

Development of Porous Carbon for High Performance Lithium-Sulphur  
Batteries

by

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## Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

## Abstract

In recent years we have seen an enormous increase in electronic device capabilities as users demand new and improved features in a smaller form factor. As a result, the power demands of these electronics are increasing at an exponentially large rate such that lithium ion-battery (LIB) technology is rapidly becoming obsolete. Tesla motors and other electric vehicle manufacturers are pushing the limit of their technology as vehicles approach 300 miles per charge. Subsequently, battery technology must evolve in tandem with the rapid improvements made on current technology. The lithium-sulphur battery (LIS) stands as a promising candidate for future energy storage needs. As an old technology thought to be too difficult to implement, LIS technology has been rediscovered as researchers across the globe race to successfully implement this technology. A typical LIS consists of a lithium anode and sulphur cathode. The sulphur component allows for increased energy density over LIB technology. Sulphur is capable of bonding to lithium at much greater ratios than LIB cathodes. With a theoretical energy density five times higher than that of LIB, LIS has the potential to replace LIB as the new energy storage standard. In order to successfully implement LIS, several inherent shortcomings must be properly dealt with. Firstly, sulphur is an insulating material, effectively restricting electronic movement towards reaction areas in the cell. Secondly, the deposition of sulphur based by-products due to the electrochemical reactions which occur between lithium and sulphur create highly insulating areas resulting in poor electrochemical performance. Attempts to remedy these issues typically take form as modifications to select components of the battery, namely the composition or structure of the electrolyte, electrodes and the separator.

It has been shown that nanoporous carbon materials are an excellent cathode option for increasing LIS battery performance as a result of increased sulphur uptake and decreased PS diffusion. This thesis will describe the development of a porous, carbonaceous material to be used as the cell cathode to improve performance. Herein, carbon spheres were synthesized as the cathode material sulphur host. These spheres are approximately 500nm in diameter and are air treated to greatly increase pore volume to promote PS retention and increase sulphur loading. The assembled cell using the air treated sample was shown to have a capacity of approximately 1100 mAh g<sup>-1</sup> with an 81% capacity retention versus the non-treated sample with a capacity of 700 mAh g<sup>-1</sup> and 68% retention.

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## List of Abbreviations

CTAB: Cetrimonium bromide

EIS: Electrochemical impedance spectroscopy

EV: Electric Vehicles

GCD: Galvanostatic Charge and Discharge

ICE: Internal combustion engine

KJB600: Ketjenblack 600 JD

LIS: Lithium-sulphur

Li-ion: Lithium ion

LIB: Lithium-ion battery

LIO: Lithium cobalt oxide

PCS: Porous carbon spheres

PS: polysulphide

SEM: Scanning Electron Microscope

TGA: Thermogravimetric Analysis

XRD: X-ray diffraction

## 1.0 Introduction

Modern electronic devices are omnipresent in the developed world. From cell phones to cars, developments in technology have allowed us to live a life of comfort and convenience. However, these devices are being built to consume greater amounts of energy at an increased rate as users demand more features in a same-sized package. As such, batteries play an incredibly vital role in the operation of nearly every electronic device. Once considered a modern technology, the lithium-ion battery is quickly approaching the upper limit of its capabilities. This coincides with the recent explosion in interest of commercially viable, mass produced hybrid/electric vehicles. These green alternatives to tradition combustion engines require a large battery to deliver a steady amount of power in order to travel an acceptable range. The Tesla Model S, one of the most iconic electric vehicles on the market, provides a range of approximately 400km. Tesla is poised to take over the electric vehicle market with a more affordable alternative to the Model S known as the Model 3 with a starting price of about 35 000 USD. The push to create cheap electric vehicles is driven by the otherwise high barrier to entry as a result of the expensive manufacturing costs associated with electric vehicles. Battery charge stations are also of great concern to Tesla in order to alleviate some range anxiety concerns as they commit themselves to creating a large network of charging stations across North America. Unfortunately this is a classic case of treating the symptom and not the cause. The real issue at hand is the batteries currently being used in EVs do not have a high enough energy density to compete with internal combustion engines (ICE). A longer lasting battery format is needed in order for a seamless transition from ICE based vehicles to EVs.

A potential replacement for lithium-ion battery technology is the lithium-sulphur battery (LIS). A typical LIS consists of a lithium anode and sulphur cathode. The sulphur component allows for increased energy density over LIB technology. Sulphur is capable of bonding to lithium at much greater ratios than LIB cathodes. With a theoretical energy density five times higher than that of LIB, LIS has the potential to replace LIB as the new energy storage standard. In order to successfully implement LIS, several inherent shortcomings must be properly dealt with. Firstly, sulphur is an insulating material, effectively restricting electronic movement towards reaction areas in the cell. Secondly, the deposition of sulphur based by-products due to the electrochemical reactions which occur between lithium and sulphur create highly insulating areas resulting in poor electrochemical performance. Attempts to remedy these issues typically take form as modifications to select components of the battery, namely the composition or structure of the electrolyte, electrodes and the separator.

In this thesis, the basic operating mechanism and limitations of lithium-ion battery technology is discussed. Lithium-sulphur batteries are then introduced as a potential candidate to replace lithium-ion with an insight on their chemistry and advantages over lithium-ion technology. The challenges facing lithium-sulphur batteries are not trivial; these will be investigated and potential solutions will be elucidated. The work presented consists of the development of two different porous carbon materials for use in lithium sulphur batteries as the carbon host for sulphur in the cathode. Also included is the synthesis, application and physical/chemical characterization of the above materials. Discussion of the obtained results is to follow.

## 2.0 Lithium Ion Batteries

The lithium ion battery is part of a larger family of rechargeable battery types where lithium ions travel in the negative to positive electrode direction upon discharging and in reverse when charging. Over the years rechargeable batteries have undergone great change as they become more and more compact and energy dense. John Goodenough pioneered the lithium metal oxide family of rechargeable batteries starting with the 4V lithium cobalt oxide ( $\text{LiCoO}_2$ ) battery around 1980. This innovation of metal oxides as positive electrode materials made lithium ion batteries commercially viable. After further refinements to the battery, the first commercialized lithium ion battery was produced by Sony and Asahi Kasei in 1991. Lithium ion batteries require low-maintenance with a high energy density and have a relatively low self-discharge rate. All of these factors contribute to their popularity and dominance over the consumer electronics market. Various research groups and corporations raced to improve upon this technology through material doping or changing the composition of the electrode. In the present day, these types of rechargeable batteries represent a 30+ billion dollar market share and are currently uncontested as the energy source of choice for consumer electronics.

### 2.1 Operating Principles

The lithium ion battery consists of a lithium-based positive electrode and a negative electrode typically made from carbon. Lithium metal oxides, such as  $\text{LiMn}_2\text{O}_4$  and  $\text{LiCoO}_2$ , are a popular choice for the positive electrode due to their stability and high performance. Lithium ion intercalation and extraction from the electrodes ultimately govern the electrochemistry in the battery. This concept of reversible intercalation into graphite and cathodic oxides was discovered by J. O. Besenhard at TU Munich. The mechanism of energy storage and the production of useful work lie in the transfer of lithium ions from the anode to become

intercalated with the cathode. A schematic depicting the general LIB operating mechanism is shown in figure 1 [30] with a  $\text{LiCoO}_2$  cathode and graphite anode.

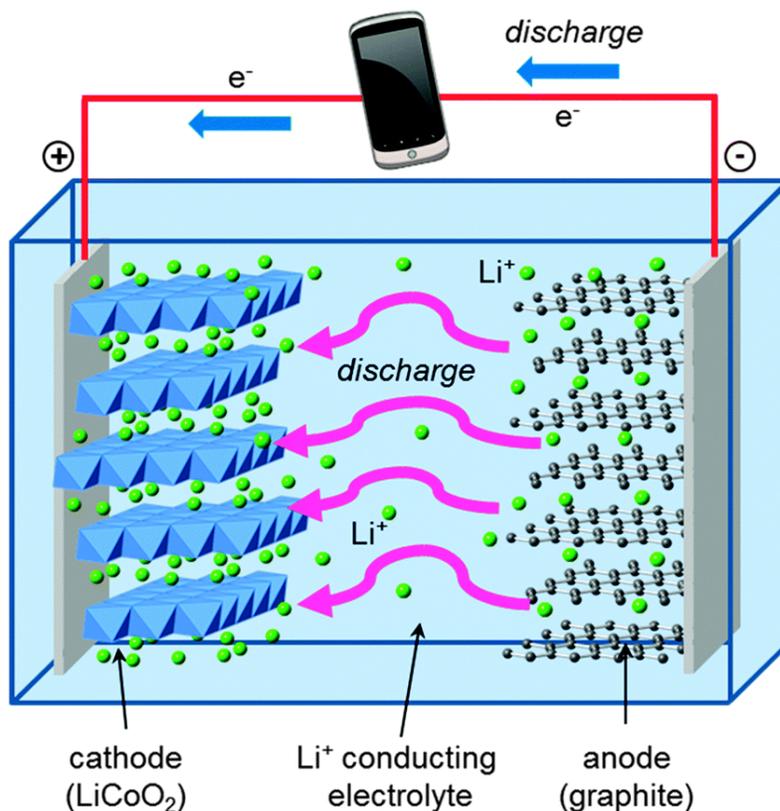


Figure 1: Schematic diagram of a first-generation Li-ion cell

During the discharge process, the positive lithium ions move from the negative electrode (typically carbon based such as graphite,  $\text{C}_6$ ) and enter the lithium containing positive electrode. The reverse of this process is charging. Through this mechanism, electrons are transferred concurrently with the lithium ions and convert the chemical potential gradient into electrical power. In order for the charging process to occur, an external voltage is necessary in order to drive the lithium ions from a lower chemical potential at the cathode to a higher chemical potential, this effectively recharges the battery and primes it for another discharge cycle. An insulating,  $\text{Li}^+$  permeable membrane is placed in the cell in order to separate the anode from the cathode, this is known as the separator. The separator ensures the transport of

the ionic charge carriers while preventing electrical short circuits between the electrodes. Additionally, lithium-ion cells usually use an organic solvent based electrolyte through which the lithium ions are easily conducted.

## 2.2 LIB limitations

There are numerous disadvantages to lithium ion batteries including high cost, low shelf life and low thermal stability among many others. Despite this, its high energy density is highly desirable and it continues to be the choice of rechargeable energy storage in a large majority of consumer electronics. A higher energy density battery allows a device to operate longer before requiring a recharge. As lithium ion battery technology matured, it has become apparent we are reaching the upper limit of the theoretical energy density for the materials typically used in LIBs.  $\text{LiCoO}_2$  (LCO) is a commonly used cathode material for LIBs due to its high theoretical specific capacity of  $273 \text{ mAh g}^{-1}$  [1], however we are nearing the theoretical capacity for this material. The limitations stem from the innate ability for free  $\text{Li}^+$  to be absorbed into the structure of the metal oxide and carbonaceous anode. This effectively limits the capacity by preventing  $\text{Li}^+$  species from undergoing redox reactions. Furthermore, upon inspection of the popular  $\text{LiCoO}_2$  material we can determine the mass ratio of useful lithium metal to lithium oxide. This ratio is approximately 1:13 (Li:Li-Oxide) where the lithium metal represents approximately 7% of the total mass of the cathode. This effect can be seen when calculating the theoretical capacity of the lithiation of the metal oxide material ( $274 \text{ mAh g}^{-1}$ ) and comparing it to practical capacities often reported in literature ( $150 \text{ mAh g}^{-1}$ ) [2]. In order to improve upon cathode performance, a new host for lithium must be developed which allows for a significantly higher density of lithium to be stored. Sulfur-based cathodes represent an attractive strategy for increasing the lithium to host material ratio.

### 3.0 Lithium Sulphur Batteries

Lithium sulphur battery technology dates back to the late 1970s when Rauh and his coworkers created a lithium/dissolved sulphur battery [3] as a proof of concept. Unlike LIBs, LIS technology does not rely on the intercalation mechanism of  $\text{Li}^+$ . Instead, sulphur dissolves from its native form ( $\text{S}_8$ ) to form polysulfide species ( $\text{S}_8^{2-}$ ). The overall reaction is given by:  $\text{S}_8 + 16\text{Li}^+ + 16\text{e}^- \Rightarrow 8\text{Li}_2\text{S}$  [4]. Under ambient conditions, sulphur exists as cyclooctasulfur as a solid. Upon accepting an electron, sulphur becomes charged as  $\text{S}_8^{2-}$  then further reduced to a  $\text{S}_6^{2-}$ . While the non-charged form is insoluble in many organic electrolytes, the charged state sulphur molecules are soluble. It has proposed that the  $\text{S}_6^{2-}$  species spontaneously form radicals as  $\text{S}_3^-$  which are almost immediately reduced to  $\text{S}_4^{2-}$  and finally to insoluble  $\text{S}^{2-}$ . Thus we may deduce that the original solid sulfur ( $\text{S}_8$ ) is stripped from the cathode host material to be deposited over the course of a single discharge cycle. Lithium is concurrently passed with the sulfur and formed intermediate polysulfides as the sulfur is reduced.

Ultimately, the discharge product formed is lithiumsulfide ( $\text{Li}_2\text{S}$ ) which possesses a greater ratio of lithium to ‘dead weight’ material than  $\text{CoO}_2$ . The theoretical capacity of sulfur for lithium is calculated to be around  $1672 \text{ mAh g}^{-1}$  [5], about five times higher than that of typical cobalt oxide lithium ion batteries. Specific capacity provides a good measure of the battery lifetime over a full charge but electrical devices require energy related to the operating voltage of the battery. The energy density of sulphur is  $2500 \text{ Wh kg}^{-1}$  in theory, but taking into account the effect of the lithium anode and other battery components (current collector, separator and electrolyte), the practical energy density becomes closer to  $700 \text{ Wh kg}^{-1}$ . Still, this represents a greatly increased theoretical practical energy density over LIB which has only shown a

practical energy density of  $210 \text{ Wh kg}^{-1}$  [4]. Thus, if successful, LIS can potentially offer more than three times the energy density of LIB technology. Unfortunately a wide variety of challenges must be overcome before LIS technology is adopted as a new battery technology.

### 3.1 LIS limitations

There are three major issues which effectively limit the LIS cycling stability and obtainable capacity. First, is the insulating property of sulphur, as we now require the host material containing sulphur to be conductive enough for effective electron transport. The next issue is the  $\sim 80\%$  volumetric expansion in sulphur after lithiation which may short circuit the battery by disconnecting the lithiated sulphur. The dissolution/deposition mechanism between sulphur and  $\text{Li}_2\text{S}$  during cell cycling may create an undesirable redistribution of sulphur among its host material. Thus, the conductive host is crucial for cell operation and the conductive additive must be homogeneously mixed with the host material and sulphur for intimate contact to ensure a good electronic conduit. Finally, and most importantly, is the effect known as the polysulfide shuttle, where the dissolution of sulphur into the electrolyte occurs during battery discharge. These soluble polysulfide (PS) species diffuse readily through the battery separator resulting in short circuiting at the anode location. Higher order PS can attach themselves and be reduced directly on the anode while PS are continuously being created at the cathode. These regenerated PS discharge upon contact with the anode resulting in a significant reduction in efficiency by producing wasteful products.

## 4.0 Applications of Porous Carbon Materials for LiS

Porous carbon materials for LiS batteries has been widely research and explored by various research groups. For lithium sulphur batteries, porous carbon is an attractive host material due to the effective entrapment of sulphur into its pores which serves as both a conductive matrix for electron transport as well as to resist PS diffusion from the pores. While interparticle pores formed by adjacent carbon structures are a key component of the pore volume, intraparticle pore volume is also of great importance. Work done by Ji et al. has proven to effectively entrap sulphur while preventing the polysulfide shuttle effect allowing for a reversible LiS battery but with much needed room for improvement [6]. Typically, there are three main areas that are targeted in order to improve batteries, the separator, the electrolyte and the electrodes all with the intention of improving performance by increasing capacity, preventing PS shuttle or by increasing cycling lifetime. More recently, electrodes have incorporated nanostructured carbon materials such as carbon nanotubes [7], graphene foams [8, 9] and other porous carbon materials [10, 11, 12] in order to increase sulphur encapsulation while maintaining a conductive matrix. In order to attract and retain the polysulfide species within the cathode a wide variety of additives and other chemicals have been incorporated into the cathode that may also aid in retaining PS [13, 14, 15, 16]. Nitrogen doping of carbonaceous materials is also another popular area of research with a wide variety of already established materials being doped for increased performance [13]. Despite all this work, we have still yet to see a commercially feasible battery to reach the market. High energy density of LIS batteries is achieved mainly through high loading of sulphur. Interestingly, the majority of reported LIS batteries have yet to greatly surpass LIB [17] with recent developments only slightly improving upon existing LIB technology. The majority of work published in the last few years have been

intensely focused on obtaining maximum performance at low loading ( $<2\text{mg cm}^{-1}$ ) under the guise of increasing performance rather than being a practical solution for real world applications [25]. In actuality it is very difficult to successfully synthesize high loading, electrodes in large part due to the mechanical instability of the thick electrode associated with higher loading [22, 26]. Somewhat more recently, an attempt has been made to create thick, high loading lithium sulphur batteries by Dr. Wang's group at Penn State University [27, 28]. Lithium sulphur is becoming more and more impressive in a laboratory setting but more work is to be done to have it leave the lab and become a commercial product. In this thesis I would like to elucidate how to obtain higher performance batteries with practical possibilities by developing a strategy that would effectively increase the performance of the sulphur electrode.

#### 4.1 Carbon-based cathode materials of lithium-sulphur batteries

Although sulphur is a suitable cathode material due to its excellent specific capacity and energy density, it is electrically insulating thus making the cathode conductivity quite poor. Thus, suitable conductive materials are needed in order to enhance the electrical conduction of the cathode. While sulphur/polymer and sulphur/metal oxide composites exist, sulphur/carbon composites are by far the most common [31]. A wide variety of carbon-based materials have been widely researched as a cathode component such as carbon black, graphene, carbon nanotubes (CNT), carbon nanofibers and hybrid composites. These hybrid composites include graphene/CNT [32-35] and combined graphene nanosheets [36]. Porous carbons, including microporous, mesoporous, hierarchical porous, and hollow-structured carbon composites, have also been researched and applied [37]. Work by Jozwiuk et al [38] compared a variety of different carbon blacks for use in LIS cathodes: Printex-A, Super C65, PrintexXE2, and Ketjen black EC-600JD and standard (Super C65 and Printex-XE2 in a ratio of 1:1). SEM images and

optical microscope images of the resulting cathodes are shown in figure 2. Ketjen black showed the highest battery specific capacity of  $>1000 \text{ mAh g}^{-1}$ . The capacities of Printex-A, Super C65, PrintexXE2 and standard were  $<600 \text{ mAh g}^{-1}$ ,  $600\text{-}700 \text{ mAh g}^{-1}$ ,  $800 \text{ mAh g}^{-1}$  and  $800\text{-}9000 \text{ mAh g}^{-1}$  respectively. It was hypothesized that the greater surface area of Ketjen black contributed to the increased capacitance and thus from this study, knowing surface area of materials would be helpful to understanding the mechanism of cathode preparation.

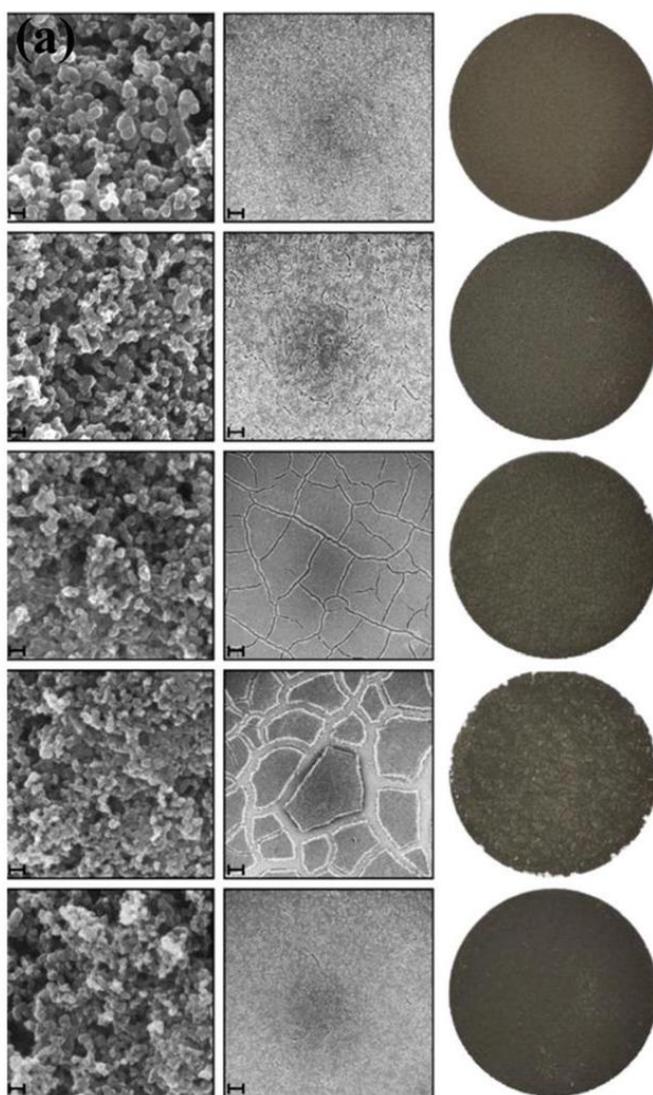


Figure 2: Column 1–2: Top view SEM images of sulfur cathodes containing different carbon blacks. Scale bar indicates 100 nm (left) and 100  $\mu\text{m}$  (right). Column 3: Optical microscope images of 13mm diameter disc electrodes. Top to Bottom: Printex-A, Super-C65, Printex-XE2, Ketjenblack EC-600JD and standard.

Structural design of the carbon host material is another research focus spurring forth from the prominent work of Ji et al in 2009 [6]. In his work, a high performance LIS battery was created with the cathode material consisting of a conductive mesoporous CMK-3 carbon framework modified by polyethylene glycol (PEG). SEM images and a schematic diagram of the CMK-3 material are shown in figure 3 [6].

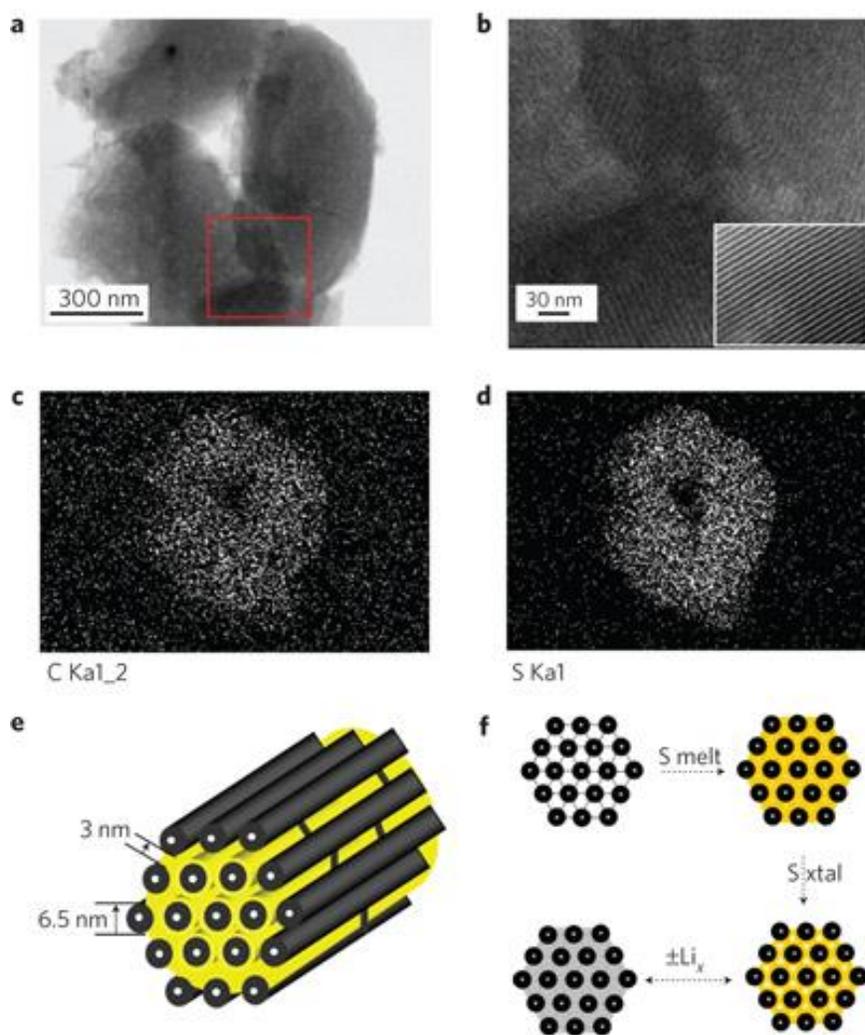


Figure 3: a) CMK-3/S-155 composite particle. b) Image expansion corresponding to the area outlined by the red square in a, where the inset shows the TEM image for pristine CMK-3 at the same magnification. c), d) Corresponding carbon and sulphur elemental maps showing the homogeneous distribution of sulphur. e), A schematic diagram of the sulphur (yellow) confined in the interconnected pore structure of mesoporous carbon, CMK-3, formed from carbon tubes that are propped apart by carbon nanofibres. f) Schematic diagram of composite synthesis by impregnation of molten sulphur, followed by its densification on crystallization. The lower diagram represents subsequent discharging-charging with Li, illustrating the strategy of pore-filling to tune for volume expansion/contraction.

This carbonaceous material was used to precisely constrain the sulphur infiltration within its channels to ensure intimate electrical contact with the sulphur. The CMK-3/sulphur composite aided in trapping PS species and the modified POG conductive polymer provided a chemical gradient to aid in diffusing the anions out from the electrode. The specific capacity of the cell reached 1320 mAh g<sup>-1</sup>. This research demonstrated an effective method for the application of nanomaterials in the cathode for the development of high-performance batteries and effectively spurred on the movement towards tailoring carbon structure for increased LIS performance.

Besides the structural designs of sulfur/carbon composite cathodes, numerous experiments and related theory show that substituting heteroatoms through doping and other similar methods can also significantly enhance electronic conductivity in addition to trapping PS species with functional groups and synthetic peptides. Cai et al [39] used porous nitrogen-doped carbon derived from silk fibroin protein as a host material for the sulphur cathode. This material had a mesoporous structure with high surface area, both of which help constrain PS within the cathode and improve conductivity. Additionally, the nitrogen doping could chemically adsorb PS. Thus the capacity retention of the battery could reach 98%, even at 1C after 200 cycles.

## 5.0 Project Objective

As an electrochemical storage device, LIBs are rapidly approaching their upper limit of theoretical performance capabilities. LIS batteries are poised to make an impact on the energy storage market boasting a respectable theoretical capacity at a low cost. A key component to the LIS cell is the cathode, where polysulfide species are reduced during discharge. The cathode serves as the host material for the sulphur that ultimately governs cell performance.

The goal of this project is to develop a strategy that would effectively increase the performance of the sulphur electrode using a method that is both simple and effective. The key to this design is to utilize an existing carbon particle and further increase its porosity to further encapsulate additional sulphur thus increasing performance. Concurrently, PS species that contribute to the PS shuttle effect will be well entrapped within the tortuous pore structure increasing diffusion resistance thus alleviating the effects of the PS shuttle. Porous carbon spheres and commercial carbon black will be used as the cathode material. The commercial carbon black, Ketjenblack 600 JD, will only be used to test the effectiveness of the air treatment activation method to determine if it is effective in increasing pore volume and surface area. The three major objectives are: 1) Synthesize carbon spheres as the LIS cathode material, 2) develop a methodology to increase carbon particle porosity, 3) high loading of electrodes to increase performance and lifetime.

## 6.0 Sphere Size

An important topic to discuss is the effect of carbon particle or sphere size on the operation of the LIS cell. A small sphere size results in an increased surface area for a more a maximized and uniform distribution of sulphur throughout the host matrix. In addition when using smaller nanosized particles, porosity of the material become less of an issue due to the interparticle spaces now act as pores. There are numerous advantages of using nanoparticles and multiple publications in the field of LIS batteries take advantage of this [22, 23]. Unfortunately these smaller sized nanoparticles are typically unable to accommodate a high load of sulphur. The mechanical stability and properties of the electrode surface is compromised using even for mass loading lower than  $3 \text{ mg cm}^{-2}$ . Crack formation on the surface of the processed electrodes resulting from interparticle stresses ultimately renders certain regions unusable [22, 24]. For large scale roll-to-roll manufacturing the quality of the electrodes is of utmost importance. An effective solution to this problem would be to increase the binder content in the slurry. The binder acts as the adhesive for the components of the slurry. Increased binder content would effectively yield a better film quality with fewer cracks. Doing so would come at a price however, with a thicker electrode required due to the reduced mass loading of sulphur. Another drawback of using smaller particle sizes is that while the interparticle pores are effective at hindering PS diffusion, lithium ions are affected negatively. In extreme cases lithium ions are unable to react with the sulphur due to the increased diffusion resistance of the interparticle pores. This work will mainly focus changing pore volume on moderate sized particles on the order of 100nm. While the focus of this work is not to determine the optimal particle size to the nearest nanometer, it is most definitely a future goal to tune the sphere size to optimize performance in a way that balances the sphere size with performance.

## 7.0 Physical & Electrochemical Characterization Methods

Materials research is highly dependent on a wide variety of characterization methods which help elucidate both physical and chemical properties of a material. Physical and electrochemical characterization of the cathode materials and LIS cells allows for quantitative analysis between samples. In order to better understand important material characteristics, techniques such as scanning electron microscopy, transmission electron microscopy, thermogravimetric analysis, Brunauer–Emmett–Teller (BET) surface area analysis and X-ray diffraction (XRD) all allow for physical characterization of materials. Electrochemical analysis of the assembled battery via Galvanostatic discharge and electrochemical impedance spectroscopy provides both performance data and may offer insight to the mass transfer which happens within the cell. This is relevany to electrochemical cells as the conductance of the charged species may vary during the cycling lifetime. The following section outlines the characterization methods used in this work.

### 7.1 Scanning Electron Microscopy (SEM)

SEM is a commonly used microscope technique which is capable of imaging nano-sized objects and surfaces. Unlike traditional light microscopes, SEM uses a focused electron beam to probe the sample surface for information. Modern SEM setups are capable of sub-nanometer resolution with minimal sample preparation required. The electron beam is mostly non-destructive and can even be used to image organic materials with some additional sample preparation. The main drawback to using SEM is that it is only capable of probing the surface of the samples and any materials or structures buried well within the sample are effectively hidden from the electron beam.

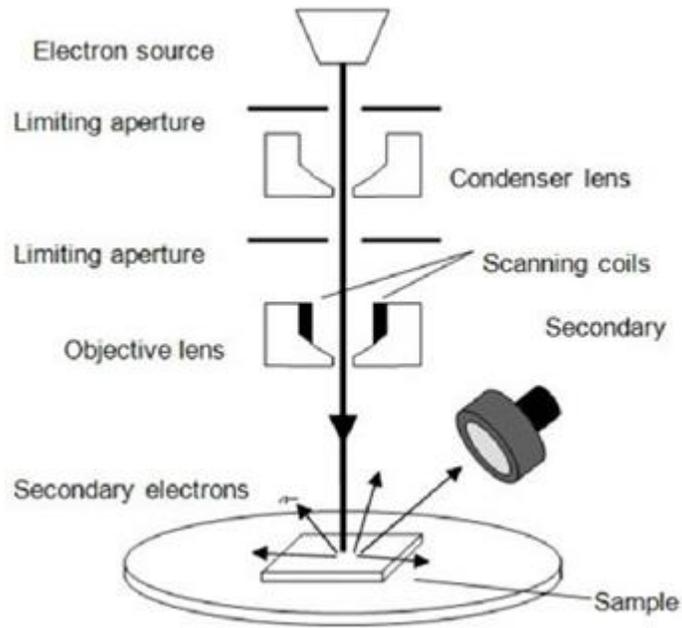


Figure 4: Schematic diagram of SEM setup

An electron gun fires an electron through a focusing lens towards the sample. The scattered electrons that result from the incident electron beam are collected and analyzed. Depending on the interaction depth and type of interaction the scattered electrons may be known as backscattered electrons (BSE) or secondary electrons (SE). Other forms of scattered energy including visible light and x-rays may also be captured. Depending on the type of detector, different information may be acquired.

SEs are low energy electrons that result from inelastic collisions with the sample. These electrons originate from a region very close to the sample surface. SE mode is one of the most commonly used modes of the SEM.

BSEs are high energy electrons that result from elastic collisions with the sample. BSEs are generally used for elemental analysis as high atomic number elements have a denser electron cloud resulting in more BSEs and thus a brighter image.

In this work SEM is used to visualize surface morphology, particle size and also to confirm pore formation.

## 7.2 Transmission Electron Microscopy (TEM)

Similar to SEM, TEM transmits a beam of focused electrons through a sample. Using a higher gun voltage, TEM is capable of much higher resolution and magnification images at the cost of additional sample preparation. This technique is capable of visualizing diffraction patterns of crystalline materials to obtain information such as stresses, crystallization, and lattice defects. Thin slices of the sample must be prepared such that the electron beam may pass through the sample.

## 7.3 Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) is a characterization method where the change in sample mass is measured in an environment where temperature is changing or at a constant temperature at an increasing timescale. This provides valuable information regarding phase transitions at certain temperatures and thermal stability. It is crucial to choose the correct gaseous atmosphere to perform TGA. For example, heating carbon in an inert atmosphere at high temperatures (>800C) will do little, if anything to the sample mass. However, in air, carbon is easily burned away. A laboratory TGA setup consists of a balance, sample pan and a furnace. The sample pan is usually made from a heat resistant material such as platinum or alumina. Precision monitoring of the mass with the set temperature or time gradient provides the output data. Generally, the processed data results in a percentage mass loss versus

temperature plot. In this work, TGA is used to determine the sulphur content within the carbon host material. At 444C, sulphur boils and evaporates out of the material. This mass change is measured to determine the percent sulphur content.

#### 7.4 Potentiostatic Electrochemical Impedance Spectroscopy

Potentiostatic electrochemical impedance spectroscopy (EIS) helps provides insight on the working mechanisms of an electrochemical cell. EIS simulates a circuit of capacitors and resistors to effectively test the cell. By applying a varying oscillating voltage and sweeping a range of frequencies, the corresponding AC current at each frequency can be obtained. Thus changes in impedance can be measured.

#### 7.5 Galvanostatic Discharge

Battery evaluation was performed using a CR2035 coin cell. In this technique, the cell is discharged then charged at a constant current. The cycle ends when the voltage reaches a specific target voltage. For LIS testing, the typical voltage window is a charge from 2.8 V vs Li/Li<sup>+</sup> followed by discharge to 1.9 V vs Li/Li<sup>+</sup> with a brief rest between the charge and discharge. An important quantity known as the the C-rate quantifies the charge/discharge current and is defined by the following equation:

$$C_{rate} = \frac{1}{Discharge\ Time}$$

Where discharge time is in hours. Rate performance evaluation was performed at a moderately low C rate.

## 7.6 Brunauer–Emmett–Teller Surface Analysis

BET surface area analysis allows for the calculation of both surface area and pore volume of a material. A known gas is introduced into a chamber containing the sample of interest. This gas adsorbs onto the sample surface and the amount of adsorbate gas corresponding to a monolayer on the sample surface is calculated. Sample preparation involves removing the gases within the sample and in the sample chamber to be filled with the gas of interest (typically nitrogen). If this outgassing is not achieved, the apparent surface area may be reduced. This technique allows me to determine the level of porosity of my carbon spheres which directly affects the amount of sulphur that may be loaded within. Tuning the experimental methods to maximize pore volume and surface area is key to improving performance.

## 8.0 Development of Porous Carbon for High Performance Lithium-Sulphur Batteries

### 8.1 Introduction

As an electrochemical storage device, LIS batteries are heavily reliant on cathode materials capable of entrapping a large amount of sulphur within their matrix. The purpose of this project is to create effective baseline materials to improve upon in future iterations. The material is a porous carbon sphere synthesized using a simple one-batch hydrothermal step. The second is an activated form of commercial Ketjenblack 600 J D. The activation processes are simple but extremely effective at increasing both pore volume and surface area.

### 8.2 Experimental

#### 8.2.1 Porous Carbon Spheres (PCS)

The following figure depicts the process for formulating the porous carbon spheres.



Figure 5: NCS synthesis schematic

Porous carbon spheres (PCS) were prepared via a hydrothermal method similar to [18]. Here, 10g of D-(+)-Glucose is well mixed with 100g of water and placed into a sealed steel autoclave. The autoclave is transferred into an oven heated to  $180^\circ\text{C}$  for 6h. The greater the

time heated, the longer the polymerization process takes place, resulting in larger spheres. The self-contained pressure and heat initiates the polycondensation and aggregation of the glucose forming spheres of uniform size [19]. A time of six hours provides us with spheres of diameter less than 1 micrometer. Fructose and sucrose are all possible sources of carbon that may be used for forming spheres. Any biomass such as corn is suitable as well although the time required for grinding and processing is undesirable for lab scale testing. Heating time is also to be optimized for the other forms of carbon biomass as longer heating times may be necessary for different compounds. In order to explore other possible morphologies, agglomerated carbon spheres were synthesized using the above method but adding 5% wt acrylic acid monomer to the hydrothermal mixture.

The resulting puce coloured mixture is then filtered through a fine (<200nm) mesh in an ethanol/water mixture until a semi-dry solid with clay like consistency is obtained. This product is placed in a vacuum oven at 60°C for at least 24 hours to remove any residual liquids. Treatment via the well-known KOH method was performed using a 3:1 mass ratio of KOH to carbon spheres in order to further increase porosity. Carbonization and KOH treatment of the resulting sample was performed by ramping from room temperature to 600°C at a rate of 5°C/minute followed by a ramp to 900°C in argon to complete carbonization. The resulting solid was washed gently with water and dried in the vacuum oven as above to remove any residual impurities. Carbonized spheres are placed into a furnace in an ammonia atmosphere and heated from room temperature to 600°C at a rate of 5°C/minute.

### 8.2.2 Air Activated Ketjenblack (KJB600-Air)

Ketjenblack EC-600JD was purchased from AkzoNobel. The KJB600 powder was washed with nitric acid steam at 90°C in a sealed steel autoclave to remove any impurities. Careful removal of the brown nitrogen dioxide gas is done under a fumehood and the material is washed with copious amounts of water to completely remove any acid remaining. Air treatment in a furnace connected to the outside environment ensured a steady airflow. The furnace was heated to 900°C with a final mass loss of approximately 60%.

### 8.2.3 Synthesis of NCS/Sulphur and KJB600-Air/Composite

A typical melt diffusion process was carried out in order to infiltrate the carbon materials with sulphur. The mass of sulphur was weighed out based on the desired sulphur to carbon ratio (60%) and was mixed in a mortar. The mixture was placed in an argon filled Teflon tube within a steel autoclave. This autoclave was heated in an oven to 155°C for 12 hours [20].

### 8.2.4 Synthesis of Electrolyte Solution

The electrolyte used is a polysulfide solution of lithium sulphide and sulphur (2:4 molar ratio) in a DOL/DME (1:1 v/v) solution. This solution was stirred at 50°C in an argon filled environment inside a glove box for 24 hours.

### 8.2.5 Electrode Fabrication

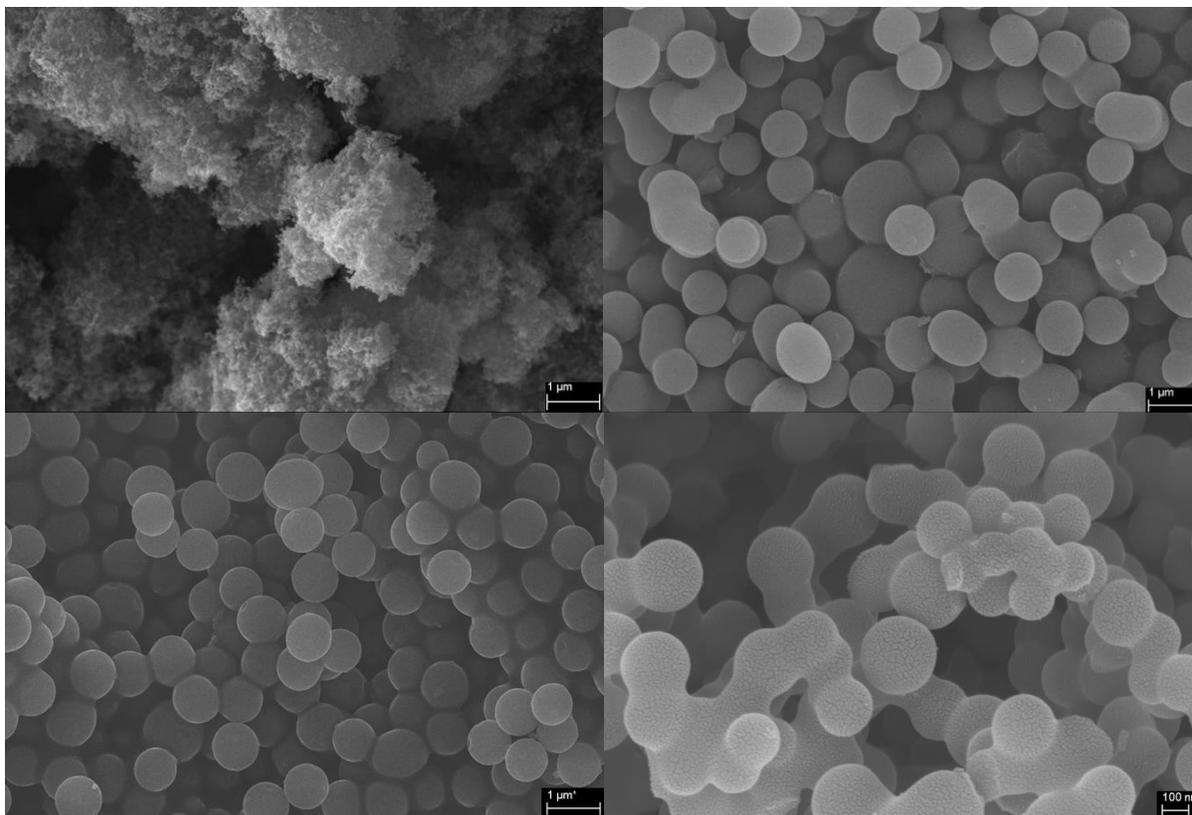
The fabricated electrode was cast from a water based slurry. The slurry consists of 15% solid content and 85% water. The solid content is composed of PCS/S, carbon nanotubes and sodium carboxymethyl cellulose in a mass ratio of 85:5:10 respectively. The slurry was well mixed and cast onto a carbon coated aluminium foil using a doctor blade to achieve a sulphur loading of approximately 1mg/cm<sup>2</sup>. The resulting electrode was dried at 60°C for 24 hours then transferred into an argon filled glovebox.

### 8.2.6 Electrochemical Tests

The electrodes were assembled to form a 2035 type coin cell using the electrolyte solution described above. Electrochemical testing was performed using a Neware testing station. The anode material is a lithium metal chip (Linyi Gelon LIB Co., Ltd) and the separator material was acquired from Celgard (Celgard 2500). The testing voltage window was 2.8V to 1.6V (vs Li/Li+) for cycling rate performance.

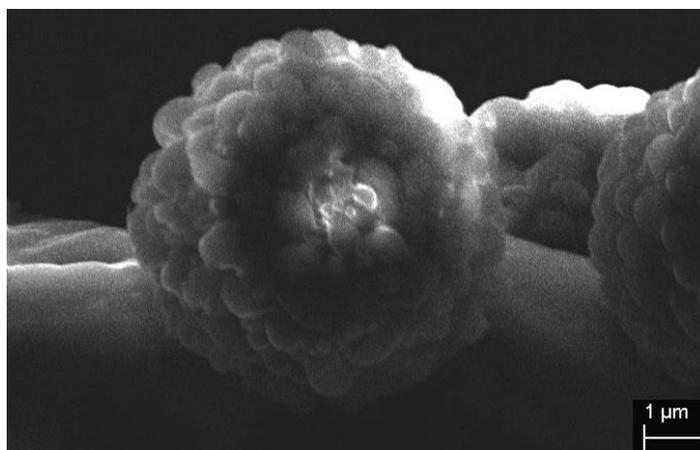
### 8.3 Results and Discussion

SEM images of the KJB600/S and PCS/S composites can be shown in Figure 2. Figure 1a shows the KJB600/S composite while Figure 1b-d shows the carbon spheres at varying stages in processing. KJB600 carbon black can be described as a fine, sparse network of carbon particles, while the carbon spheres show a more defined morphology. As shown in Figure 2b, the spheres are not entirely disconnected and form a ‘peapod’ structure. A disconnected morphology was achieved using a low amount (5 wt%) of charged surfactant, cetrimonium bromide (CTAB), to form distinct spheres as shown in Figure 2c. Although we suspected that the distinct spheres would shorten the sulphur diffusion pathway to potentially increase performance, preliminary electrochemical testing revealed little to no difference in performance, surface area and pore volume using the interconnected and distinct sphere morphologies and as such we performed the final activation processes on the connected ‘peapod’ spheres to remove an unnecessary step in the synthesis. Figure 2d demonstrates the fine micro-mesoporous voids forming surface cracks after air and KOH activation. Sphere diameters generally ranged from ~500nm to 1µm with the average particle size being around 600nm.



*Figure 5: SEM images of (a) KJB600, (b) carbon spheres formed without surfactant, (c) carbon spheres formed with surfactant, (d) air-treated carbon spheres*

To briefly explore other sphere morphologies, agglomerated carbon spheres were also formed by adding 5 wt% of acrylic acid to the glucose solution prior to hydrothermal treatment. Figure 4 shows the morphologies of the materials prepared in the presence of acrylic acid. Here, the addition of acrylic acid induces a drastic change in sphere morphology and growth mechanism with the particle surface appearing to be formed of smaller aggregated particles [29]. Acrylic acid appears to stabilize the initial small sized spheres with similar morphology depicted in Figure 3, thus preventing them from further growth, as might occur in the pure glucose case. This shows the numerous possibilities that additives have in sphere formation whether it is tuning particle size or overall morphology.



TEM images of KJB600 taken before and after air activation is shown in Figure 3. The fine carbon particles of KJB are roughly 20 nm in diameter. Figure 3a shows the material prior to air treatment with the dark regions indicating low porosity, highly dense areas of KJB600. Figure 3b shows the material post activation with nearly all the dark regions gone indicating that the air treatment was successful in removing material and creating voids.

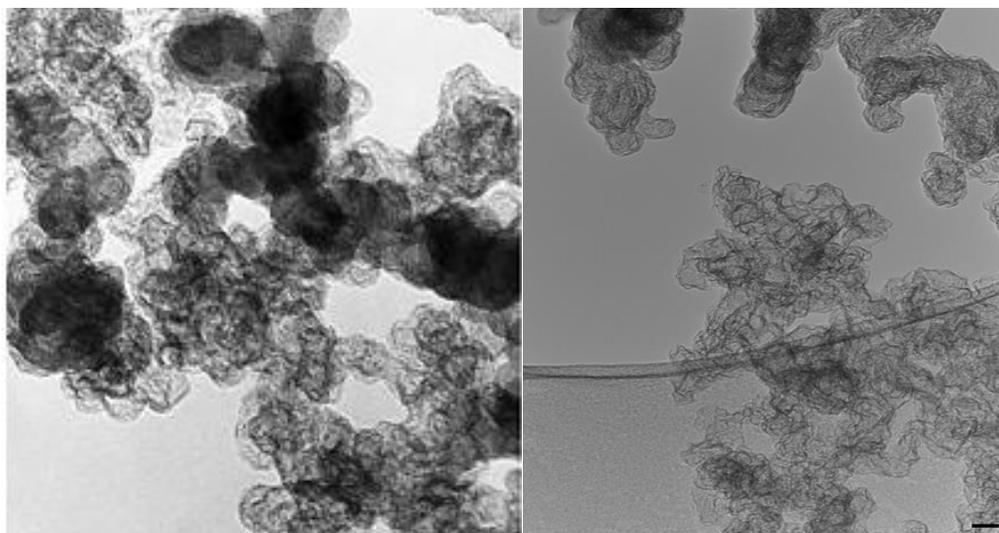


Figure 6: TEM images of (a) KJB without any treatment, (b) KJB activated in air

BET testing revealed that the PCS surface area with no air or KOH treatment to be  $414 \text{ m}^2 \text{ g}^{-1}$  and a pore volume of  $0.731 \text{ cm}^3 \text{ g}^{-1}$ . Increasing pore volume is crucial in order to maximize the amount of sulphur that can be contained within the carbon matrix, thus various treatments have

been developed such as KOH activation [21] or steam activation. Here, we activate PCS through two methods: KOH activation and air activation. For KOH activation, we mix the carbonaceous material with KOH pellets at a 3:1 a ratio and heat at high temperatures in an inert environment. Air activation is simply carbonization at high temperatures in an open environment. The oxygen in the air allows for the oxidation of the carbonaceous materials producing voids within the material. This method is both effective and simple and can easily be scaled up for larger batches of PCS. With this method the surface area of PCS increased to  $725 \text{ m}^2 \text{ g}^{-1}$  and the pore volume to  $1.5 \text{ cm}^3 \text{ g}^{-1}$ . As shown in Figure 4a, the majority of the pores from the PCS sample are micropores (2.5 to 10 nm) represent a much greater fraction of the pores than mesopores. These pores are likely formed due to the volatile species generated during the KOH and air treatments. The porous nature of this material is crucial for maximizing the uptake of sufficient sulphur within the carbon matrix and not on the surface. Surface sulphur is easily lose during cell cycling and has adverse effects on electrochemical performance. This method also works with other types of carbon blacks with very low pore volume and surface area such as Super P from Alfa Aesar as shown in Figure 4b. Micropores were created from a starting material which was essentially void of any porous voids. Air treatment increased surface area from  $4.4 \text{ m}^2 \text{ g}^{-1}$  to  $92.8 \text{ m}^2 \text{ g}^{-1}$  and pore volume from  $0.025 \text{ cm}^3 \text{ g}^{-1}$  to  $0.157 \text{ cm}^3 \text{ g}^{-1}$ , a marked difference. The changes in a wide variety of materials strongly suggests that this air treatment method is capable of being effective with a wide variety of carbonaceous materials not solely limited to spheres.

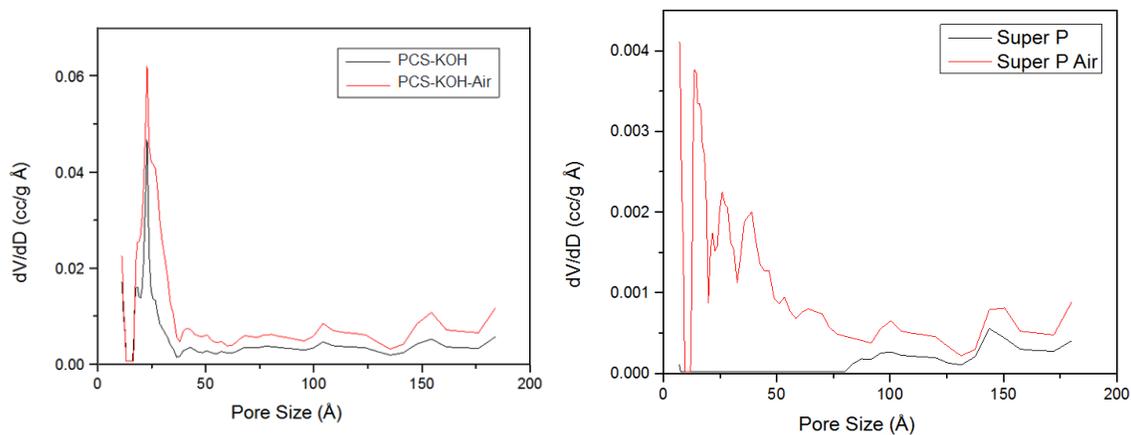


Figure 7: Pore size distribution of PCS

THA was performed in a nitrogen gas environment thus any mass loss can be contributed to sulphur boiling out in gaseous form from the carbon host. The mass loss continues until all the sulphur has been removed and the mass change is stable at a higher temperature. TGA results shown in figure 5 successfully confirm a sulphur loading of approximately 75%. Using the same mass percent of sulphur, the additional air treatment of PCS resulted in an additional 10 percent loss of mass over the non-treated sample, thus the air treatment was effective in producing additional pores for more sulphur containment. Furthermore, at the 300 to 450 degree range we notice an unusual change in slope for the air treated sample. This slower rate of mass loss may be attributed to the well entrapped sulphur, likely the result of the increased entrapment in the created micropores over the non-air treated sample. This data shows evidence in support of the idea that the increased pore volume due to air treatment not only increased sulphur content but also retains sulphur better within its tortuous micropores.

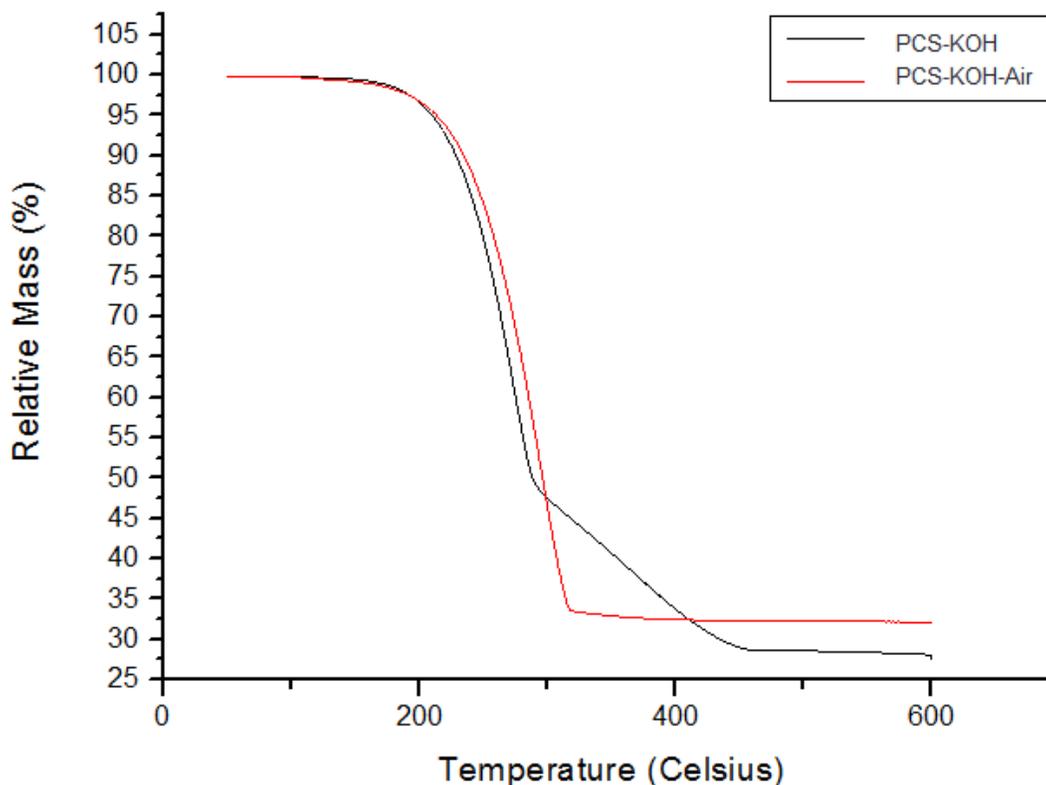


Figure 8: TGA curve of PCS/S composite

The electrochemical cycling stability data obtained is shown in Figure 6 demonstrating a capacity retention of 81% for the air treated sample versus 68% for the sample with no treatment. The cycling stability of the cathode is highly dependant on the materials' electron mobility towards its contained sulphur during a single charge/discharge cycle. The columbic efficiency is defined as the percentage of the full charget set by the user that is achieved versus the subsequent cycle. Thus the high coulombic effeciency demonstrated by the air treated PCS means the energy rquired to charge the cell is comparable to the energy produced by the cell. The rapidly decreased performance of the non-treated PCS is likely attributed to a more pronounced shuttle effect as the polysulfide species escape from the caron matrix and creates short circuits on the anode in the less porous material without as many micropores. The good

cycling stability of the air treated sample is attributed to the effective entrapment of PS species preventing short circuiting on the anode.

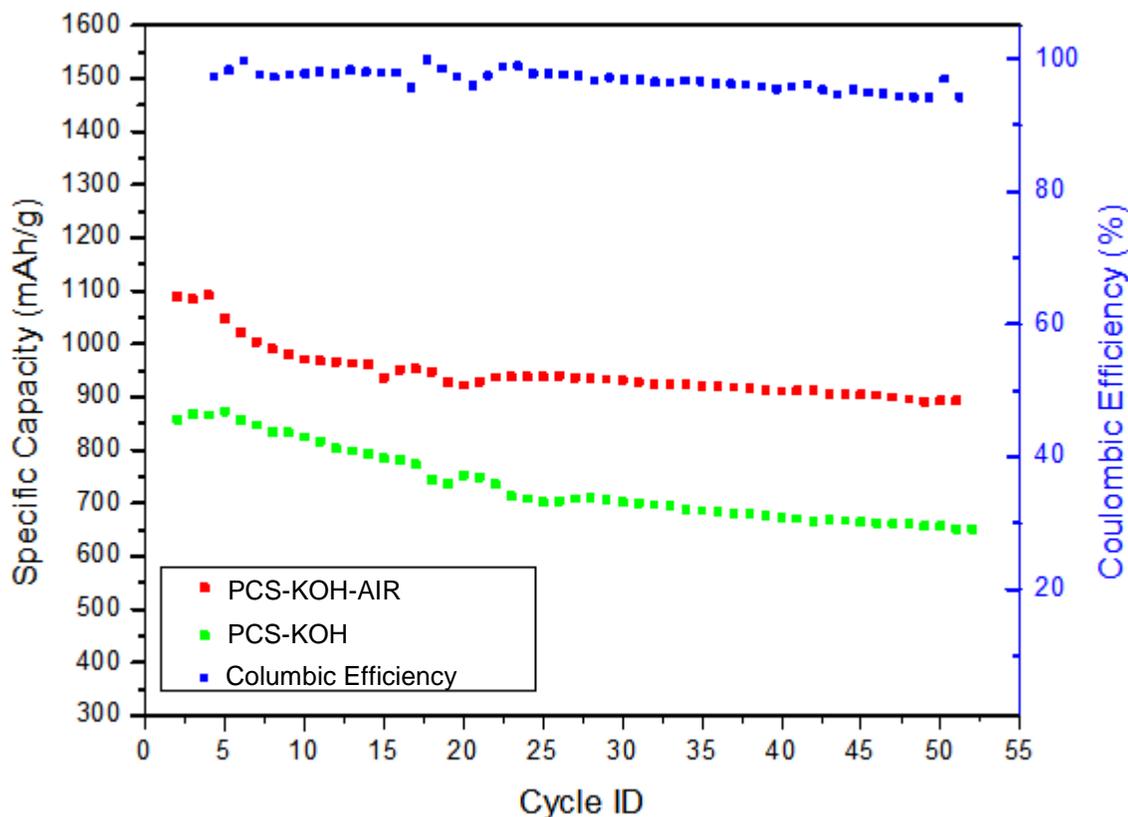


Figure 9: Cycling performance and coulombic efficiency of PCS

The diffusion and shuttling of PS species from cathode to the anode is adversely affecting the act of charging. Since the non-air treated PCS sample lacks additional pores to limit the diffusion of PS, the PS is more likely to escape and cause short circuiting at the anode interface, effectively limiting the capacity of the cell. The air treated sample on the other hand reduces the energy required to charge the cell by ensuring less wasted energy goes towards the PS shuttle thus improving capacity and coulombic efficiency. Ensuring a somewhat difficult diffusion pathway for PS is key to reducing permanent capacity loss caused by PS.

## 9.0 Conclusions and Future Directions

LIS batteries have a promising future as the next generation electrochemical storage platform for use in both consumer and industrial markets. The major drawback preventing current LIS technology from entering the market is the lower capacities due to the polysulfide shuttle effect limiting the capacity. Introducing new nanoporous materials as cathode materials is an effective strategy for increasing performance. Increased sulphur content and increasing the diffusion pathway for PS species also aid in performance. Other effective strategies include tuning the electrolyte solution or separator to suppress the shuttle effect. Herein, successful efforts were made to develop a porous carbon material for the cell cathode for increased performance. Uniform porous carbon spheres of ~500nm diameter were synthesized from glucose from which a LIS cathode was made. This material was then treated with KOH followed by treatment in air to greatly increase pore volume and surface area thus allowing for more sulphur to be contained within the material providing additional diffusion pathways for lithium while retaining PS species.

Increasing pore volume by increasing the amount of tortuous micro/mesopores within the carbon spheres serves two distinct functions: 1) increase the amount of sulphur contained within the material and 2) retain PS species thus alleviating some of the negative effects of the PS shuttle mechanism. This should ultimately lead to increased capacity and performance.

Despite the promising increase in pore volume and electrochemical performance, more work needs to be done to increase both loading and cycling stability. Additional nitrogen doping would also be beneficial to change the type of carbon present to increase performance. Tuning sphere size to optimize the interparticle pores as well as to potentially increase performance is another avenue of approach.'

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