OPTIMISING Li_2S FORMATION: PROGRESS IN LITHIUM-SULFUR CATHODE DESIGN

The effect of heteroatomic doping in anode-free Li-S cells

Nathan Njoku, Thomas Miller, Roby Soni

1. Project Introduction

Lithium-sulfur (Li-S) technology offers high energy density, but experiences material loss and activation issues [1]. This project looks at *in-situ* Li_2S conversion inside pores of nitrogen-doped 3D graphene: nano-size Li_2S lowers activation barriers, whilst N-heteroatoms counter the shuttle effect, enhancing cycle life for energy storage applications.

Li-S cell chemistry: $S_8 + 16Li^+ + 16e^- \rightleftharpoons 8Li_2S$

Operating at 1.7-2.8 V

Activation Voltage: 4 V [2]

Stages: $S_8 + 2Li \rightleftharpoons Li_2S_8 \rightleftharpoons Li_2S_6 \rightleftharpoons Li_2S_4 \rightleftharpoons Li_2S_3 \rightleftharpoons Li_2S_2 \rightleftharpoons Li_2S$

Conversion Issue: Shuttle Effect
Soluble polysulfides can move across separator, causing active material loss

Solution: Polysulfide Trapping
Immobilisation of polysulfides through electrostatic interactions (using B, N, P, S)

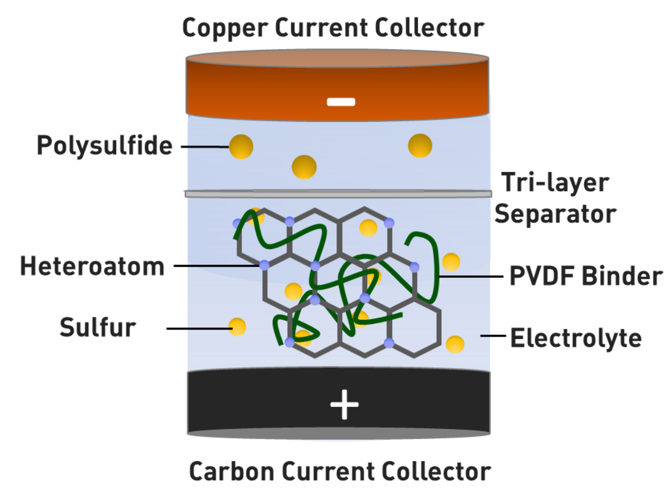

Figure 1: Schematic of a discharging Li-S coin cell

Negative Electrode
- Copper: cheap, light-weight and conductive
- Anode-free: no excess Li or active materials, for increased safety and energy density

Positive Electrode
- Sulfur: light-weight, high capacity (1675 mAh g^{-1}) active material for Li reaction
- Graphene: conductive host material for sulfur
- Binder: for holding electrode materials together

2. Method – Coin Cell Fabrication

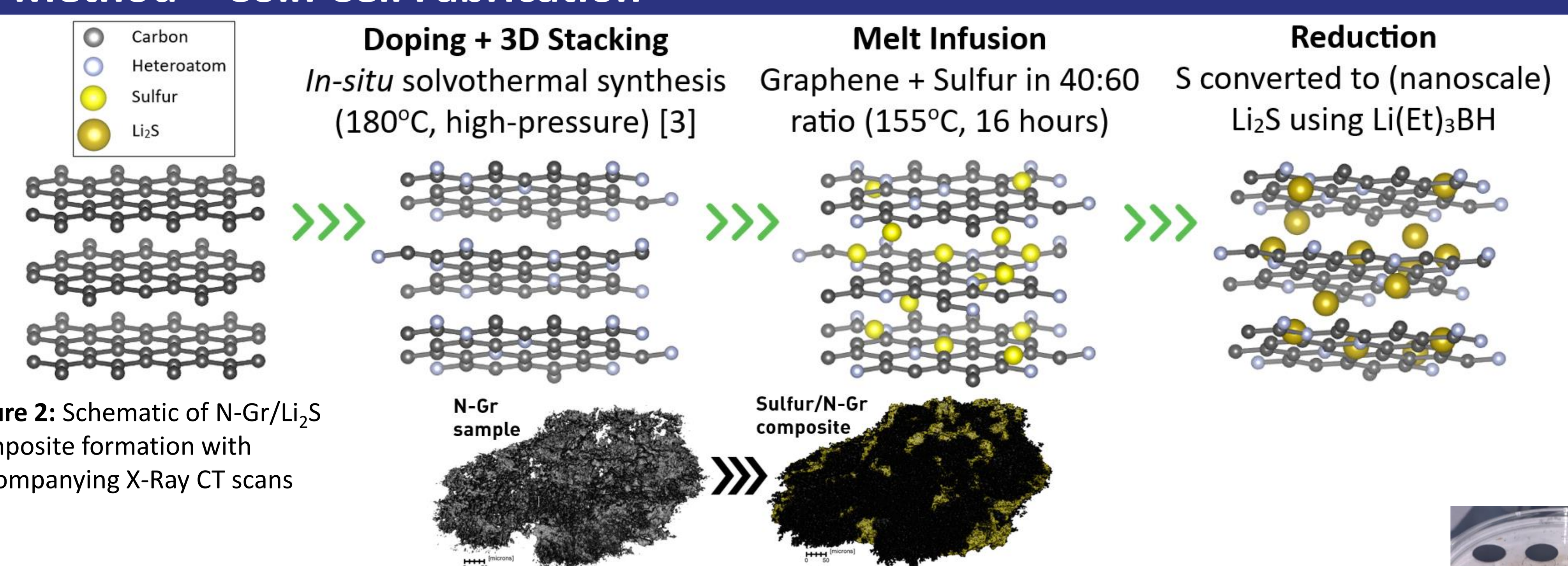

Figure 2: Schematic of N-Gr/Li_2S composite formation with accompanying X-Ray CT scans

Cathode Formation: N-Gr/Li_2S composite + PVDF combined in 90:10 ratio
Assembly: Cathode and Cu collector wetted in 1 M LiTFSI + 1 M $LiNO_3$ electrolyte
Testing: Compared against micron-scale C65/Li_2S control

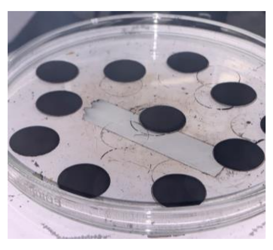

Figure 3: Image of prepared cathode

3. Evidence of *in-situ* Conversion

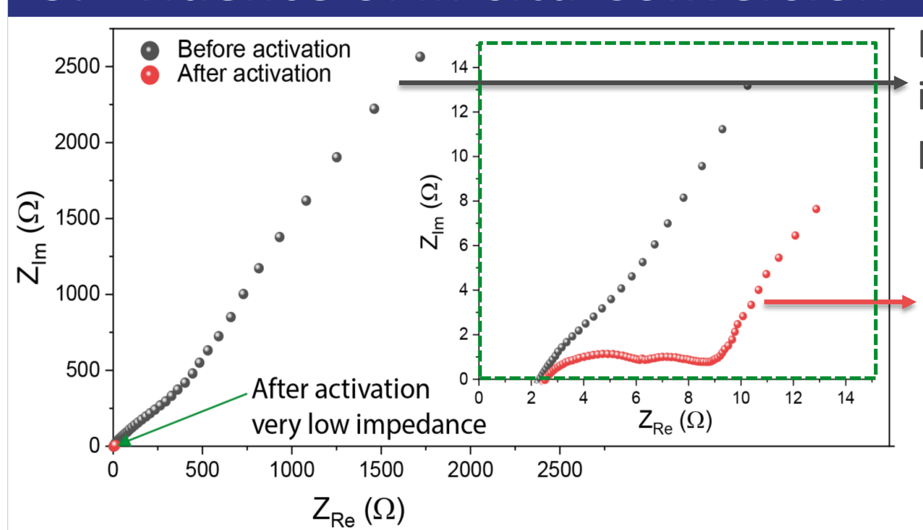

Figure 4: Electrochemical Impedance Spectroscopy data for an anode-free cell before and after testing

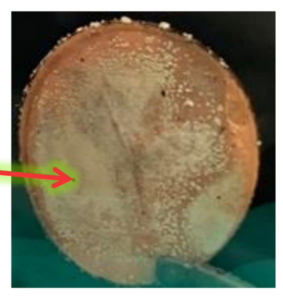

Figure 5: Image showing copper current collector with white coating

4. Results – Material Performance and Characterisation

N-Gr/Li_2S PERFORMANCE WITH LITHIUM HALF CELL

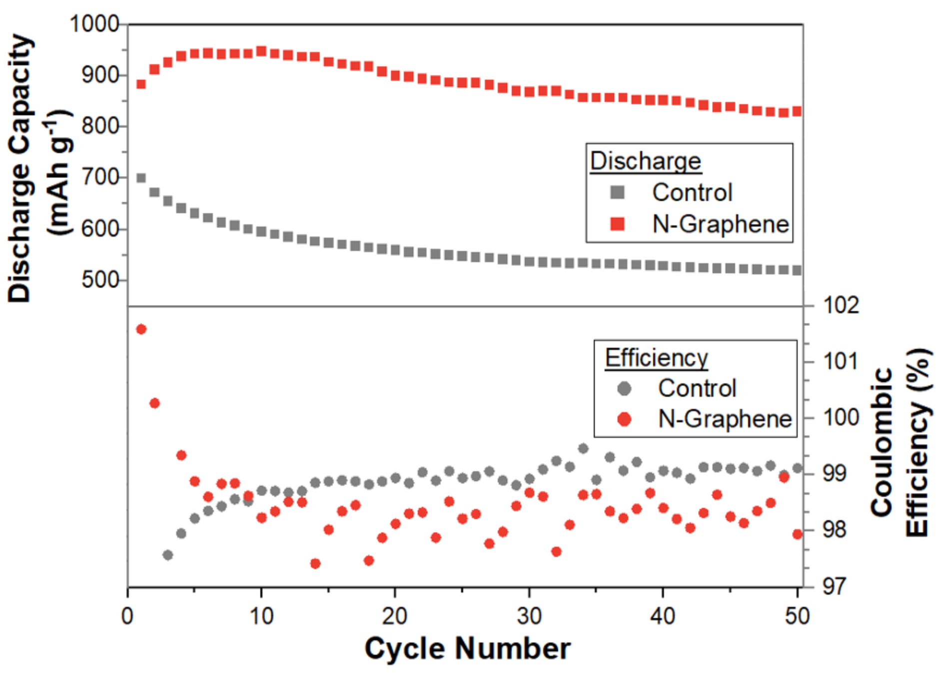

Figure 6: Discharging Capacity and Efficiency graphs for commercial Li_2S/C65 cell and for N-doped graphene cell (C5)

Capacity
- Higher capacity achieved by N-Gr/Li_2S
  → Nano-sized Li_2S is utilised better
- N-Gr/Li_2S shows less capacity loss than commercial Li_2S (10% vs. 26%)
  → Better stability in N-Gr attributed to reduced polysulfide shuttling

Efficiency
- Similar average efficiency (99% for control vs. 98.4% N-Gr)

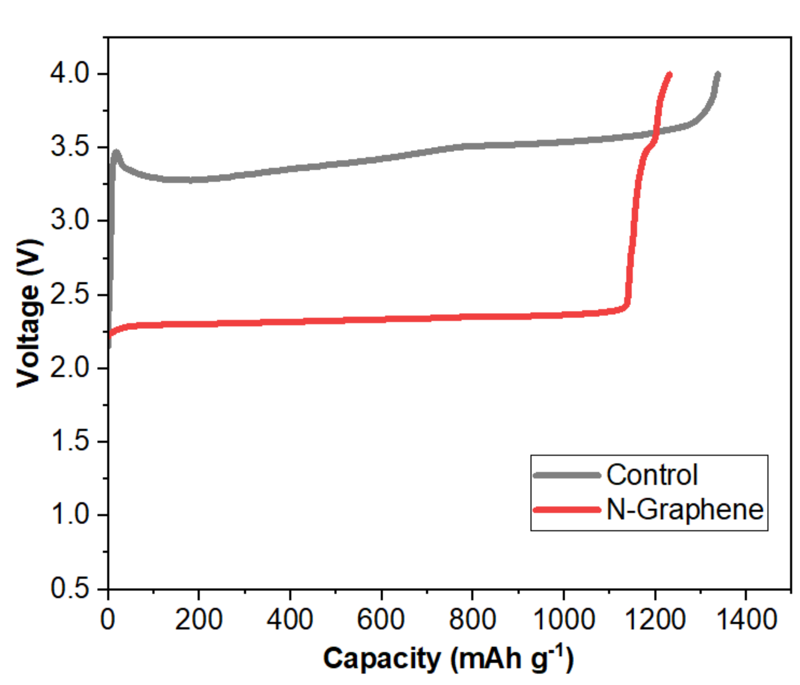

Figure 7: Activation (voltage vs capacity) graphs for Li_2S/C65 cell and for N-doped graphene cell

Activation
- N-Gr/Li_2S shows lower overpotential for activation
  → Nano-sized Li_2S provides large surface area and reduces Li-ion diffusion distance, aiding activation [2]

N-Gr/Li_2S PERFORMANCE IN ANODE-FREE SYSTEM

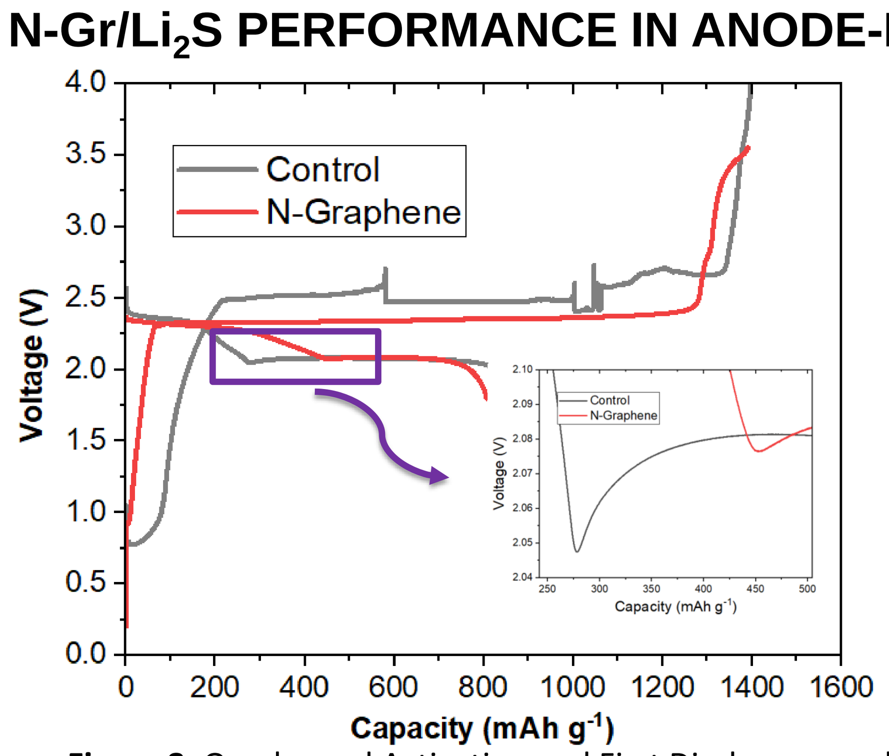

Figure 8: Overlapped Activation and First Discharge graphs for anode-free Li_2S/C65 and N-doped graphene cells

First Discharge
- **Liquid to Solid conversion:** smaller barrier for transition is observed for N-Gr/Li_2S (0.01 V vs 0.04 V)
  → Increased surface area and catalytic properties of nanoparticles improve reaction kinetics

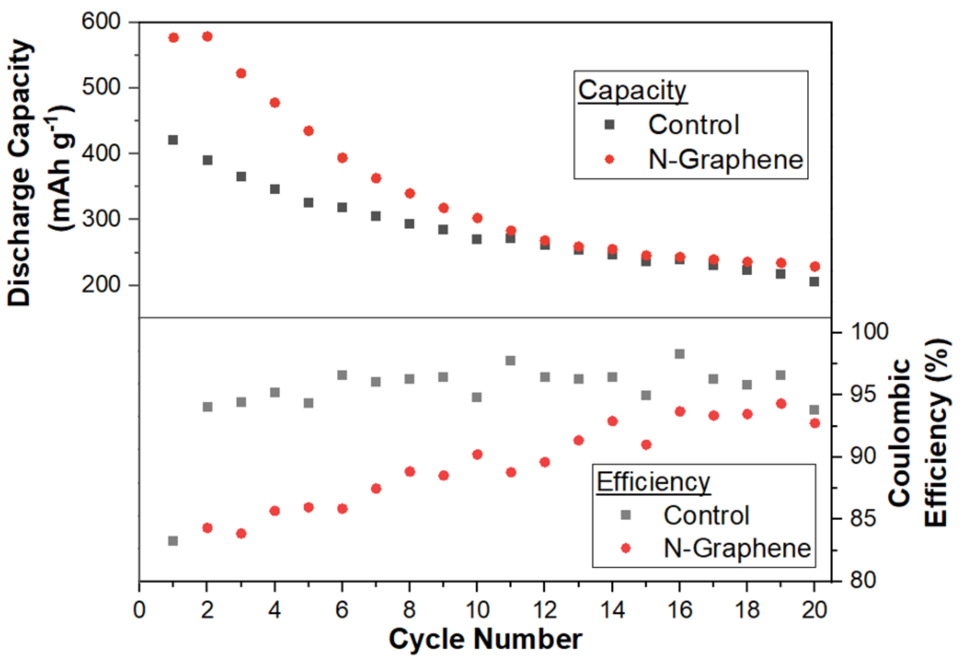

Figure 9: Discharging Capacity and Efficiency graphs for anode-free Li_2S/C65 and N-doped graphene cells (C5)

Capacity
- N-Gr/Li_2S shows higher capacity (580 mAh g^{-1} vs. 420 mAh g^{-1})
- N-Gr retains higher capacity than commercial Li_2S after 20 cycles

Efficiency
- N-Gr initially lower, but efficiencies both end steady around 94%

6. Project Aims / Conclusions

6. Project Aims	Conclusions
Li_2S optimisation	✓ Successful *in-situ* synthesis *(seen from EIS and deposition imaging)* ✓ Nanoparticles functioning in structure *(Lower activation overpotential)*
Heteroatom Doping (novel material synthesis + characterisation)	✓ Support for Polysulfide Trapping seen *(Improved Cycling- 90% Capacity retention after 50 cycles)*
Anode-Free Coin Cell Fabrication	✓ Over 85% Efficiency *(Maintained over 20 cycles despite uneven Li deposition)*
Progression of Li-S batteries	✓ Promising developments for future use *Potential use in Transportation, Portable Electronic & Energy Storage industries*

7. Next Steps – Further Testing

→ **Different Dopants + Amounts:** (e.g. Boron & Phosphorus) to further study the process of polysulfide immobilisation

→ **Material Development**: Modifying Cu collector to improve Li deposition and Cycling Efficiency

→ **Industrial Viability**: Progressing to pouch cell development, with additional safety testing and Life Cycle Assessment

References

[1] M.R. Kaiser et al, "Lithium sulfide-based cathode for lithium-ion/sulfur battery: Recent progress and challenges". *Energy Storage Materials*. 2019; vol 19: pp 1-15.

[2] H. Ye et al, "Activating Li2S as the lithium-containing cathode in lithium–sulfur batteries". *ACS Energy Lett*. 2020; vol 5: pp 2234-45.

[3] N. Manna et al, "A NiFe layered double hydroxide-decorated N-doped entangled-graphene framework: a robust water oxidation electrocatalyst". *Nanoscale Advances*. 2020; vol 2: pp 1709-1717.

[4] X. Ji et al, "Advances in Li-S batteries". *Journal of Materials Chemistry.* 2010; vol 20: pp 9821-9826

Intern bio

Nathan is in the 2nd year of his Chemistry undergrad at the University of Cambridge. He completed this research project whilst at UCL, within the Department of Chemical Engineering.

He is interested in sustainable technologies, particularly MOF carbon capture and battery energy storage. Looking to the future, he intends to contribute to research in these fields.

LinkedIn: Visit Nathan Njoku's Page

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