Investigating Cathode Composition and preparation in Lithium-Sulphur batteries

Optimising synthesis pathways for capacity realisation and retention

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Abstract

Commercialisation of Lithium-Sulphur (Li-S) batteries requires an increase in Sulphur utilization within the cathode so that the overall experimental capacity and cycling stability is improved. Cathodes must be consistent and high performing. Using a range of analysis techiniques, this project investigated different synthesis methods and cathode compositions to determine and understand how cell performance can be improved.

Motivation

As the demand for large scale energy storage increases, cheaper, more ethically sourced and environmentally friendly resources are important. The natural abundance of Sulphur and its higher theoretical capacity (1675 mAg^{-1} of Sulphur) makes Li-S batteries an attractive alternative to Li-ion batteries. (1) Li-S batteries have a theoretical specific energy of 2.6kWhkg $^{-1}$. This is much higher than the theoretical specific energy of Li-ion batteries (~0.4kWhkg $^{-1}$) (2)

Method

Make cathode

- Weigh out and mix Carbon-Sulphur composite
- Heat to 155 °C or 120°C for 12 hours (or don't heat)
- Dissolve in NMP and mix with binder and additive
- Coat evenly onto current collector and leave to dry

Build coin cell

Cycle the cells

Cells were cycled in Biologic battery cyclers.
Types of Data collection:

- Galvanostatic
- Cyclic Voltammetry
- EIS
- Rate change

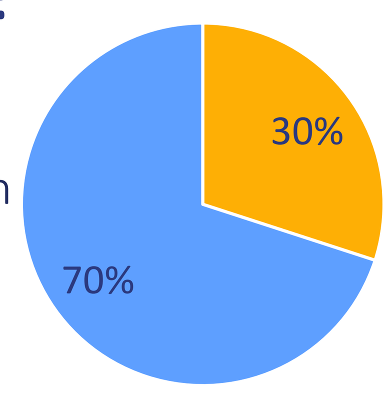
*All compositions have approximately 30wt% Sulphur overall so that they are easily comparable

Characterise the electrodes

- SEM and EDX
- X-ray tomography
- Tomograms analysed in Avizo to observe distribution, shape and size of observable Sulphur

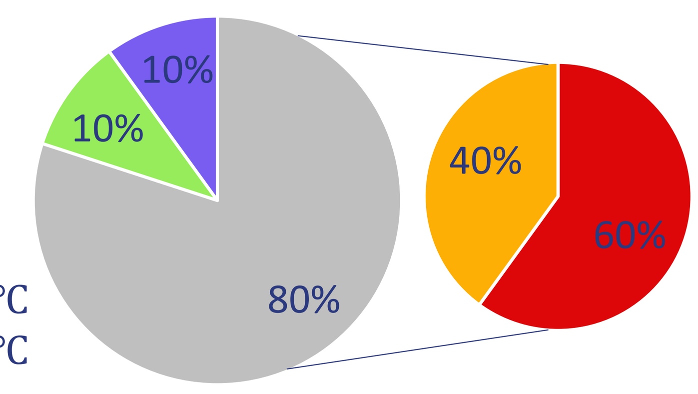
2 Compositions:

30wt% Sulphur melted onto Carbon paper current collector at 155 °C



60:40 Carbon:Sulphur composite on carbon coated Aluminium

1. Unheated composite
2. Composite heated to 120 ℃
3. Composite heated to 155 ℃



Cathode Performance

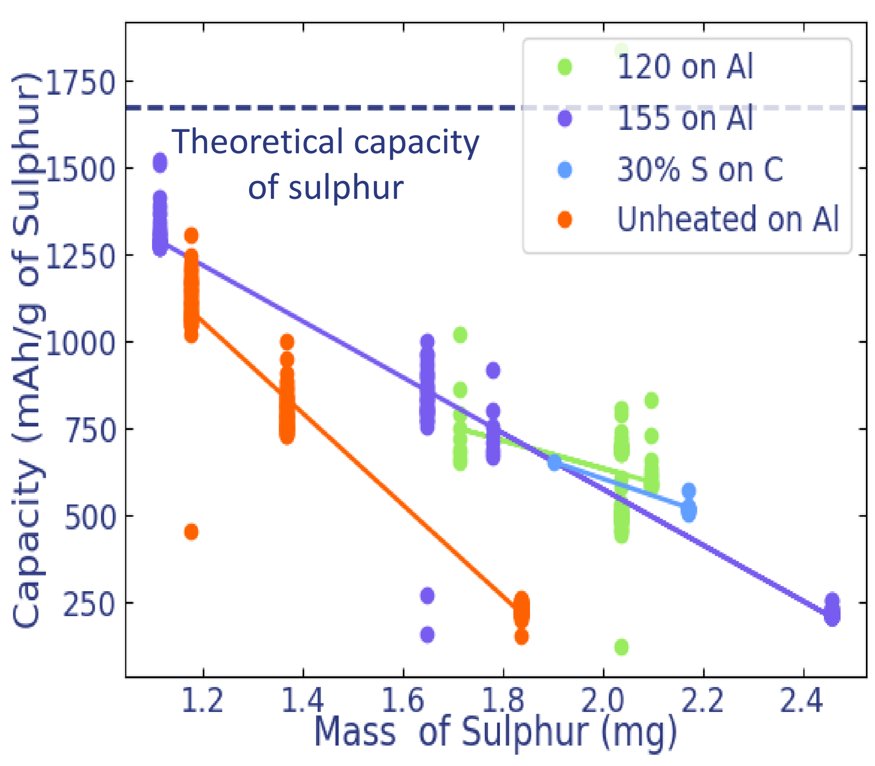


Fig. 1: Capacity vs Sulphur mass in cathode

Gravimetric capacity is negatively correlated to the mass of sulphur in the cathode over the range of masses studied **(Fig. 1).** This means that the higher the gradient of the line of best fit, the less the overall capacity (mAh) will increase upon adding more active material (sulphur).

- There isn't a drastic difference in the performances at similar masses. This will require further investigation to reach a statistically significant conclusion.
- The cathodes with unheated composites performed inconsistently; the distribution of sulphur was heterogeneous so it was difficult to predict the amount of sulphur per cathode. This led to one cell appearing to have a capacity above 100% of the theoretical capacity based on predicted sulphur content. Most of these cells failed.
- The cathodes that had composites heated to 155℃ consistently performed with high capacities and a low failure rate compared to those with composites heated to 120℃. This could be due to the "120" cathodes being thicker (and containing more sulphur.)

Sulphur distribution

Heating Temp of composite	155℃	120℃
Sulphur wt%	46%	42%
Particles	Fewer, larger	More, smaller
Sphericity	Lower	Higher
Mudcracks	Smaller	Larger

- Particles were smaller, closer to the current collector
- When the 155 cell was discharged, little sulphur was observed within the cathode **(Fig 4)** and Li_2S precipitated on the surface of the cathode.
- Li_2S is electronically insulating, so over time this precipitate could lead to poor sulphur utilization and capacity degradation.(3)

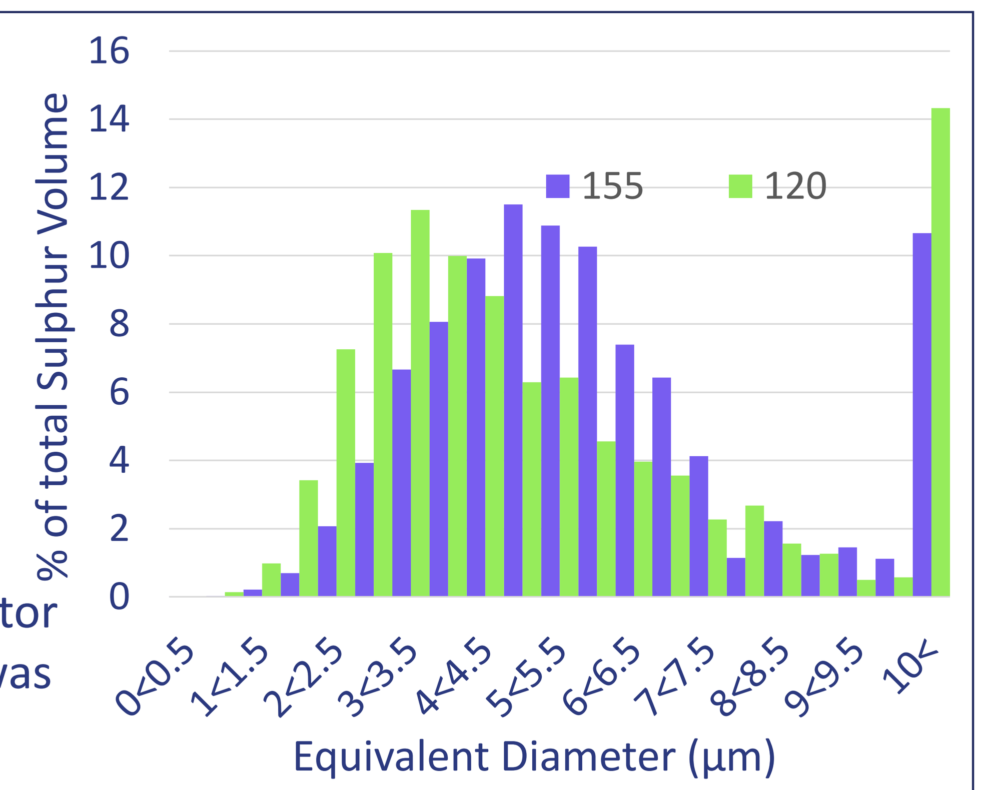


Fig 2: Comparing size distribution of sulphur particles

The hypothesis is that by heating to 155°C, the Sulphur melts to its lowest viscosity and more evenly coats the Carbon, leading to more contact with the carbon and greater current collection. Higher Sphericity of particles in the "120" cell suggests that Heating to 155 °C results in better coating of the Carbon.

Fig. 3: Sulphur distribution

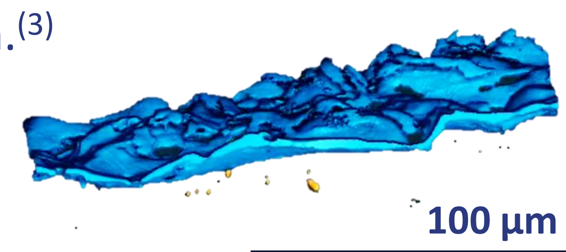


Fig 4: Sulphur (yellow) and Li_2S (blue) in discharged "155" cell

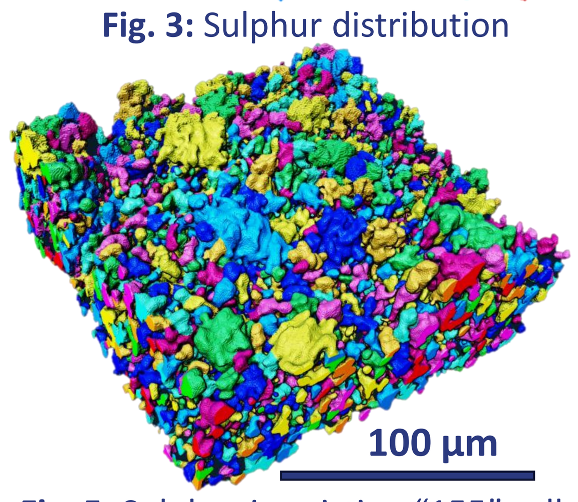


Fig. 5: Sulphur in pristine "155" cell

Link to X-ray tomography animations, SEM and EDX images

bit.ly/FUSE-SEM-EDX

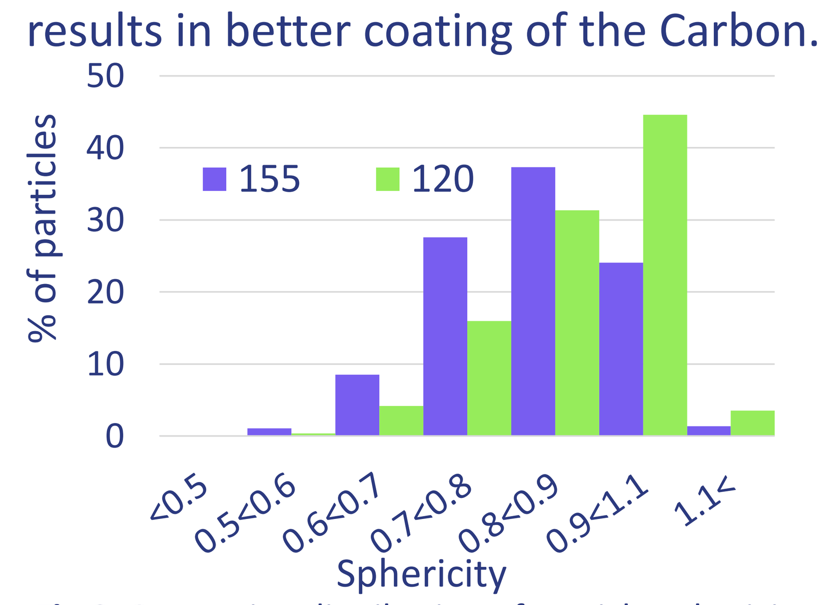


Fig 6: Comparing distribution of particle sphericity

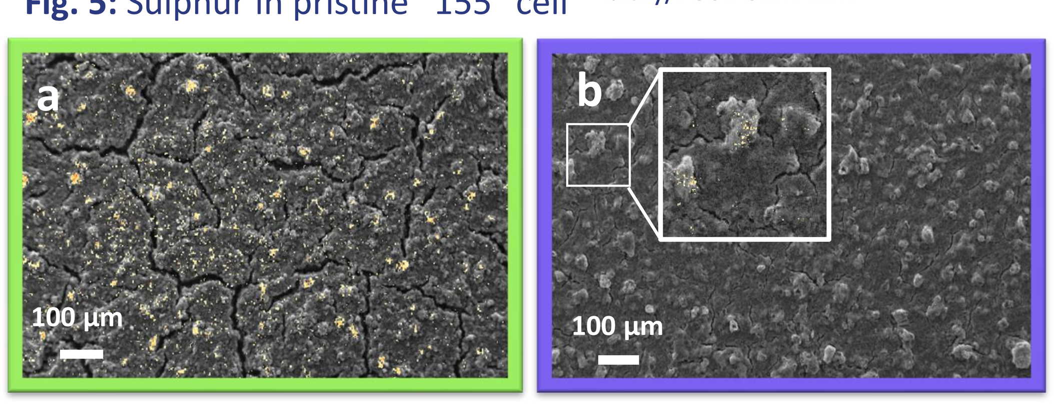


Fig 7: SEM and EDX of electrodes heated to a) 120 °C and b)155 °C

Comparing the EDX of the cathodes heated to 120 °C (a)and 155 °C (b), the sulphur (yellow) has agglomerated at the surface of the cathode more in the "120" cell than the "155" cell.

Conclusions

- Heating the composite to 155℃ melts the sulphur to its lowest viscosity. This results in a lower sphericity of sulphur particles in the cathode, suggesting higher surface contact of sulphur and carbon.
- Not heating the sulphur and carbon composite results in a heterogeneous and unreliable cathode
- Sulphur accessibility and utilization is the most important factor for improvement in capacity; despite increasing the mass of sulphur contained in the cathode, the amount of sulphur contributing to the capacity of the cell appears constant beyond an optimum sulphur: electrolyte: carbon ratio.

Next steps

- Collect more data so statistically significant conclusions can be reached
- ➢ (Ensure thickness and sulphur: electrolyte ratio is accounted for)
- Conduct further post-mortem x-ray tomographs in discharged and recharged state to observe sulphur redistribution.
- Heat the composite to 96 °C (the temperature β-sulphur is formed) to see if improves carbon-sulphur contact
- Investigate other compositions

References

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Biography

Alex Ellerington recently finished her first year studying Natural Sciences (Physics and Chemistry) at the University of Bath.
This project has piqued her interest in the battery industry; specifically in finding alternatives to Lithium-ion batteries for large scale, sustainable energy storage. It has inspired her to consider a career in research.

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