL:DME, 0.25M LiSO_3CF_3 (LiTf) and 0.25M LiNO_3 . This electrolyte is similar to the one used in this work, differing in the choice and concentration of electrolyte salt (0.25M LiTf rather than 1M LiTFSI), lacking $\text{Pyr}_{14}\text{TFSI}$ as a cosolvent and

using a DOL:DME ratio of 1:1wt. These variances should not effect the conclusion of the result, but may affect the cycle at which degradation occurs, the rate of stability loss and the E/S ratio at which this effect manifests.

At an E/S of 6.5 cycle stability degrades abruptly after the 50th cycle. Zhang suggests that an abundance of polysulfides in solution lead to increased shuttle activity, which consumes sulfur from the cathode, lowering capacity by depleting the cathode.

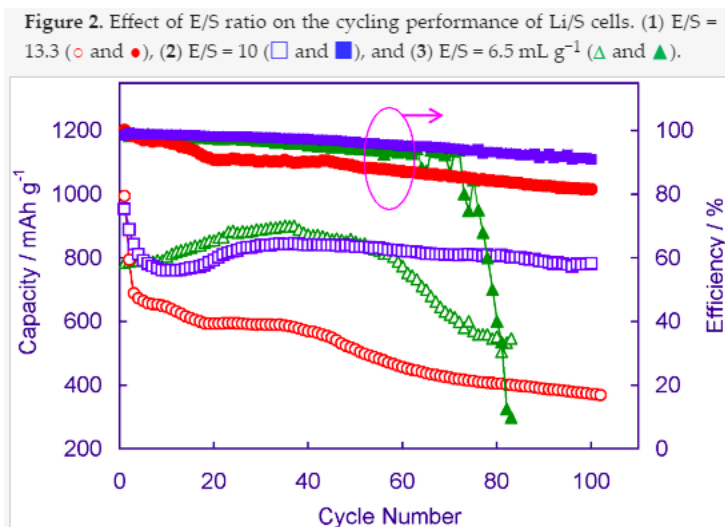


Figure 36 - Cycle stability as a function of E/S ratio in Li/S cells. (Zhang, 2012)

Moreover, the redeposition of insulating polysulfide species either on the surface of the cathode or the anode may drive up internal cell resistance, leading to lower capacities reached under the same voltage cutoffs. Indeed, the activation of Li₂S during charge (125) appears to consistently soften, suggesting a high presence of polysulfides in solution, catalyzing the activation of Li₂S, reducing the voltage necessary in the first step of the charge cycle. This is articulated in the following plot for one of the two 10 E/S cells, highlighted in the inset.

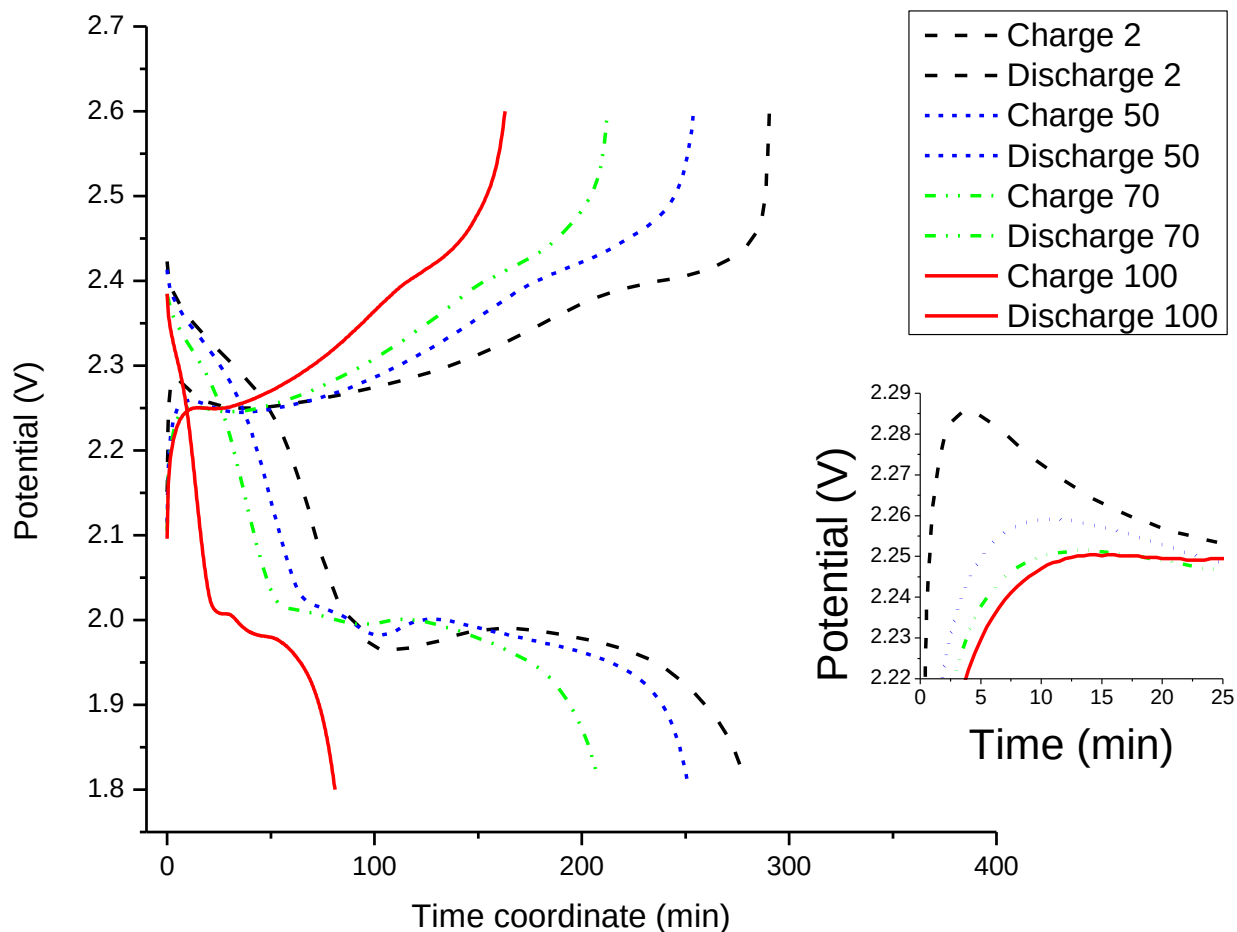


Figure 37 - Four discrete charge and discharge cycles shown for a 3N2S cathode, Mix #2, 10 E/S, cycling at a rate of C/10.

The sharp decrease in capacity retention after the 60th cycle suggests a saturation of PS in the electrolyte solution, driving more aggressive reaction of the PS at the anode.

The empirical method suggested by Zhang for optimizing the E/S ratio is unfortunately inapplicable to a Li₂S@C cathode, because it undergoes a charge step prior to its first discharge, unlike a S@C cathode. Zhang suggests observation of a voltage delay upon the first discharge, which indicates too low an E/S ratio; that the minimum electrolyte content possible where this delay disappears indicates the optimum ratio. However, since cells

assembled with $\text{Li}_2\text{S}@C$ cathodes experience a charge step first, the phenomenon indicated by Zhang, of resistive diffusion of Li_2S_8 which appears only upon first charge, does not appear in $\text{Li}_2\text{S}@C$ cells, as first-cycle processes have already occurred by the time the cell is discharged. 3N2S cells assembled with an E/S of 8, (even lower than the 10 we see the

stability fade in), do not show this feature, noted with Arrow 3 in the figure from (Zhang, 2012), upon first discharge.

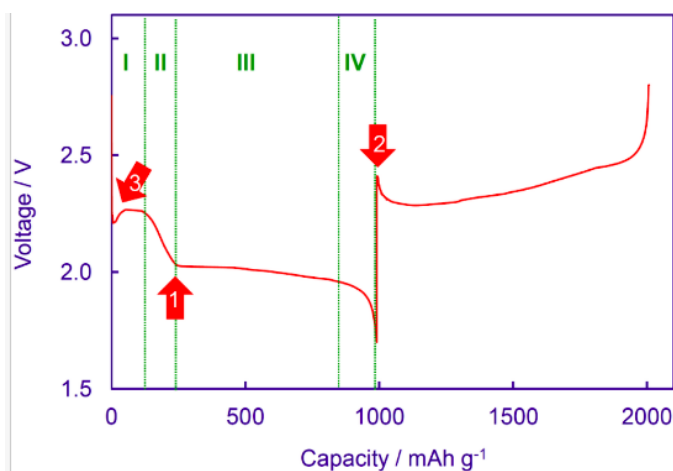


Figure 38 - First charge and discharge cycle for a Li-S cell with E/S of 10. (Zhang, 2012)

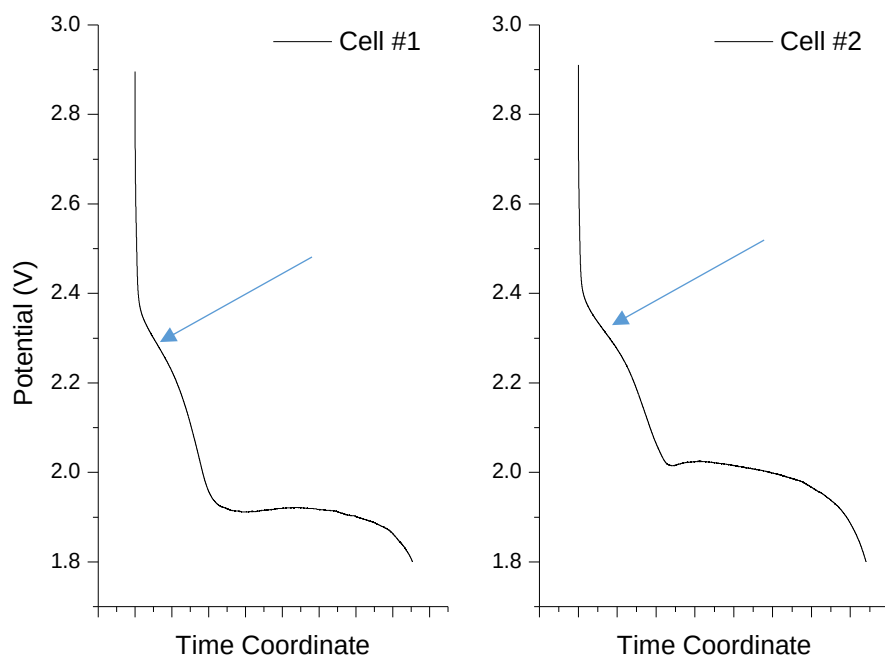


Figure 39 - First discharge for two 3N2S cells with E/S of 8. Note the lack of voltage delay in either, as (Zhang, 2012) suggests would be expected.

As such, barring the technique suggested by Zhang, the optimal electrolyte to sulfur ratio is a question of staying ahead of PS saturation in the electrolyte. As such, given DME as the highest PS solubility component of the electrolyte, an unknown PS solubility in the electrolyte mixes, an optimal mix will not necessarily have the same E/S ratio throughout this study. A combination of 10 and 12 E/S were attempted for various mixes, accommodating for either high DME content, or low cathode masses available in the limited batch size.

3.4.1.3.2 Voltage Efficiency as a performance metric

When comparing poor performing cells, the differences tend to be sufficiently high to offer easy distinction. High performing cells however, represent the apex of performance that can be extracted by manipulating a particular variable. The difference between high performers may be difficult to ascertain, as the optimal selection may only incrementally better than alternate selections. This begs quantification. As a metric, Coulombic Efficiency (CE) in a Li-S cell can be interpreted to consider the activity of irreversible side reactions; as inefficiency here represents more reactions occurring upon charge than in discharge. This inefficiency is born out of the shuttle effect, where higher order PS react with the lithium anode to form lower order PS, drawing out further sulfur content from the cathode. Coulombic Efficiency is calculated as such,

$$CE = \frac{\text{Discharge Current(Ah)}}{\text{Charge Current (Ah)}}$$

Since current is a direct measurement of electron count, any difference in current between charge and discharge represents a difference in the quantity of reaction. CE does not directly describe the reactions occurring, merely that they are occurring.

Overall energy efficiency offers a broader context of the efficiency of the cell, considering the total energy invested in the cell, upon charge, versus the energy retrieved from the cell, upon discharge. Overall energy is calculated as such,

$$\text{Overall Energy Efficiency} = \frac{\text{Discharge Energy (Wh)}}{\text{Charge Energy (Wh)}}$$

A consideration of overall energy efficiency envelopes both losses to irreversible reactions as well as losses to an overpotential. As such, by assessing cells by their overall energy efficiency, one cannot ask about losses to the overpotential alone.

As articulated by the Tafel Equation, to get the true potential of a cell, the current applied to it must be very low. This is an impractical proposition in Li-S cells, as such a low current would lag behind the diffusion of PS in the electrolyte, leading to extensive shuttling. As such, the Voltage Efficiency of these cells, is not reasonably assessed. Moreover, such a test does not represent C rates relevant to real world applications. As such, rather than measure the voltage efficiency of charge or discharge, as the ratio of the actual voltage to the thermodynamic voltage for each half cycle; we measure the voltage of discharge versus that of charge, suggesting the voltage efficiency of a full cycle (FCVE). This can conceptually be considered equivalent, as such,

$$\text{Full Cycle Voltage Eff. (FCVE)} = \frac{\text{Discharge Voltage Eff.}}{\text{Charge Voltage Eff.}} = \frac{\frac{\text{Measured Discharge (V)}}{\text{Thermodynamic (V)}}}{\frac{\text{Measured Charge (V)}}{\text{Thermodynamic (V)}}}$$

Considering that the thermodynamic voltage of a fully reversible reaction should be equivalent going backwards or forwards, we can conceptually cancel the Thermodynamic Voltage term. We are then left with the following,

$$\begin{aligned} \text{Full Cycle Voltage Eff. (FCVE)} &= \frac{\frac{\text{Measured Discharge (V)}}{\text{Thermodynamic (V)}}}{\frac{\text{Measured Charge (V)}}{\text{Thermodynamic (V)}}} \\ &= \frac{\text{Measured Discharge (V)}}{\text{Measured Charge (V)}} \end{aligned}$$

Measured voltage across a half cycle (charge or discharge) is not however a single average value. Indeed, a half cycle in a Li-S is replete with several reaction regimes. Arguably, a ratio of discharge over charge should be an apples to apples comparison. Due to the shuttle effect however, this is not the case. Comparing a charge that occurred over a longer period than a discharge, which is invariably the situation in a Li-S cell, makes for an inappropriate ratio in terms of voltage. As such, we may want to arrive at the FCVE through a different route.

Consider that work is the product of current and voltage, as such,

$$\text{Work (W)} = \text{Voltage (V)} * \text{Current(A)}$$

Multiplying both sides by time we yield,

$$\text{Energy (Wh)} = \text{Voltage (V)} * \text{Charge(Ah)}$$

Rearranged we have,

$$\text{Voltage (V)} = \frac{\text{Energy (Wh)}}{\text{Charge(Ah)}}$$

A further leap allows us to consider, within significant limitations, the following ratio of discharge versus charge ratio,

$$\text{Quasi Voltaic Eff. (V}_D\text{/V}_C\text{)} = \frac{\text{Overall Energy Eff. (Wh}_D\text{/Wh}_C\text{)}}{\text{Coulombic Eff. (Ah}_D\text{/Ah}_C\text{)}}$$

The limitations of this metric warrant the term “quasi” as a qualifier. The act of dividing by the Coulombic Efficiency essentially collapses the capacity axis, so that charge and discharge capacity (in units Ah) are matched. This inherently ignores the presence of irreversible reactions as a part of the charge and discharge half cycles. The shuttle effect specifically, an irreversible reaction that occurs at relatively high voltage, effects the value derived in the above calculation. As such, deriving the Quasi Voltaic Efficiency (QVE) does not inherently qualify a cell as “excellent” overall. The QVE may however serve as a compressed metric for tracking the evolution of cell resistance as born out of cell capacity retention with cycling.

Electrochemical impedance spectroscopy (EIS) is the standard of ascertaining resistance sources in a cell, and can be applied at different points during cell life, often in the rest periods prior to the beginning of charge or discharge cycles. EIS however takes a snapshot of resistance in an infinitesimally active cell, via rapid pulses, which are not representative of currents applied during charge and discharge; as such EIS does not effectively describe an actively cycling cell. As shown by Carbone et al, (126), EIS can be taken at several steps during a cycle, thus comparing the changing environment throughout, rather than the same

point at multiple cycles. Even then however, the cell is relatively at rest. QVE describes the relation of discharge voltage over charge voltage, albeit imprecisely, during cycling. It is a useful tool for describing the resistance environment of cells as they cycle and how this environment evolves.

Another advantage of QVE is that data can be extracted from low capacity cells as well high capacity cells. Since significant variation is present among cathodes, due to incomplete mixing of the active material, carbon additive and binder; as well as varying levels of conversion and degradation in the H₂S post treatment. With QVE, the relationship in question is a unitless ratio of voltage to voltage, irrespective of actual capacity observed. Resistances related to electrolyte viscosity would theoretically be the same in a 300mAh/g cell as they are in a 500mAh/g cell; as would SEI evolution, polarization, etc.

4 RESULTS AND ANALYSIS

4.1 CAPACITY DRIVEN ANALYSIS

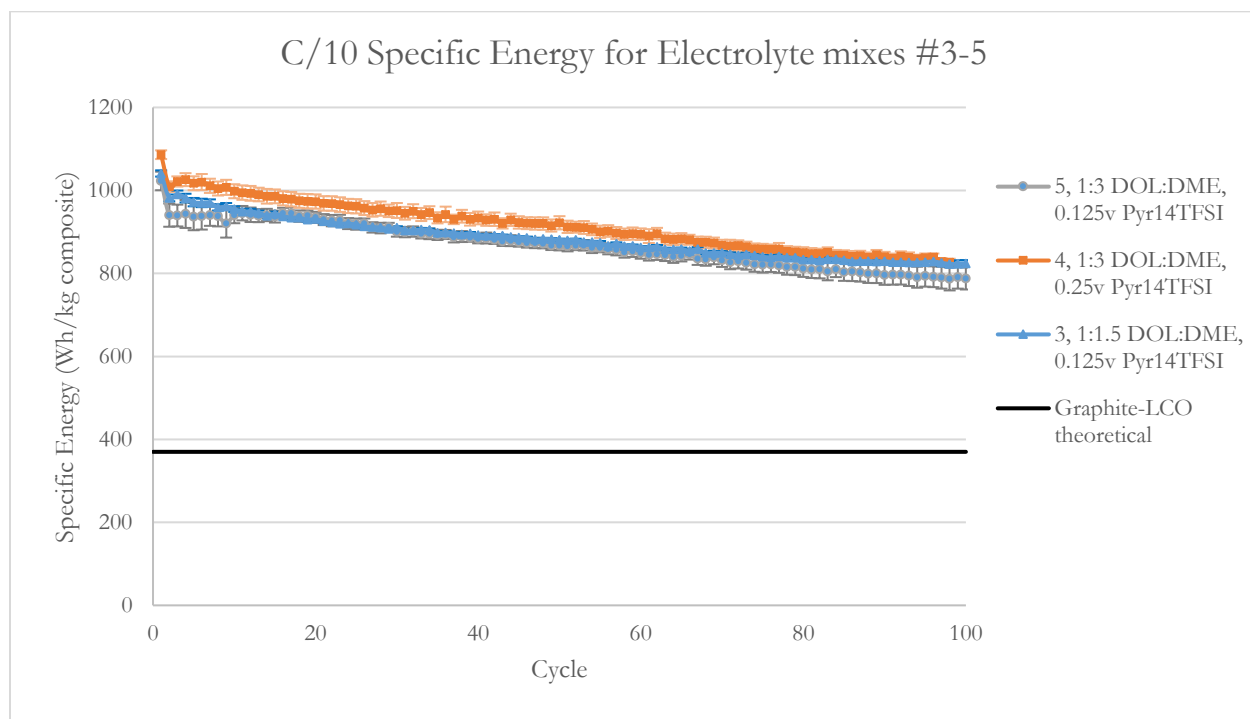


Figure 40 - Specific energy of discharged 3N2S cells in various electrolyte mixtures. Each curve represents an average of three cells. Compared to theoretical specific energy possible in a typical Graphite-LCO li-ion cell.

Arguably the most important metric for an energy storage technology geared toward high specific energy is its initial capacity. High initial capacity means a cell will weigh the device down less. This is key to enabling applications hampered by market offerings that are just too cumbersome, such as aerospace and automotive applications. A direct comparison of the Li-Li₂S@C system, considering the 3N2S composite shows a promising lead against the

theoretical specific energy of the graphite-LCO system. Graphite-LCO, however, is a relatively mature technology, which benefits from superior cathode conductivity and a meaningfully lower electrolyte content, roughly ten times less.

True to the time of this writing, the winning electrolyte formulation, at a C/10 rate, is not yet clear. A closer examination suggests that the capacity degradation of #4 and #5 are relatively linear, and track together. Whereas the capacity degradation of #3 appears to be slowing.

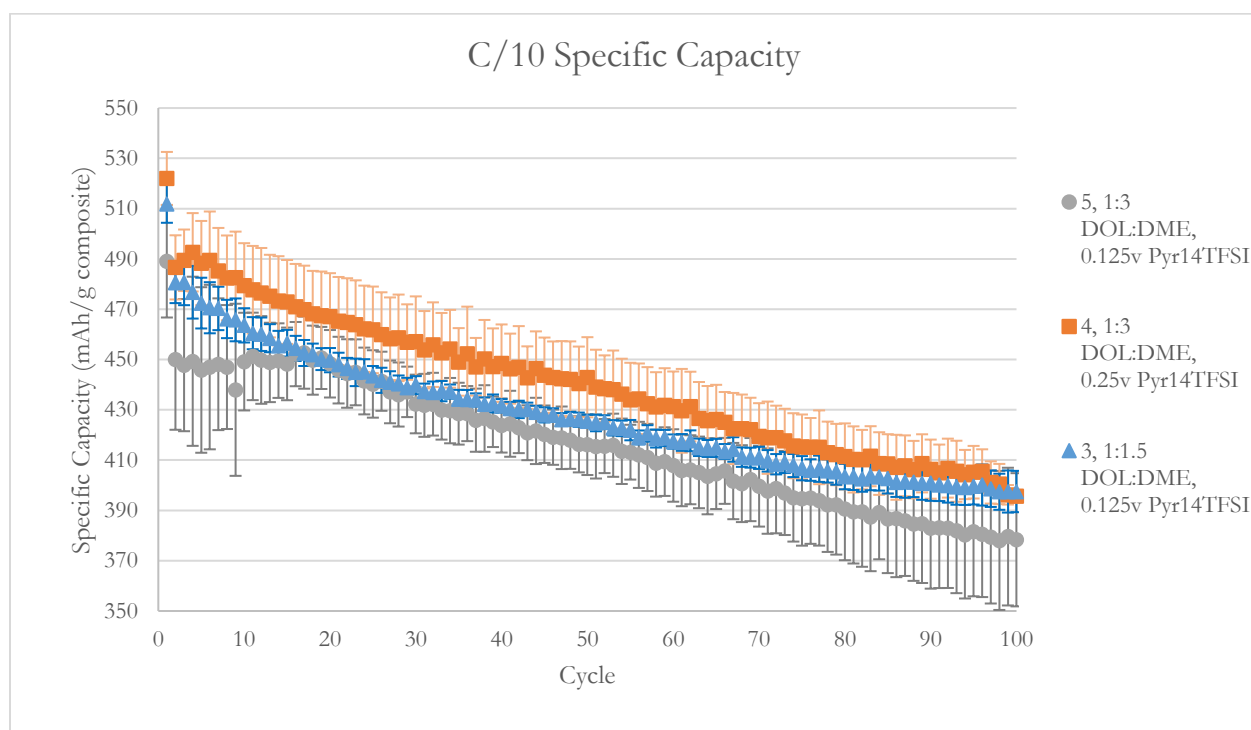


Figure 41 - Cycle stability of 3N2S cells, with varying electrolyte mixes #3, 4 & 5.

Consideration of capacity degradation itself is less clear. Where a mean capacity degradation is often cited in literature, the value of such a statement is dubious at best, without consideration of error.

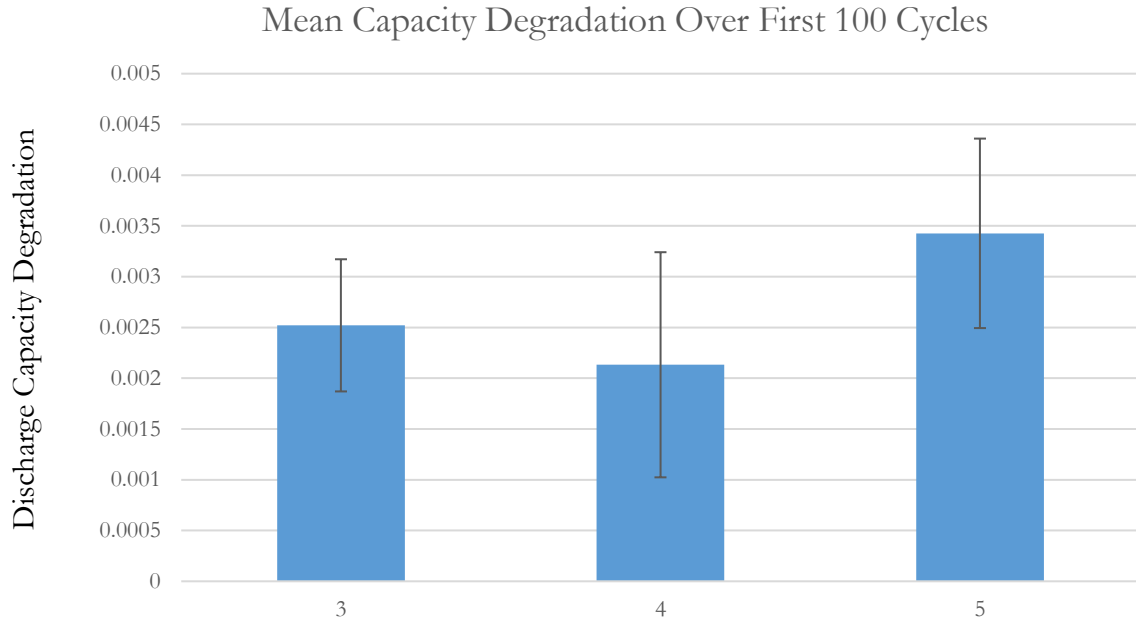


Figure 42 - Capacity degradation, in fraction of capacity lost per cycle, of 3N2S cells in electrolytes #3, 4 & 5 respectively, from cycle 2 to 100.

Capacity degradation is defined as such,

$$\text{Cap. Degradation} = 1 - \frac{\text{Discharge Cap. } \left(\frac{\text{mAh}}{\text{g}}\right)_{\text{Cycle } n}}{\text{Discharge Cap. } \left(\frac{\text{mAh}}{\text{g}}\right)_{\text{Cycle } n-1}}$$

Since this statement is a fraction, it is subject to the behavior of fractions; whereby an increase of X% is not as significant as a decrease of X%. As such, while mean capacity degradation of #4 is lower than that of #3, the error of #4 is meaningfully larger, suggesting larger swings about zero. This can be seen in the following plot, where capacity degradation for #3 presents as the least erratic of the three electrolyte compositions.

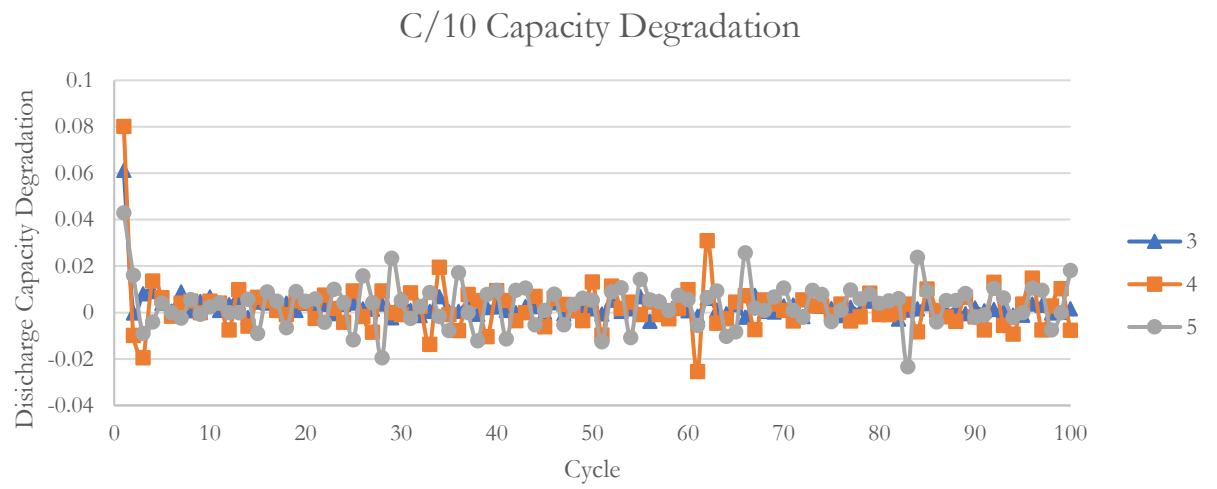


Figure 43 - Capacity Degradation across 100 cycles for electrolytes #3, 4, & 5, in 3N2S cells.

4.2 QVE ANALYSIS IN C/5 CYCLING CELLS

A comparison of the 1:1.5 DOL:DME ratio electrolytes, from the lens of QVE, shows a clear trend in terms of viscosity in the first 100 cycles.

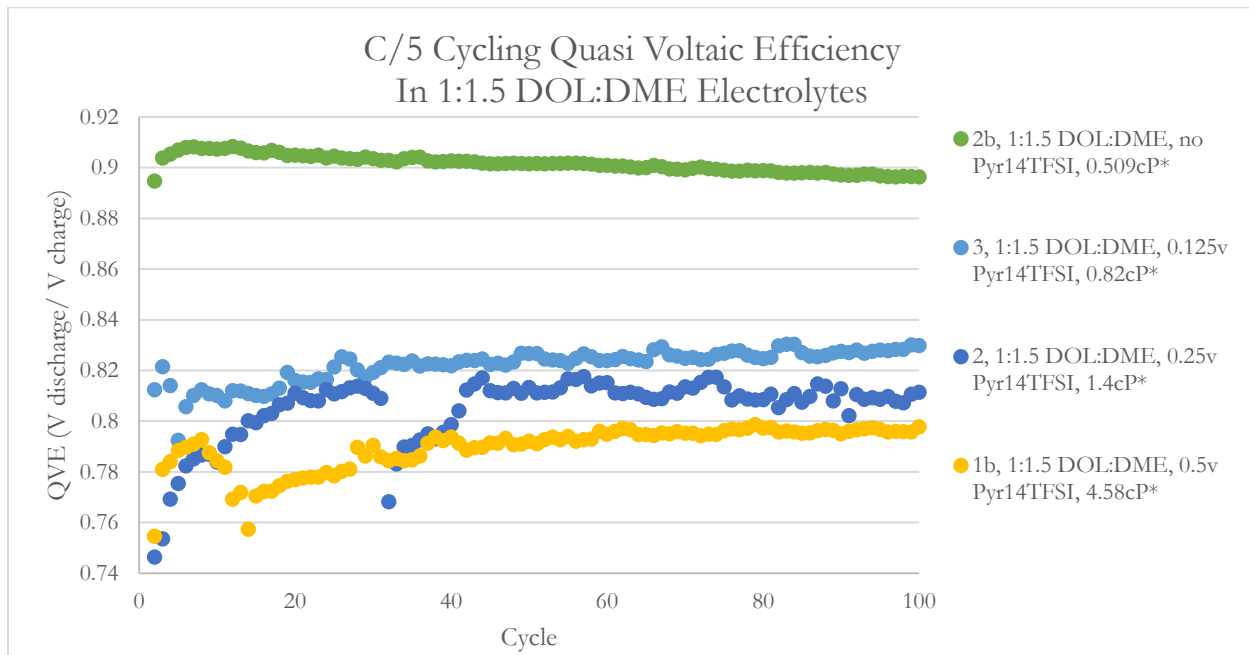


Figure 44 - Quasi Voltaic Efficiency of 1:1.5 DOL:DME electrolytes, for 3N2S cathodes, cycled at C/5.¹¹

Differing in ionic liquid content, demarked by volume fraction, a trend emerges over the first 100 cycles. Here we see that the higher the Pyr₁₄TFSI content, which will increase solvent viscosity, leads to lower initial QVE, but yields an upward trend over the observed cycling period. The lower initial QVE of higher viscosity solvent mixes can be explained in the context of lithium cation diffusion limitation. The upward trend of QVE for higher Pyr₁₄TFSI mixes may not specifically represent a contribution of the ionic liquid itself to lowering the hysteresis from cycle to cycle; instead this may suggest that the tendency of cells

¹¹ * Viscosity values refer to calculated solvent mix viscosity, absent of LiTFSI and LiNO₃.

at this stage of cycling is inherently to drop in hysteresis, and that the higher viscosity of these cells inhibits a QVE degradation mechanism.

In low viscosity cells, the diffusion of PS would be less inhibited, allowing faster migration and shuttling, leading to an increasingly thickening and resistive SEI at the anode. In high viscosity cells, this migration is relatively limited; allowing for the cells to mature without increasing internal resistance.

Increasing QVE over time is possibly associated with incremental redistribution of Li_2S at the cathode. While elemental sulfur has been shown to dissolve in DOL:DME electrolytes (5), Li_2S does not. Cathode material precipitates out of the electrolyte solution at the end of discharge (Li_2S), the film formed by deposition may vary from cycle to cycle (127), (113), (128); beginning with the crystalline Li_2S resultant from the H_2S treatment, to a thinning, more disperse film, as the cycles proceed.

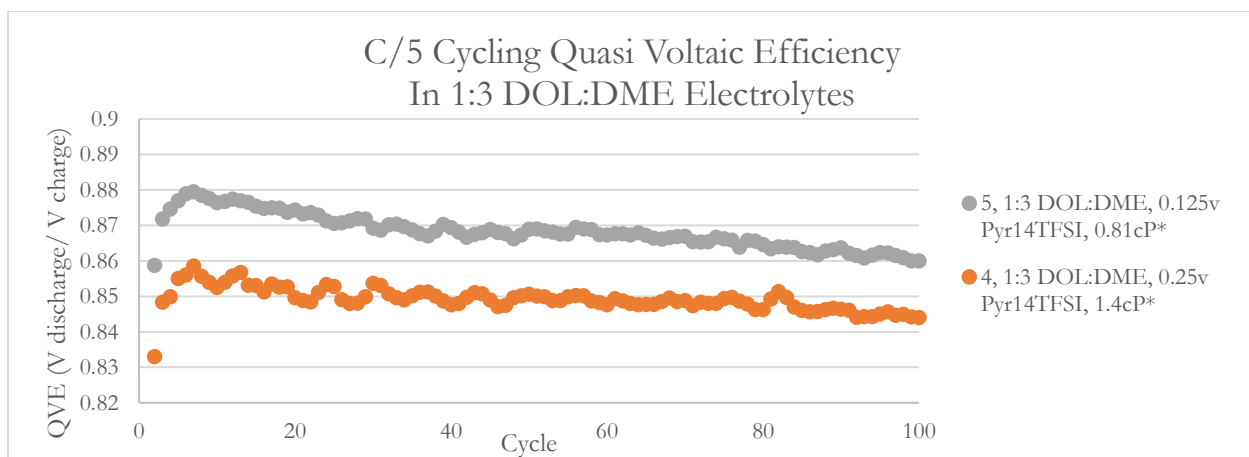


Figure 45 - Quasi Voltaic Efficiency of 1:3 DOL:DME electrolytes, for 3N2S cathodes, cycled at C/5.

The 1:3 DOL:DME electrolytes tell a similar story, relative to each other. Whereby the lower the solvent system viscosity, the higher the initial QVE.

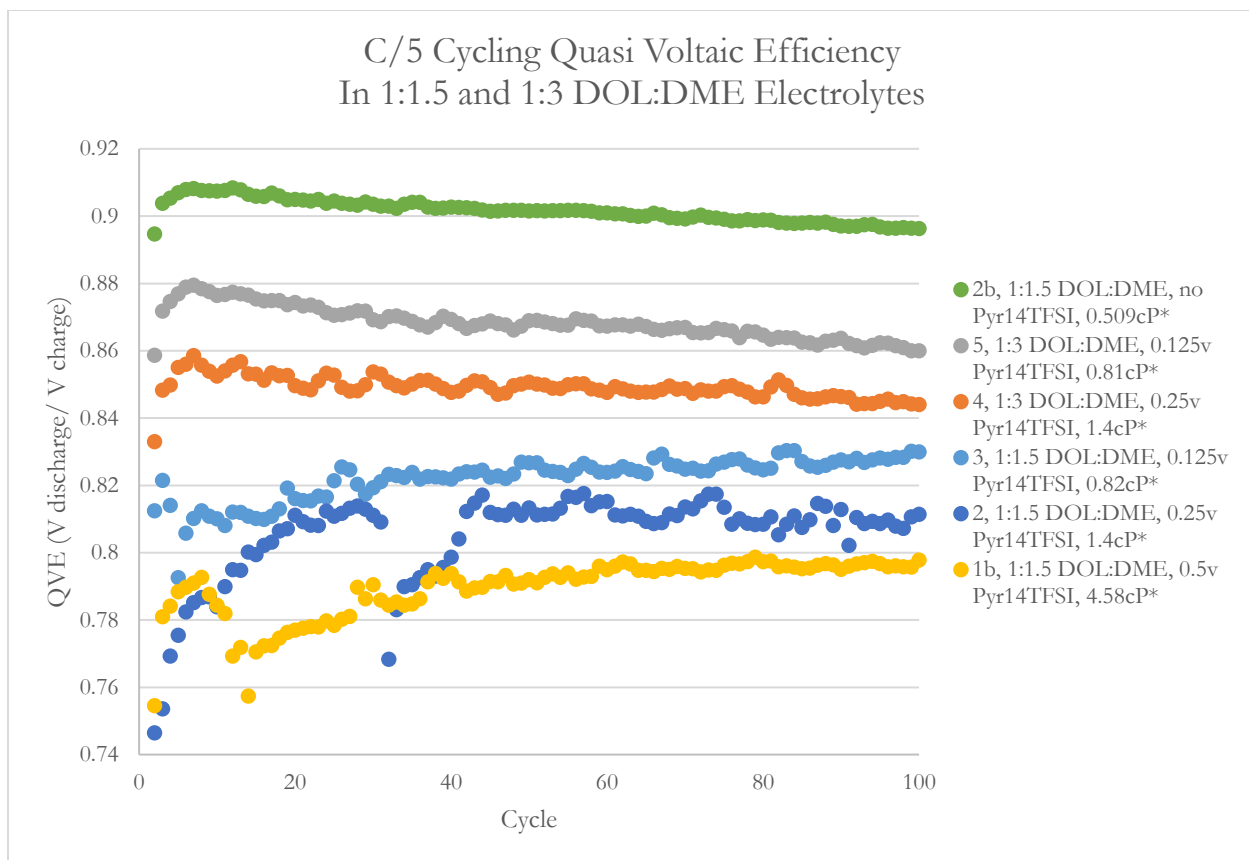


Figure 46 - Quasi Voltaic Efficiency of 1.5 and 1:3 DOL:DME electrolytes, for 3N2S cathodes, cycled at C/5.

Taken as a whole, however, another context emerges. By comparing 1:1.5 and the 1:3 DOL:DME electrolytes, we see a staggering in terms of viscosity, whereby #4, with a higher viscosity than #3, begins with a higher QVE. This suggests that viscosity is not the only factor in QVE. (Zhang, 2012) suggests that the higher the DME content relative to DOL, the greater the PS solubility. As such, the 1:3 electrolytes would hold a higher PS content than the 1:1.5 electrolytes, offering higher availability of PS in solution, for reaction and eventual deposition at the cathode. Here a higher concentration gradient PS expresses as sulfur availability at the cathode, just as it would at the anode; rather than deposit cathode

material at the anode, which represents an irreversible loss of capacity, it aids in the redeposition of cathode material at the cathode, which results in healthy cell cycling.

This higher PS solubility for the 1:3 DOL:DME electrolytes comes at an obvious cost of degrading QVE over time. Just as the high concentration of PS makes for robust redeposition at the cathode, so too does it offer robust deposition at the anode (129).

Note that since QVE would drop with extensive shuttle activity, which is known to occur at a relatively high voltage during the charge cycle, higher QVEs in high PS mobility electrolytes (2b, 4 and 5)

suggests that extensive periods of end of charge shuttling do not in fact occur.

Instead, deposition over time, as a result of the

concentration gradient appear to be the case. The following

figure displays a typical low resistance cell over the course

of one charge and discharge cycle. In this cell, vigorous

shuttle activity would appear above 2.4V during charge

(38), in the segment that appears to flatten out. The

following curve, from (130),

comparing a $\text{Li}_2\text{S}@C$

composite with physically

mixed Li_2S and C illustrated this clearly. While in curve (a) shuttle activity is relatively

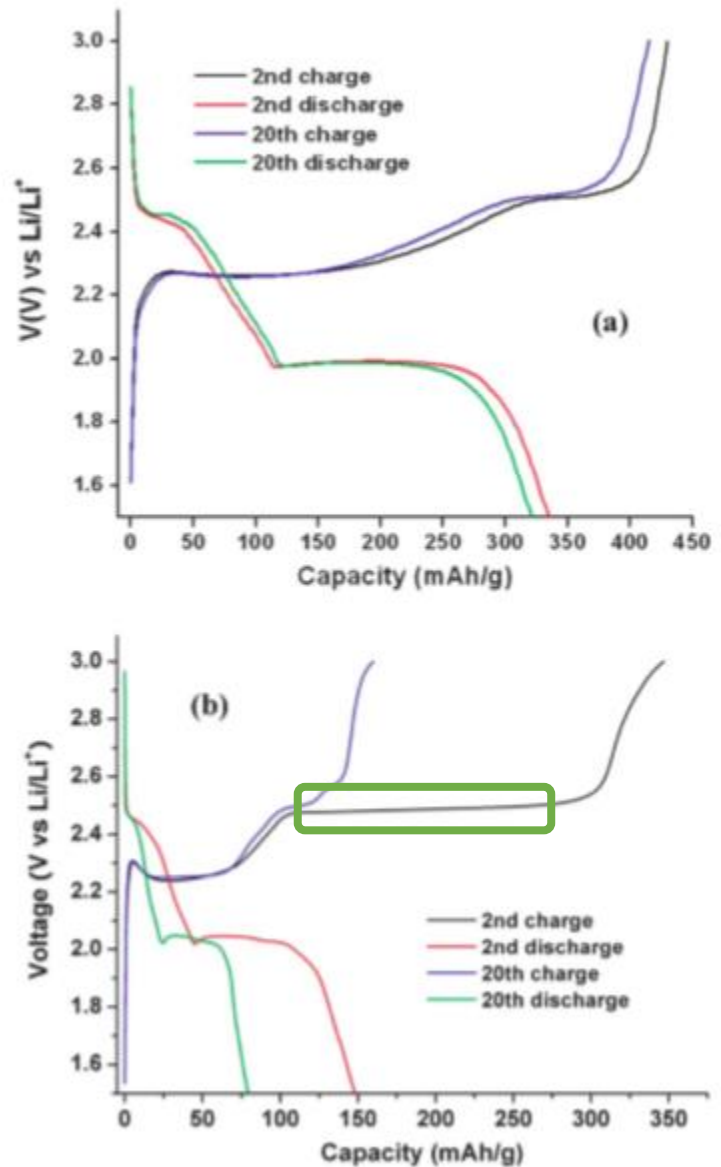


Figure 47 - Charge and discharge curves for (a) $\text{Li}_2\text{S}@C$ vs (b) Li_2S mixed with C. Performed in an electrolyte of 1M LiTFSI in tetraglyme. Green box added here to point out the region where shuttle effect is most vigorous. (130)

suppressed, the lack of rationally designed protection in curve (b) shows vigorous shuttle activity above 2.4V and the subsequent dramatic loss of capacity.

This period is dominated by the formation of S_8 , presumably by consumption of Li_2S_8 , suggesting the predominance of Li_2S_8 in solution, relative to other PS species at this moment in the cycle. This bears out from in-situ XRD as shown in (131).

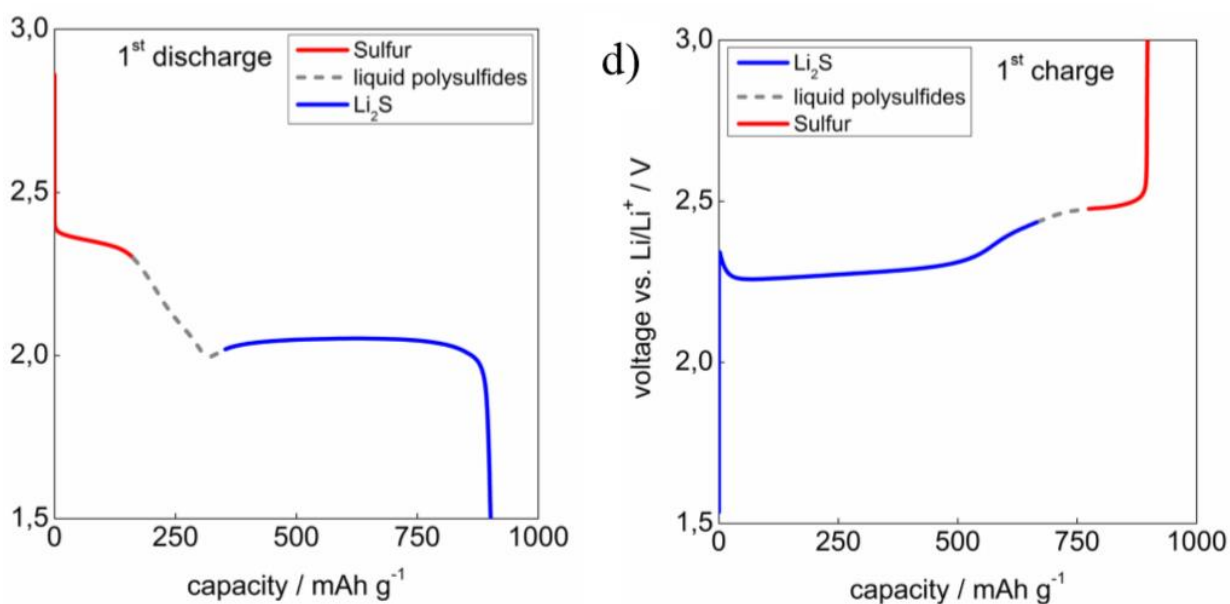


Figure 48 - Charge and discharge curve for a Li-S cell. Red highlight marks the indication of elemental sulfur during in-situ XRD, while blue indicates the presence of Li_2S . The dashed section indicates a period where neither specie is observed.

(131)

Li_2S_8 is recognized as the most soluble of PS species, leading to high relative concentration in electrolyte and vigorous shuttle activity. It is the high voltage of this conversion step, and the prevalence of Li_2S_8 at this time, that would drop QVE values. Since high PS mobility electrolytes show high relative QVE, this suggests shuttling is not robust during this step.

Another aspect worth noting is the increased effect of temperature cycling on higher viscosity cells. Note that the more viscous the electrolyte, the more erratic the QVE appears to be. This is a reflection of the erratic energy density results, as affected by the fluctuating temperature in the building. In already high viscosity cells, exemplified by the #1b electrolyte, fluctuations downward in temperature have a severe impact on viscosity and as such on performance. In contrast, 2b, which employs no Pyr₁₄TFSI, appears to ignore temperature fluctuations altogether. This in and of itself is an important matter in designing appropriate electrolyte systems, where consistent performance is important, or for cold

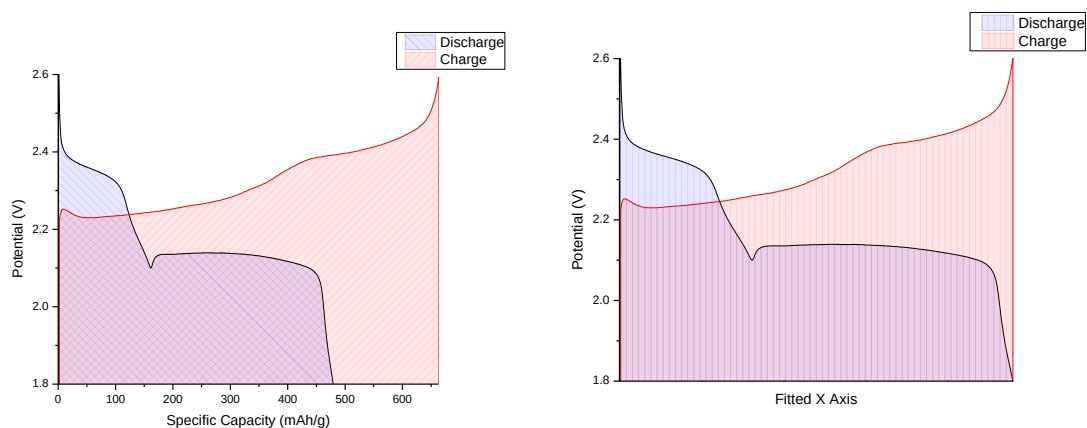


Figure 49 - Left, untreated charge and discharge curve of second cycle 3N2S cell, #2b electrolyte, 1:1.5 DOL:DME electrolyte cell. Right, QVE treated cycle plot of same cell.

weather applications.

4.3 QVE ANALYSIS IN C/10 CYCLING CELLS

The C/10 series displays a series of more mature cells, where yet a further narrative unfolds. While actual measurement of the electrolyte content is necessary to confirm these assertions, it is instructive to note that all three electrolytes explored display a pattern of three distinct

regimes. In the Regime A, which at just over 50 cycles is roughly equivalent to the time scale of the 100 cycles shown for the C/5 set above, we see a similar distribution, with 1:3 DOL:DME electrolytes starting with a higher QVE, but drop over time. Whereas the 1:1.5 DOL:DME electrolyte increases with time. It is the author's opinion, as discussed in (124), that the electrolyte saturates with PS around this time. As the cells mature into Regime B, rapid deposition of PS onto the anode, driven by a saturated solution and an aggressive gradient, leads to increasing resistances in the cell. The process of building a thicker PS driven SEI layer occurs over the course of roughly 30 cycles, upon which a sufficiently thick SEI is no longer attractive to the deposition of PS at the anode. At this point continuing rearrangement of sulfur species within the cathode proceeds to improve distribution and deposition/dissolution at the cathode. It is possible that Regime C even see loss of PS from the electrolyte into the cathode, leading to lower viscosity and more favorable conditions for the diffusivity of lithium ions.

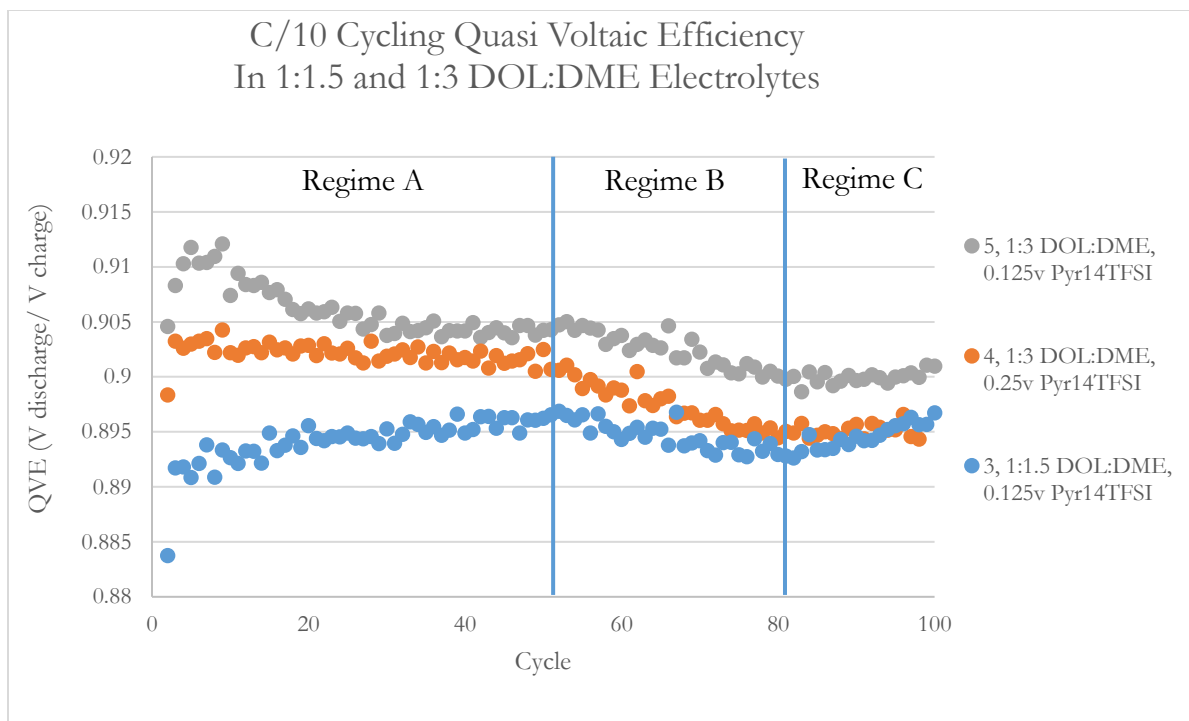


Figure 50 - Quasi Voltaic Efficiency of 1.5 and 1:3 DOL:DME electrolytes, for 3N2S cathodes, cycled at C/10

An alternative mechanism which would agree more closely with the continuing, though slow loss of capacity, even at Regime C, is the redissolution of lithium salts. As PS depletes out of solution, LiTFSI and LiNO₃ which may have precipitated due to the common-ion effect, may return into the solution, alleviating an ion blocking presence of large crystalline grains, thus promoting better ion transport and increasing the QVE. This latter hypothesis arises from the observation of crystalline deposition in the electrolyte vials over time. Despite having dissolved initially, lithium salts in the electrolyte systems appear to settle and grow over time. The presence of PS in solution will only exacerbate the situation, as two Li⁺ cations are introduced into solution per PS unit.

In the case of this behavior, QVE certainly does not identify the mechanism of action, but it does highlight that a shift in behavior is happening, which is suggested by inflection points in

the curve; suggesting that a new regime of phenomena prominence has initiated. Observing the same cycle in specific capacity data displays none of this narrative.

4.3.1 Performance comparison

Cycling data at rates of C/10 and C/5 comparing the three compositions show distinct differences in performance.

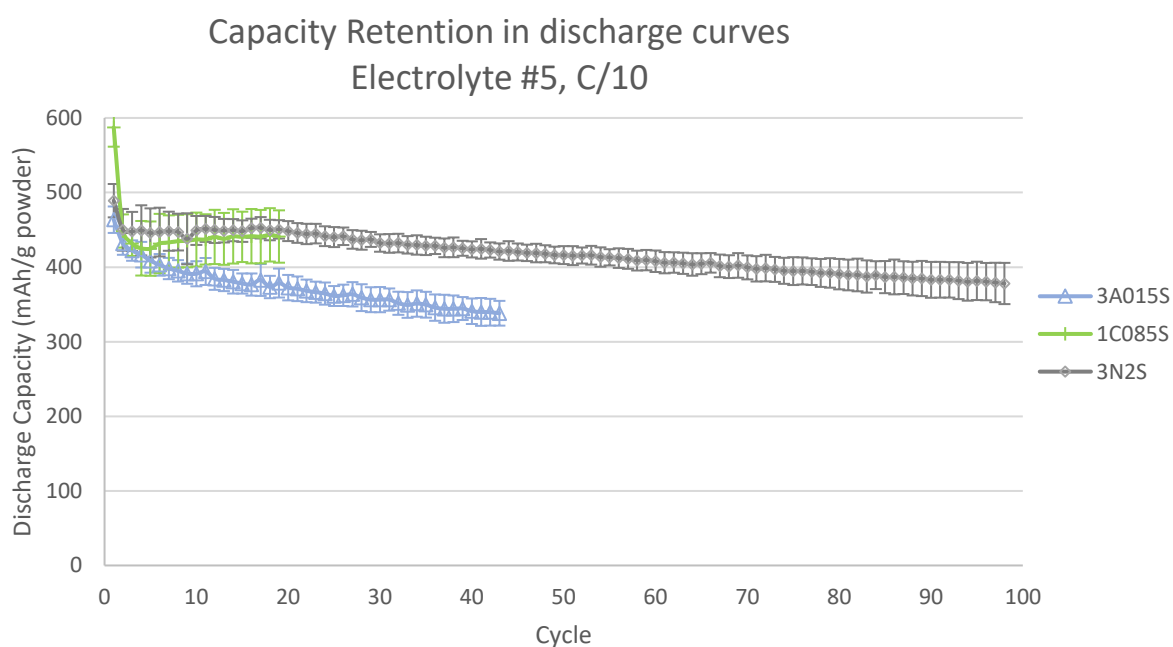


Figure 51 - Discharge Specific Capacity in Electrolyte 5 for cells produced with 3N2S, 1C085S and 3A015S precursor systems, cycled at C rate of C/10.

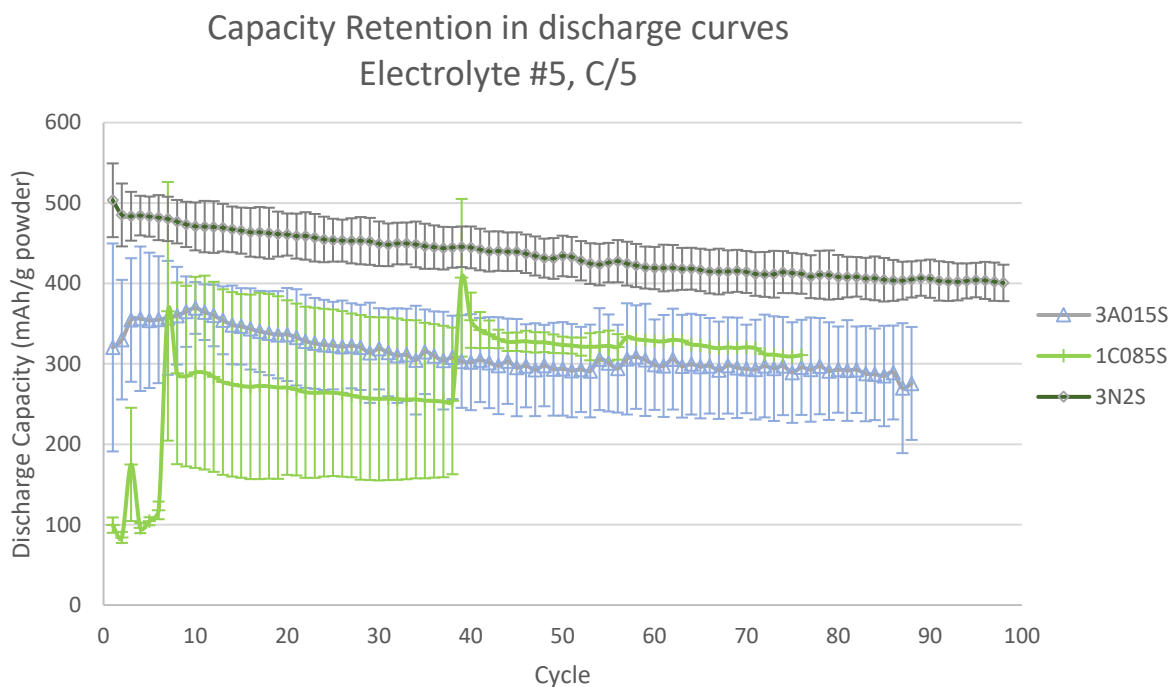


Figure 52 - Discharge Specific Capacity in Electrolyte 5 for cells produced with 3N2S, 1C085S and 3A015S precursor systems, cycled at C rate of C/5.

4.3.2 Precursor Selection Comparison - SEM and TEM Analysis

The following sets of images show the composite particle from three compositional perspectives. First, SEM images of the pyrolysis product, $\text{Li}_2\text{CO}_3@\text{C}$, are presented as is.

This set contrasts the different architectures inherent in the NitS, CarS and AceS precursor formulations, when tailored to have similar carbon contents (20-25%).

Second, SEM of the $\text{Li}_2\text{CO}_3@\text{C}$ particles, washed with HCl show the carbon host alone.

This offers a glimpse at the host structure itself and its integrity under strains in solution.

Third, $\text{Li}_2\text{S}@C$ particles are HCl washed and SEM images are presented. Since $\text{Li}_2\text{S}@C$ would not survive as is in transport to imaging, HCl washing clears it out, offering a glimpse of the host post H_2S treatment.

The same sequence is then followed up with TEM.

4.3.2.1.1 SEM Analysis

4.3.2.1.1.1 $\text{Li}_2\text{CO}_3@C$ particles

SEM images of $\text{Li}_2\text{CO}_3@C$ particles reveal a wide distribution of particle sizing, where the largest of the particles are subject to rupture (upper left image), presumably due to off-gassing through a relatively large radius of carbon host, leading to sufficient pressure buildup to cause rupture.



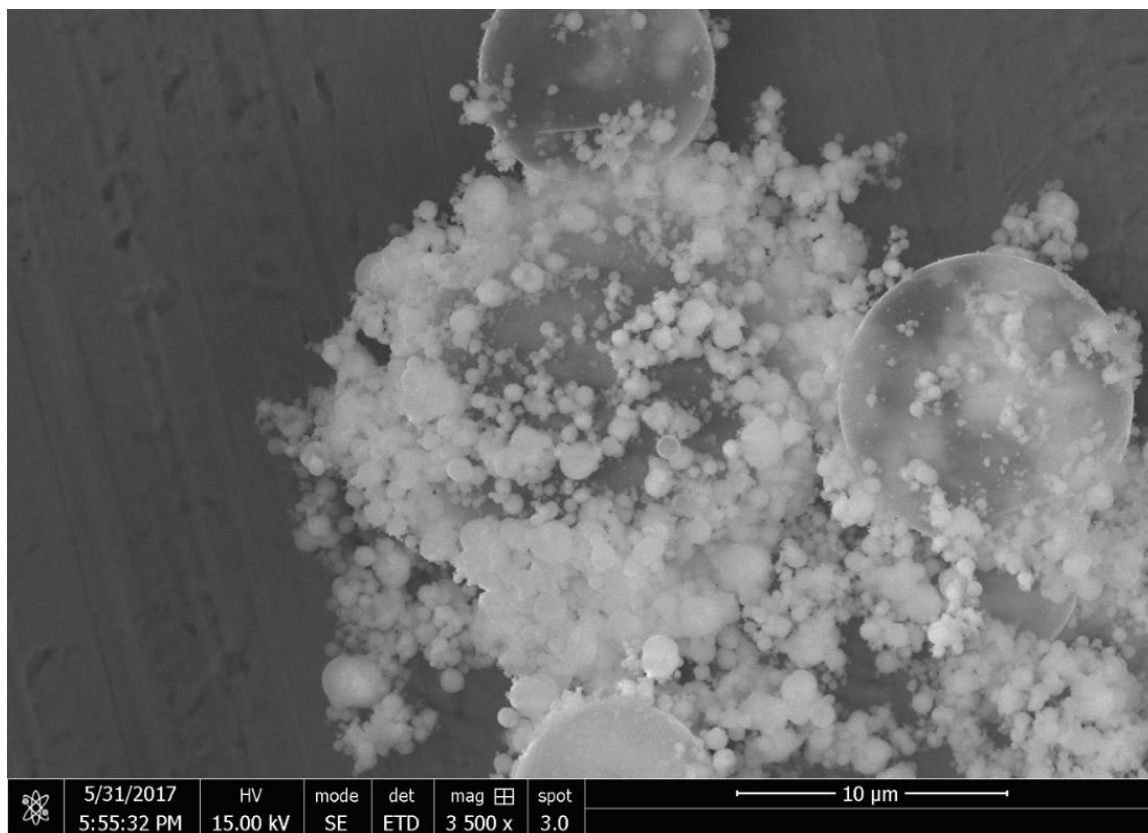


Figure 53 - Set of SEM images of 3N2S $\text{Li}_2\text{CO}_3@\text{C}$ particles.

4.3.2.1.1.2 $\text{Li}_2\text{CO}_3@\text{C}$ HCl washed particles

HCl wash of these particles reveals the effect of washing away the Li_2CO_3 content. Larger particles appear to collapse (upper right), while the largest host particles may be a mere skin (bottom most), which deflate like a balloon after the removal of the lithium salt content.

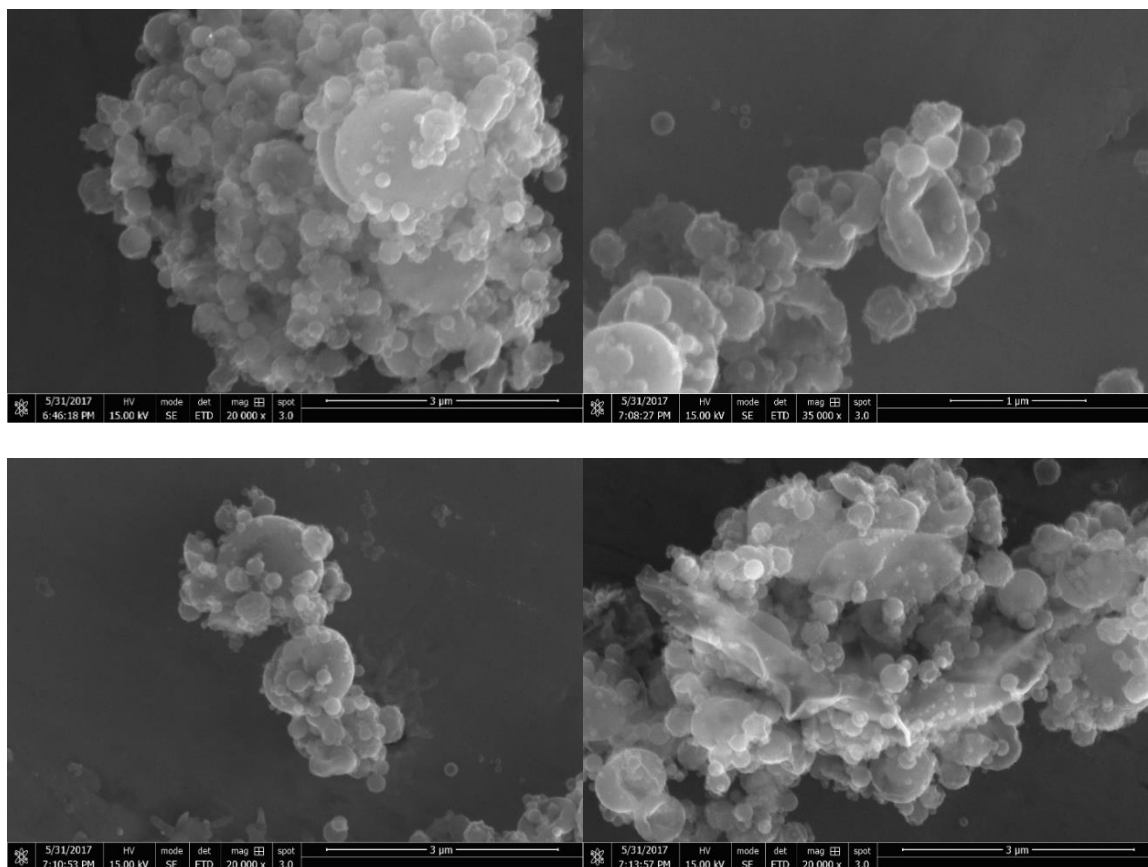


Figure 54 - Figure 43 - SEM images of 3N2S derived $\text{Li}_2\text{CO}_3@\text{C}$ particles, after HCl wash

4.3.2.1.1.3 $\text{Li}_2\text{S}@C$ HCl washed particles

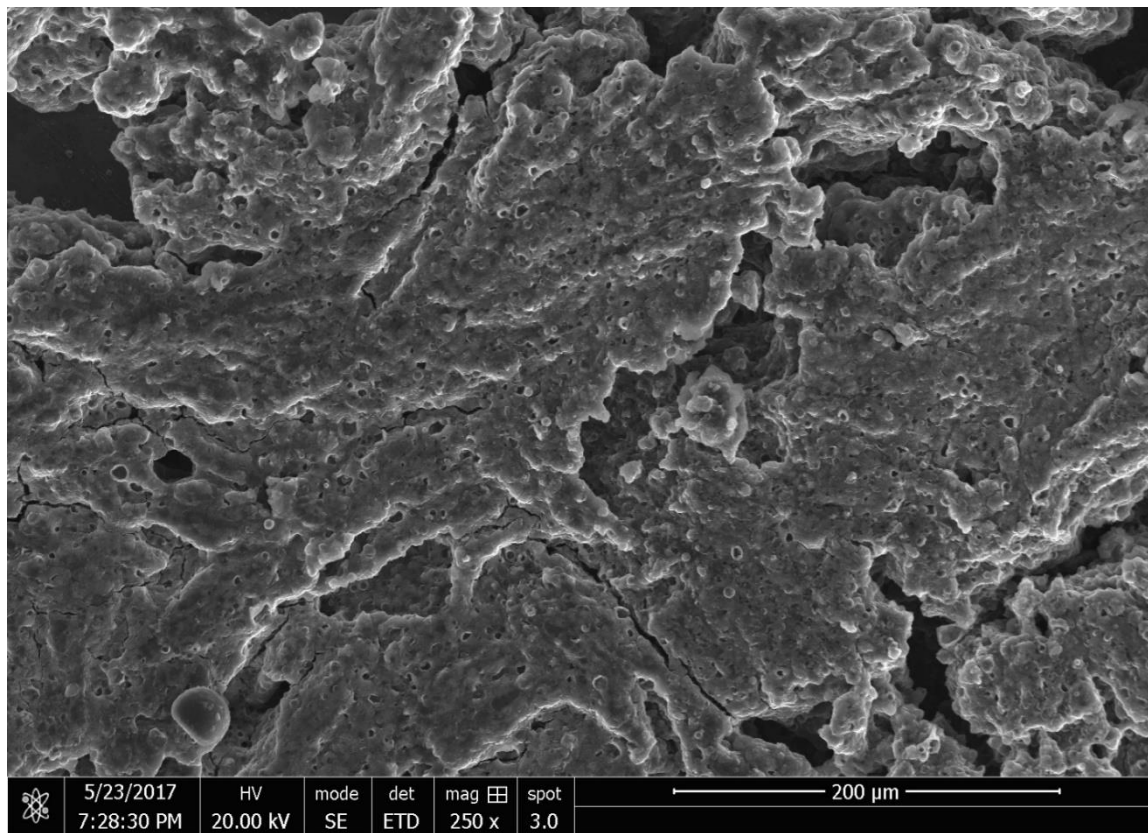


Figure 55 - Figure 43 - SEM images of 3N2S derived $\text{Li}_2\text{S}@C$ particles, after HCl wash

HCl wash of $\text{Li}_2\text{S}@C$ reveals a very different architecture. Massive agglomerates of carbon host, pocked with holes remain, where previously distinct, mostly submicron particles existed. TGA of $\text{Li}_2\text{S}@C$ shows continuing carbonization, even below 500°C, suggesting that there is certainly carbonization taking place in the reaction environment of the H_2S treatment. These images suggest that as carbonization proceeds, the carbon host particles fuse into larger networks.

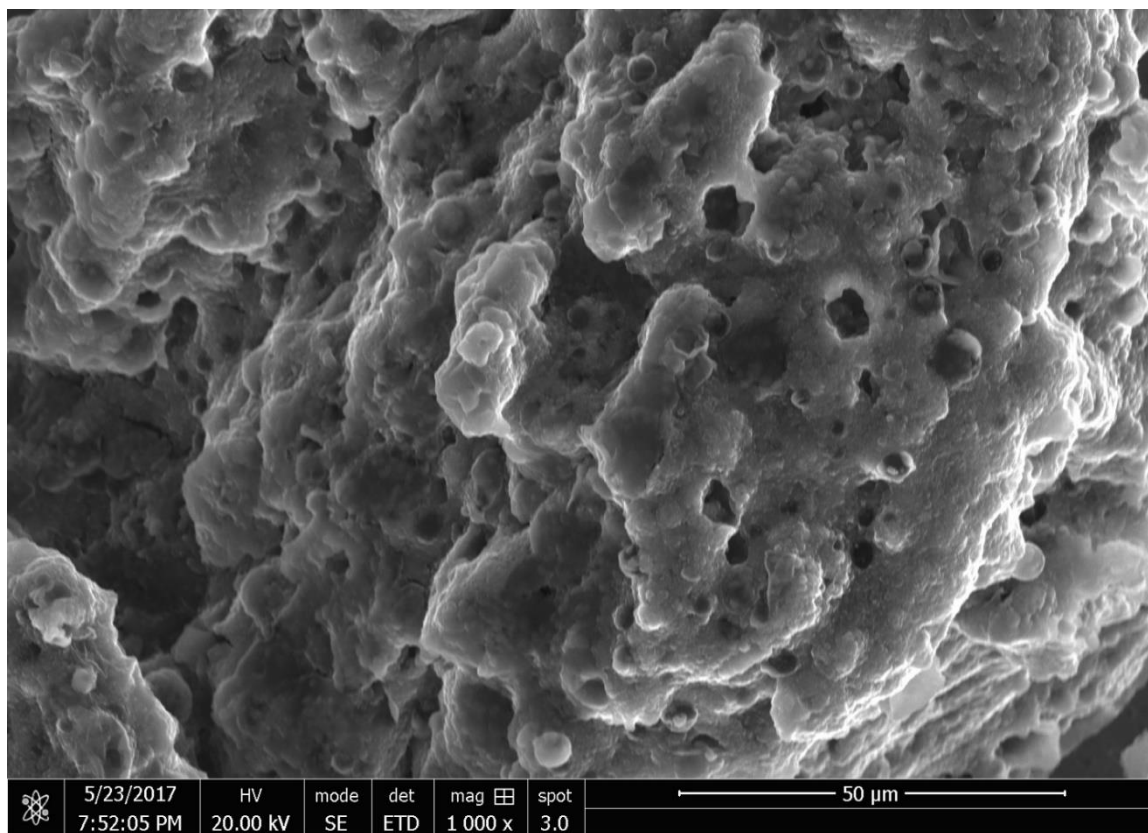


Figure 56 - SEM images of 3N2S derived $\text{Li}_2\text{CO}_3@\text{C}$ particles, after HCl wash.

A closer look reveals the prevalence of the holes. This is likely the result of off-gassing, as CO_2 is released from the $\text{Li}_2\text{CO}_3@\text{C}$ particles and H_2O is emitted as a result of reaction with H_2S . Such holes would offer the electrolyte deeper access into this architecture, promoting deeper sulfur utilization and better rate performance. This is likely to come at a cost of capacity degradation, as electrolyte access will promote PS dissolution.

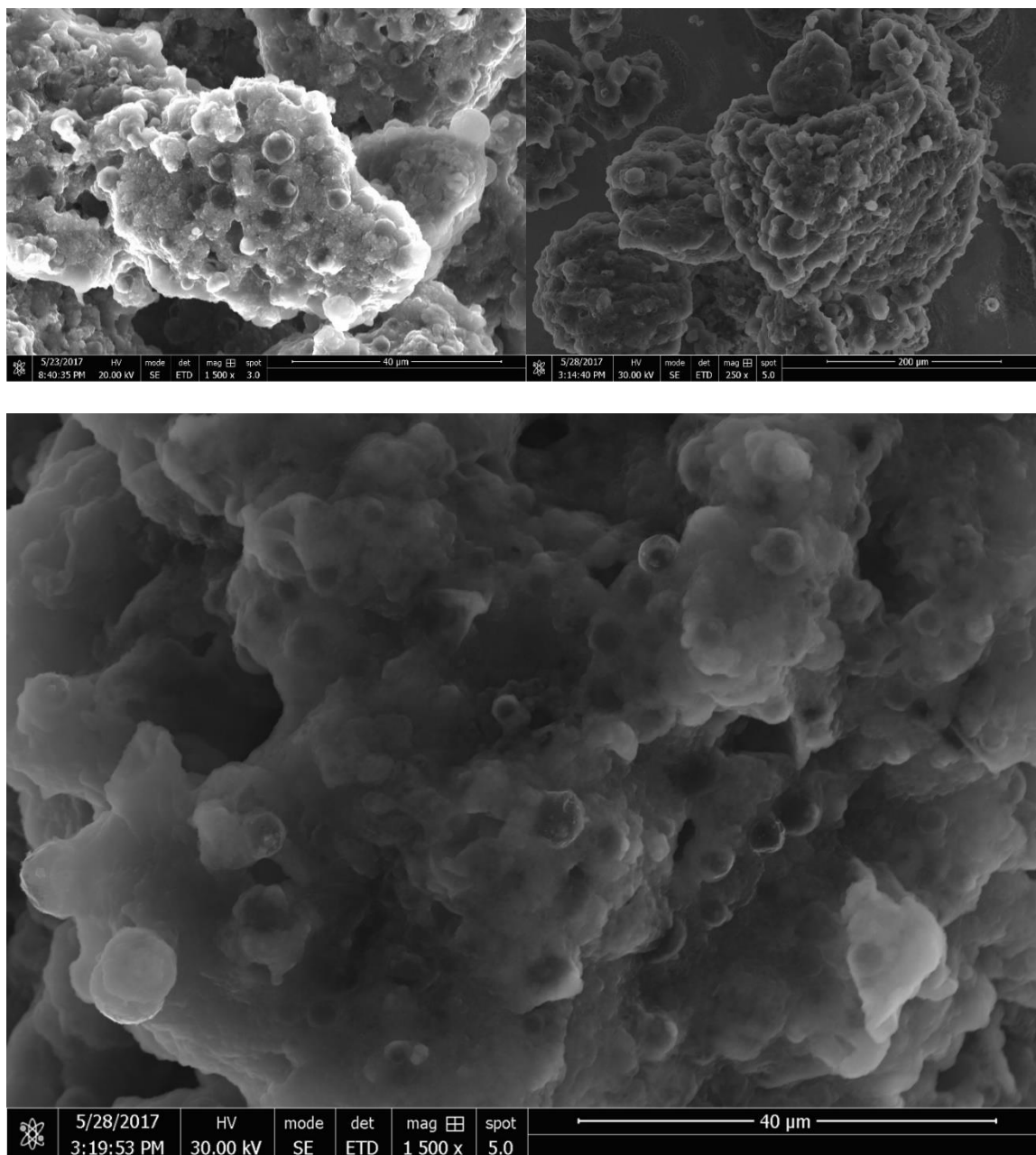


Figure 57 - SEM images of 3N2S derived $\text{Li}_2\text{S}@C$ particles, after HCl wash.

Close analysis also reveals small spherical features, suggestive of the spherical particles seen for the $\text{Li}_2\text{CO}_3@C$ particles.

4.3.2.1.2 TEM Analysis

4.3.2.1.2.1 $\text{Li}_2\text{CO}_3@\text{C}$ particles

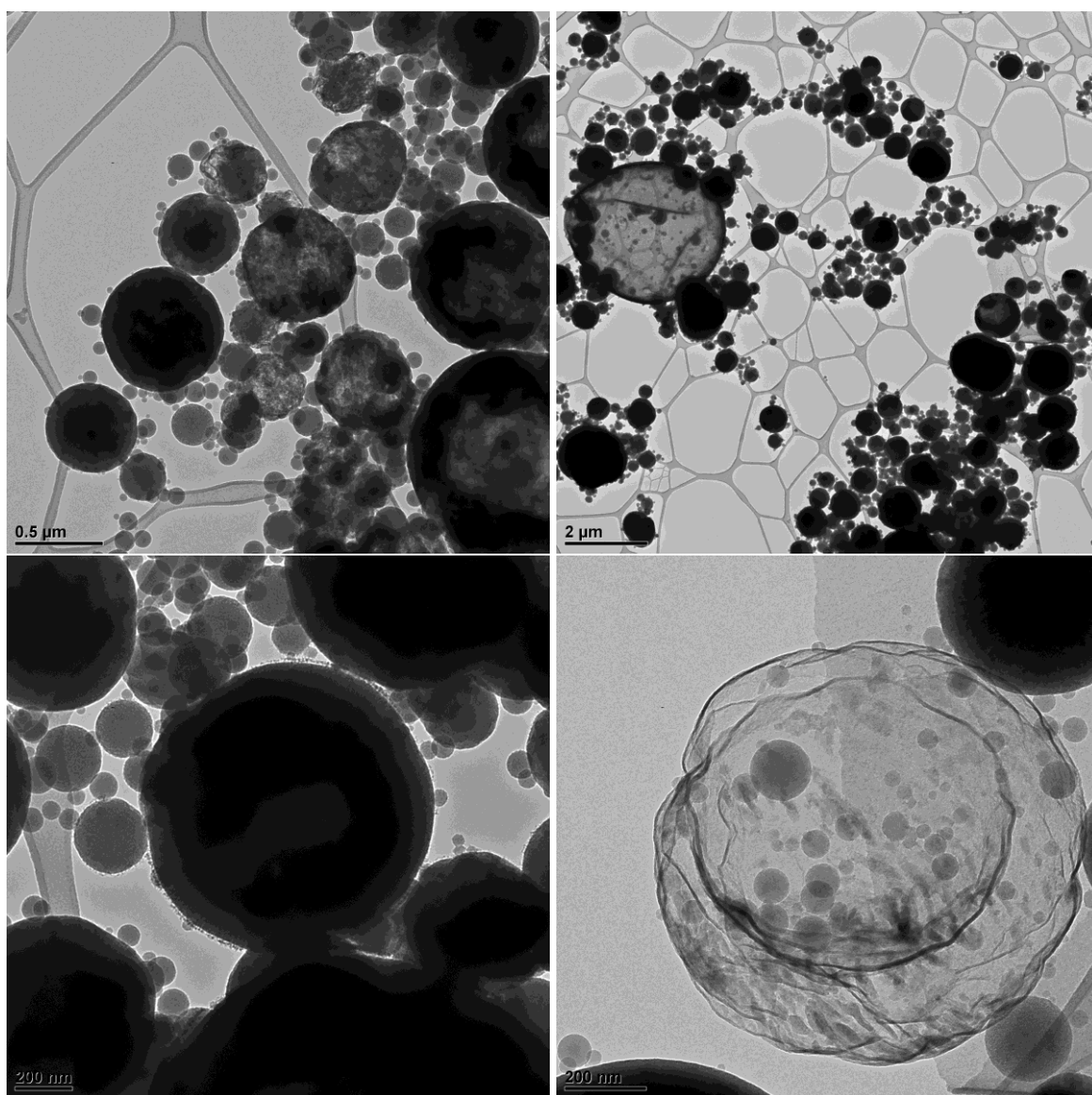


Figure 58 - TEM images of 3N2S derived $\text{Li}_2\text{CO}_3@\text{C}$ particles showing a wide particle size distribution and resultant architectures.

The above set of TEM images articulates the variety of particle sizes produced by ASP of 3N2S. Dense particle (where a consistent color appears throughout the diameter of the particle) can be seen ranging from sub 50nm to over 2 μ m. Note that some of the largest particles of the set, in the bottom and top right, present as little more than a loose skin. This level of variation cannot be expected to deliver a tightly refined behavior. Whereas the dense particles can rationally be expected to maintain high cycle stability, the medium skinned particles, such as the bottom right corner of the upper left image, may be better suited to faster rate performance. This mix suggests that the cells should perform well across a wide range of C rates. This is not however the case, as C/2 cycling, hardly the fastest in literature, scarcely engages the second plateau in discharge, offering only the initial conversion of elemental sulfur to polysulfides.

The final image in this set highlights burst particles, a behavior specific to the 3N2S particles. Thought to be related to off gassing as a result of thermal decomposition of LiNO_3 and consumptive reaction of the released O_2 and NO_x species with the carbon precursor. These cracks suggest better access to the internal Li_2S of larger particles; offering higher rate performance at the cost of cycle stability.

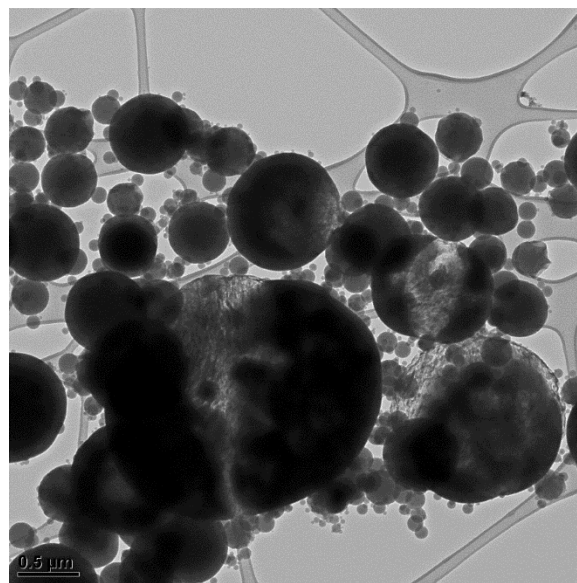


Figure 59 - TEM image of 3N2S derived $\text{Li}_2\text{CO}_3@\text{C}$ particles.

4.3.2.1.2.2 $\text{Li}_2\text{CO}_3@\text{C}$ HCl washed particles

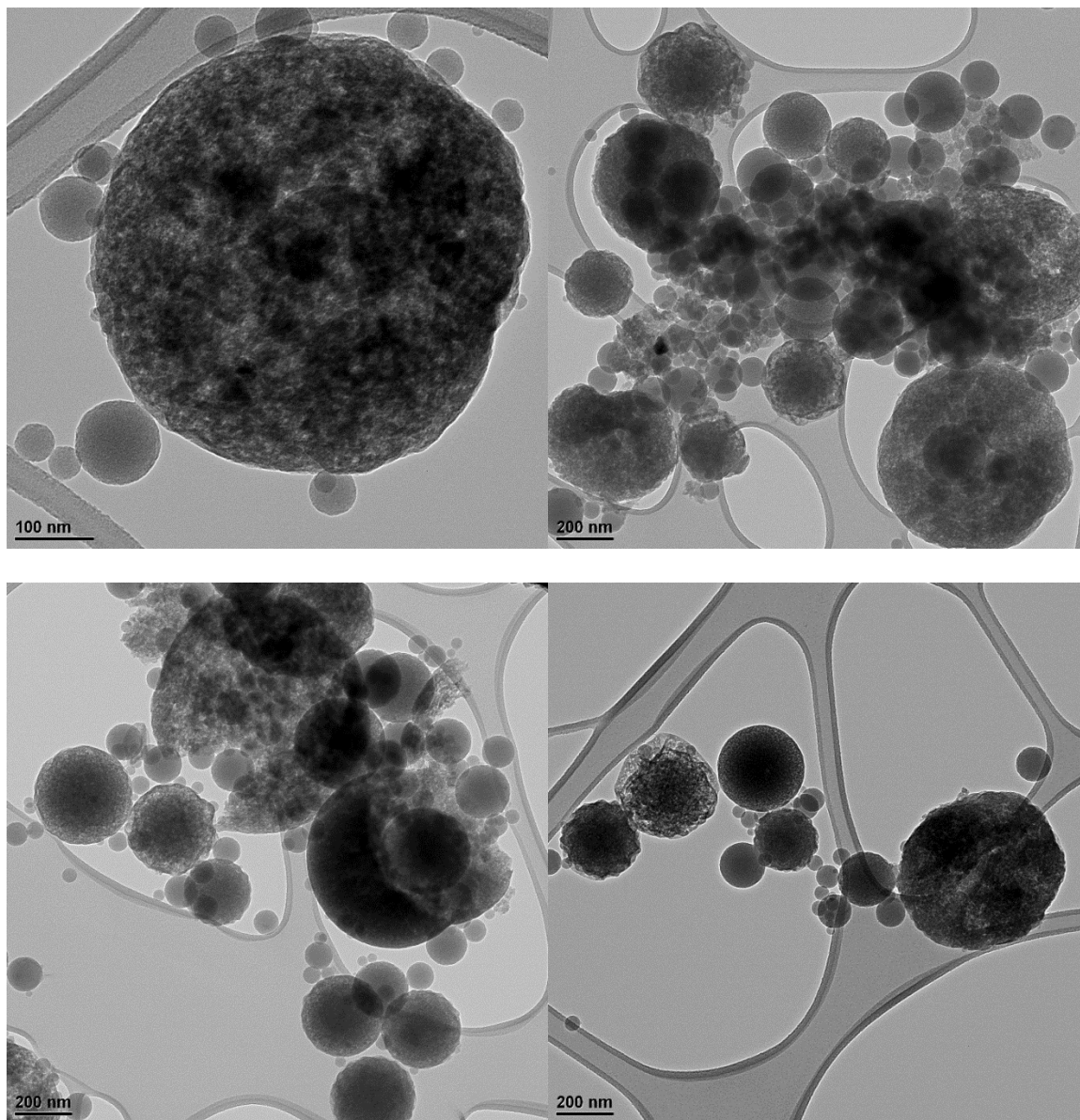


Figure 60 - TEM images of 3N2S derived $\text{Li}_2\text{CO}_3@\text{C}$ particles, after HCl wash.

The HCl wash reveals significantly less contrast in larger particles. This suggests that the Li_2CO_3 content and by extension Li_2S content, is concentrated in the larger particles and the more numerous, finer particles, may not hold meaningful Li_2CO_3 content. A system that

selects for a tighter particle size distribution may allow for lowering the carbon content, while maintaining appropriate coverage of the internal Li_2S .

4.3.2.1.2.3 $\text{Li}_2\text{S}@C$ HCl washed particles

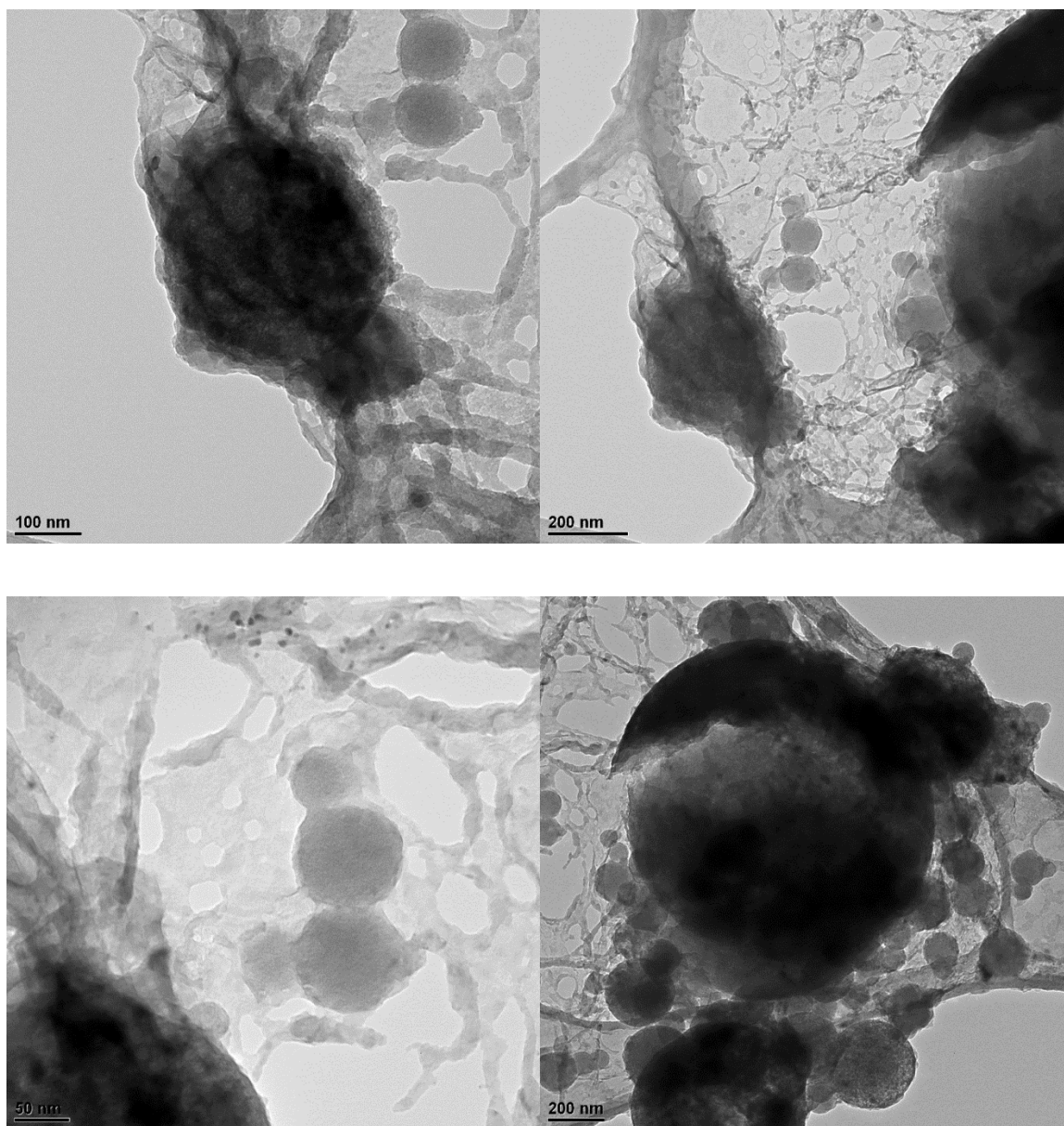


Figure 61 - TEM images of 3N2S derived $\text{Li}_2\text{S}@C$ particles, after HCl wash.

The final set of 3N2S TEM images articulates a mix of small spherical particles, a predictably ruptured large particle, and what appears to be a sloughed skin of carbon material draped across the population. Differences between this set and that observed under SEM may come down to biases in application and selection of field. In TEM the lacy carbon of the grid may cause the deposited population to spread across the film more evenly. Moreover, to get a useful image in TEM, a thinner cluster of particles yields clearer images. This suggests that the massive clusters seen in SEM may well be a population of ruptured and intact spheres, draped with the skins of the larger, balloon like particles. What is clear is that the H₂S treatment does not leave neat spherical particles behind; suggesting either that the H₂S treatment reaction environment is too severe, by time and or temperature, or that the particles as placed in the H₂S treatment environment are ill-suited for such a severe treatment.

5 CONCLUSION

5.1 SUMMARY

The above work has shown how a $\text{Li}_2\text{S}@C$ composite can be generated and utilized as cathode in an electrochemical cell. Observation of cycle stability suggests that the $\text{Li}_2\text{S}@C$ composite, as delivered in this work, does not in and of itself effectively entrap polysulfides, resulting in performance that is largely dependent on electrolyte composition and content. Performance of the composite cannot be taken as a standalone fact, but must be considered against the physicochemical environment in which the composite functions. As such, continuing improvements to the electrolyte in particular, as well as electrode pasting and cell assembly techniques, may show improved performance from the $\text{Li}_2\text{S}@C$ composites delivered herein.

The performance driven focus of this project and the complexity involved, have contributed to the difficulty to translate literature suggestions into practice within the work. Since conclusions delivered in literature are specific to a particular cathode architecture, sulfur areal loading, electrode thickness, binder selection, cycling rate, electrolyte composition, etc.; conclusions derived from one system will scarcely be applicable to another. As such, techniques relevant to advancing a project, on its own steam, become more relevant. To this end, QVE analysis may be helpful in identifying moments where the internal environment of the cell experiences a shift in predominant phenomena, suggesting opportune moments for the performance of lengthy or destructive tests on a cell.

Given the inherent limitations of measuring Li_2S directly, the devised TGA method allows for the measurement of a cathode's lithium content and as such ascertain the composition of a Li_2S composite powder; placing the product into sharper focus in comparison to performance described in literature. This method is particularly powerful for the estimation of composite carbon content, as the fate of this component, in post treatment, is difficult to gauge.

5.2 FUTURE WORK AND OUTLOOK

Much remains to be improved on, surrounding the cathode material itself. Incremental improvements in electrochemically inactive components offer mass reduction, bringing the cell ever closer to the theoretical capacity offered by lithium and sulfur.

The inclusion of CVD carbon coating may improve performance (132), (133), while allowing the overall reduction of cathode carbon content by decreasing carbon precursor (e.g. Sucrose, PVP, citric acid, etc.) in the initial solution and reducing the need for carbon additive (e.g. C65, Super P, Ketjen Black, etc.) content. Modification to the electrolyte chemistry, leading to more stable SEI (64) (118) (121), reducing the incidence of dendrite growth (134) (135) (136) (137) (138) (139) (140) (141) (142), preventing parasitic reactions (143) (144), conditioning cycle protocols (145) (143), or alternative reaction pathways (146) (147), or the adoption of solid state electrolytes (148) (149) (150) (151), suggest the possibility of greater capacity retention. Lower viscosity and lower interference with interface conductivity may offer better rate performance.

6 APPENDIX

6.1 PRODUCTION

6.1.1 Electrode compounding

After post treatment, both ASP and FD yield a $\text{Li}_2\text{S}@C$ composite and as such must be handled in a glovebox, in a low moisture ($\leq 0.5\text{ppm}$) and low oxygen ($\leq 0.1\text{ppm}$), Argon environment. The $\text{Li}_2\text{S}@C$ active material is mixed with a carbon additive and binder, at a mass ratio of 70:20:10 respectively, in sufficient toluene to allow for stir bar mixing. Mixing proceeds for 24 hours, in a sealed vial. The mixed slurry is smeared onto carbon coated aluminum foil (MTIXTL inc.) using a spatula, limiting the pasting area to yield cathodes of a desirable loading. The film is allowed to dry in the glove box environment, for ten minutes.

An upper limit of around 3mg composite material loading (translating to a potential maximum 2.1mg sulfur) per cathode is realized in this method, as a result flaking of the cathode material off of the foil. This is addressed in (152) whereby above a critical thickness of film of certain properties, the energy barrier associated with cracking is finally overcome by the stresses induced during drying. A slower evaporating solvent than toluene may alleviate these stresses and allow for a thicker, uncracked film. This upper limit suggests the methods used (compounding ratio, toluene as compounding solvent, type of binder, spatula pasting, glovebox temperature drying before oven baking) are inappropriate for commercially relevant loadings. As discussed in (153), the areal loading of sulfur (mg/cm^2) has a dramatic effect on commercial viability of a Li-S system. In Hagen’s study, with a

cathode composed of sulfur, carbon nanotube frameworks and no binder, even a loading of $15\text{mg}/\text{cm}^2$ was shown to be uncompetitive with a graphite-NCA cell.



Figure 62 - High areal loading electrode paste, derived of 3A015S.

6.1.1.1 A note on the compounding ratio

70:20:10 is not an optimized ratio, but a compromise between realizing commercially relevant performance (by limiting the binder and carbon additive content) and demonstrating functionality of the cathode, even for poor performing composites (by having sufficient binder and carbon additive).

6.1.2 Punching, drying, preservation in glovebox

The cathode film is hole punched with a $\frac{1}{2}$ " punch, over paper. The punched electrodes are collected into an open scintillating vial and dried in a muffle furnace, in the glove box, at

120°C for two hours, to remove any remaining toluene. The dried cathodes are then sealed in the vial and kept in a glovebox. Cathode performance appears to degrade, with time in glovebox, suggesting that even in the protective environment of the glovebox, $\text{Li}_2\text{S}@C$ is still reactive and as such suffers from a limited shelf life.

6.1.3 2032 cell assembly

The 1/2" cathode is weighed four times on a microbalance. The weight of the cathode itself is given by,

$$\text{Avg. Mass of 1/2" punch} - 0.0054\text{g} = \text{Mass of Cathode}$$

This calculation subtracts the mass of the foil (ascertained as 0.0054g on average, from 29 measurements) from that of the entire 1/2" punch. The cathode is loaded face up into the bottom cap of the coin cell. A volume of electrolyte is dropped onto the cathode, at a ratio of 10-15 μl electrolyte per 1mg Sulfur. Sulfur content is calculated by assuming the entirety of the active material is Li_2S , then stoichiometrically converted to Sulfur. A 3/4", diameter 25 μm thick PP-PE-PP (poly-propylene poly-ethylene poly-propylene) porous separator (MTIXTL inc.) is placed quickly over of the wetted cathode. A 5/8" punch of lithium metal is pressed onto the separator.

Steel spacer is placed on top of the lithium, and can be used to press the lithium into the separator. A steel spring is placed above the spacer. The top cap is placed atop the spring and closes the cell. The cell is flipped over and placed into a crimper (MTIXTL inc.). The crimper is pumped to 900psi. The crimper is then relaxed and the cell is removed.

6.1.3.1 Notes on assembly

For a sulfur based cathode, it is important to limit the electrolyte loading so as to reduce the solvent's ability to dissolve polysulfides and as such prevent capacity fade during cycling. As such the lower the electrolyte to active material ratio (here, 10:1), the better. Indeed, to be competitive with lithium ion cells on a gravimetric energy (Wh/kg) basis, the ratio should be close to 1:4. Dropping this ratio below 10:1 however, resulted in poor engagement of the cathode and a recurrent failure of the cells to charge. The minimal ratio was arrived at with 12:1 (roughly equivalent to 10:1 with DOL:DME in, (124)). Note that optimization would require significant lowering of this ratio, as both weight of the electrolyte and its costs at such a high volume adversely affect the \$/kWh metric.

The use of a 3/4" separator and a 5/8" lithium metal foil were arrived at as a way of standardizing and control the assembly. This configuration leads to a folding over of the separator around the lithium, and their firm lodging within the bottom cap. While this repeatable arrangement lead to a greater fraction of the assembled cells functioning, by preventing short circuits, it also means that the area of the separator is 225% that of the cathode itself, while the area of the lithium punch is above 150% that of the cathode. Separators this size were measured to hold roughly 10 μ l of electrolyte, after being patted dry. This means that a significant amount of electrolyte was used just to ensure good ion transport through excessive separator area, making it difficult to test cathodes of lower mass, below an E/S ratio of 30. Such a large lithium punch, moreover, leads to increased surface area for the consumptive reaction of PS on the lithium surface, expediting capacity loss. An optimized cell, such as a pouch configuration, where both electrodes and the separator are

roughly matched in size, would show cells with lower PS consumption and as such, better capacity retention. It would also allow the testing of lower loading cathodes, to study behavior at low E/S ratios more closely. This may be helpful in studying aspects which would be affected by thicker cathodes, such as diffusion characteristics.

6.2 ERROR

The error bars provided in the cycling capacity calculations represent the error of two dimensions: the deviation in capacities within a sample, which describes reproducibility of the material's behavior; and the error associated with weighing the cathodes, which describes the accuracy of estimation of cathode material.

For the former, this speaks to the reproducibility associated with the electrolyte (which may change properties over time due to lithium-salt precipitation, uneven cosolvent evaporation and solvent evaporation resulting in changes in solute concentration) as well as the reproducibility resulting from a particular composition (which speaks to how consistent a pyrolysis product is yielded, by architecture and sizing, the level of conversion in post treatment and the any inherent reproducibility issues stemming from the particular precursors used).

The latter describes the accuracy of teasing out the actual active material mass, which is a calculation based on the following two values: the 1/2" cathode punch of the battery measured (of which four measurements are taken on a microbalance) and a representative sample of clean aluminum foil 1/2" punches (a set of 60 such foils). The variation of the cathode punch is calculated as a function of (n) with excel's VAR.P function, while the latter

is calculated as a function of (n-1) with excel's VAR.S, since one degree of freedom is expended in estimating the mean. All calculations were scaled to compare with each other. Since capacity measurements are performed in mAh/g, capacity values are left as is, while weight values are scaled from milligrams to grams.

VAR.S is calculated as such,

$$S^2 = \frac{\sum (x_i - \bar{x})^2}{n - 1}$$

Where S^2 is the sample variance, x_i is the term in the data set, $\bar{x}$ is the sample mean, and n is the population size.

VAR.P is calculated as such,

$$\sigma^2 = \frac{\sum (x_i - \mu)^2}{n}$$

Where σ^2 is the population variance, x_i is the term in the data set, μ is the population mean, and n is the population size.

Variances of uncorrelated variables are additive, per the Bienaymé formula (154). Since the sample of foils used to ascertain the foil mass were not used in the cathodes, it is reasonable, for lack of knowledge, to consider the two variances uncorrelated, permitting the use of the Bienaymé formula. The standard deviation of weights is the square root of the added variances, and was calculated as such,

$$SD_{\text{weight}} = \sqrt{((\sigma^2)_{\text{Cathode 1}}^2 + \dots + (\sigma^2)_{\text{Cathode n}}^2 + n * (S^2)_{\text{foils}}^2)}$$

Standard deviation of cell capacity were taken as such, treating the cells as a representative sample, rather than the whole population,

$$SD_{\text{capacity}} = \frac{\sum (x_i - \mu)^2}{n - 1}$$

Standard error were calculated as such, scaling SD_{weight} to grams,

$$SE = \frac{\sqrt{(SD_{\text{capacity}})^2 + (1000 * SD_{\text{weight}})^2}}{\sqrt{n - 1}}$$

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