

Multimodal Operando Characterisation of Degradation in Lithium-Sulfur Batteries

Revealing morphological evolution and sulfur species distribution



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Background

Why do we need Lithium-Sulfur batteries?

Li-S batteries can largely contribute to the next-generation energy storage sector for decarbonisation as they have lower cost, more secure supply chains and much higher theoretical energy density.

How does Lithium-Sulfur battery work?

For the Conventional liquid-system li-s batteries, we have a lithium negative electrode, and a carbon-sulfur composite electrode.

During discharge, the solids at the cathode dissolve into the liquid electrolyte and this give the raise to some substantial challenges.

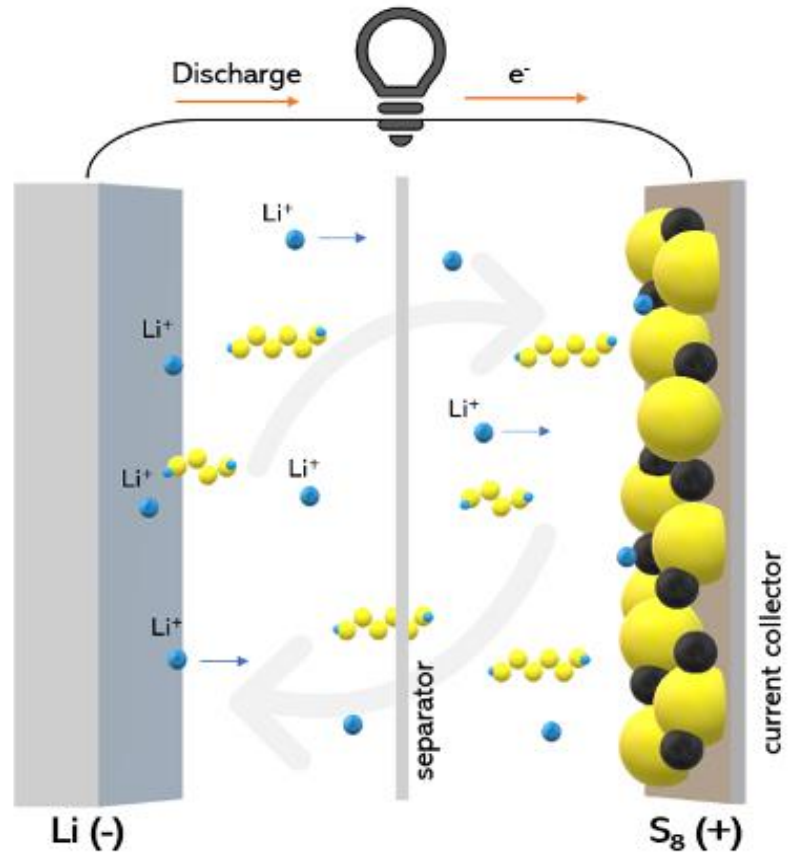
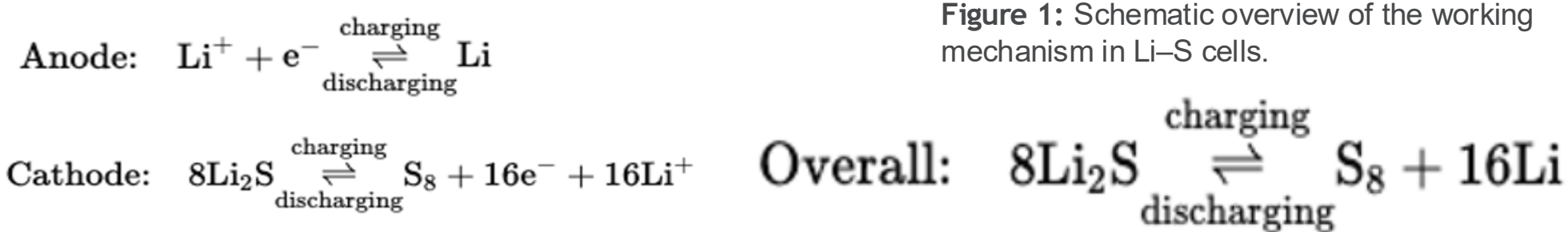


Figure 1: Schematic overview of the working mechanism in Li-S cells.

Main Challenge of Li-S batteries: Degradation Processes

- Multiple processes occur in the cell
- Degradation Processes:
 1. Lithium dendrites formation
 2. Anode corrosion
 3. PS shuttle effect
 4. Cracking of SEI layer
 5. Gas formation
 6. Insulating Li₂S on cathode
 7. Corrosion of current collector
 8. Structural collapse of cathode
- Many of the degradation processes are highly interdependent, with complex interactions that collectively contribute to cell failure, capacity fade, and safety issues.

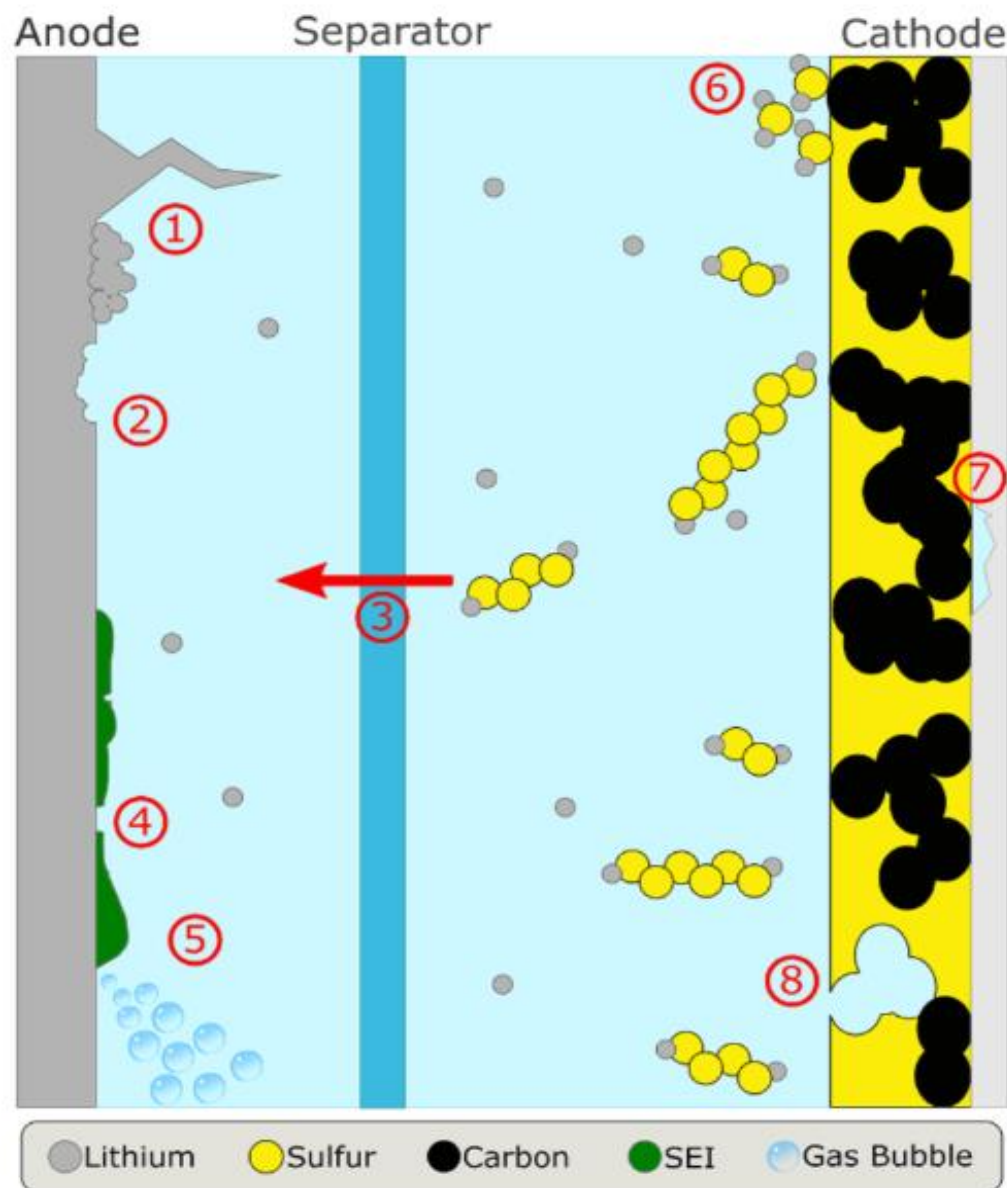


Figure 2: Schematic overview of the degradation processes in Li-S cells. Reproduced from [1].

Lab Characterisation: Operando Optical Microscopy

- Electrochemical tests coupled with Operando digital microscopy, showing the formation and growth of lithium dendrite and colour evolution of electrolytes because of polysulfides shuttle effect.

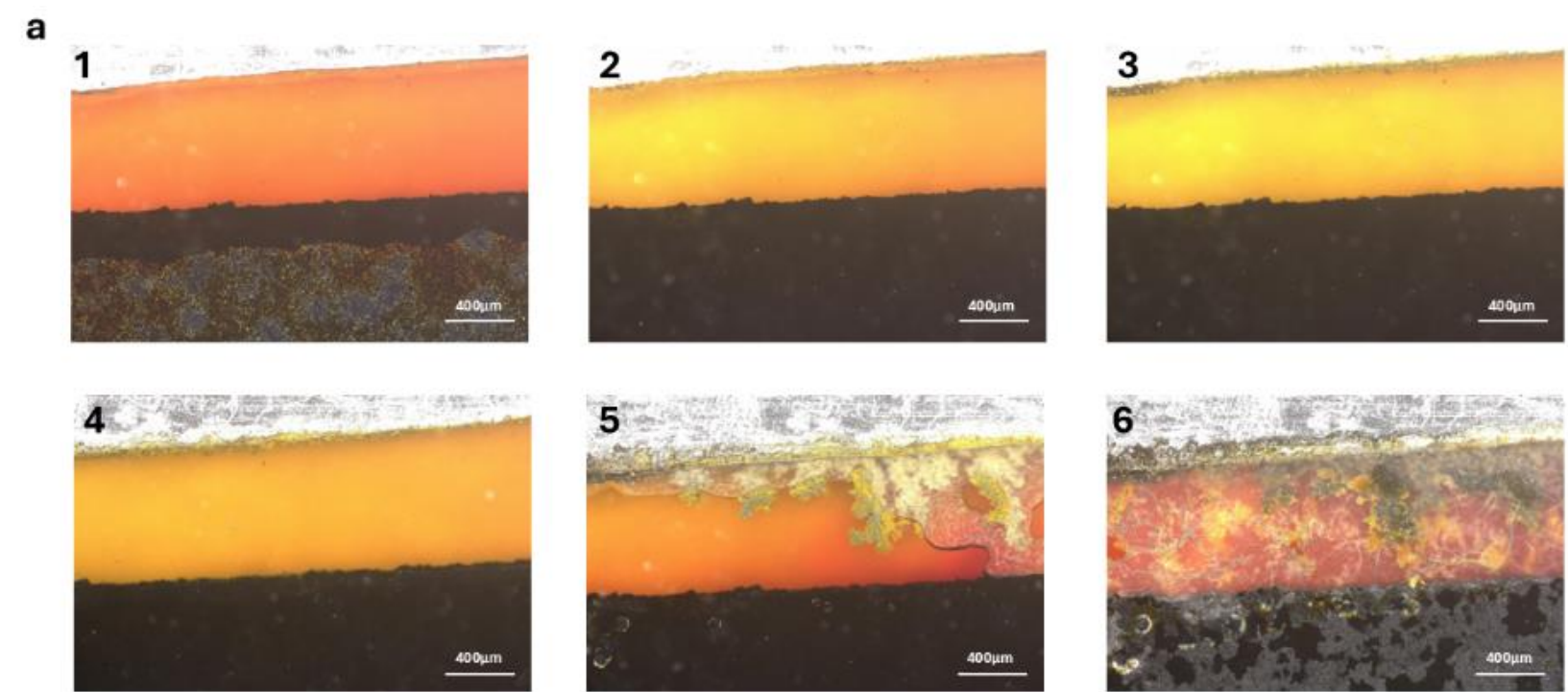
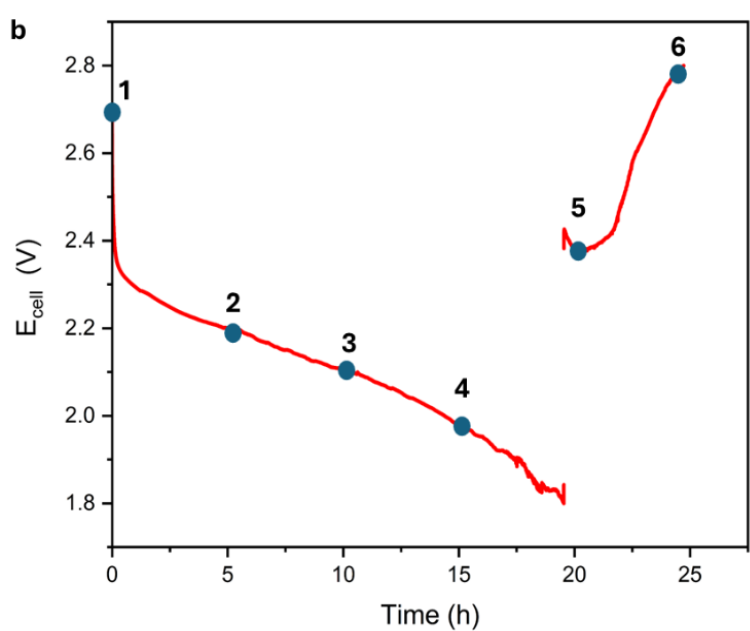


Figure 3: a. Optical images at various points across the first discharge and charge, the time at which each numbered image was recorded is shown in (b) of this figure. Scale bar = 400 μm. b. Voltage profile of operando cell's first discharge and charge.

Synchrotron In-situ X-ray Tomography Data

3mm diameter Swagelok cells were imaged using computed tomography (Fig 4). Sulfur-containing solids deposit on the lithium anode surface during cycling and keep spreading during the discharging process, which indicates the polysulfides shuttling effect and corrosion layer formation on the anode surface.

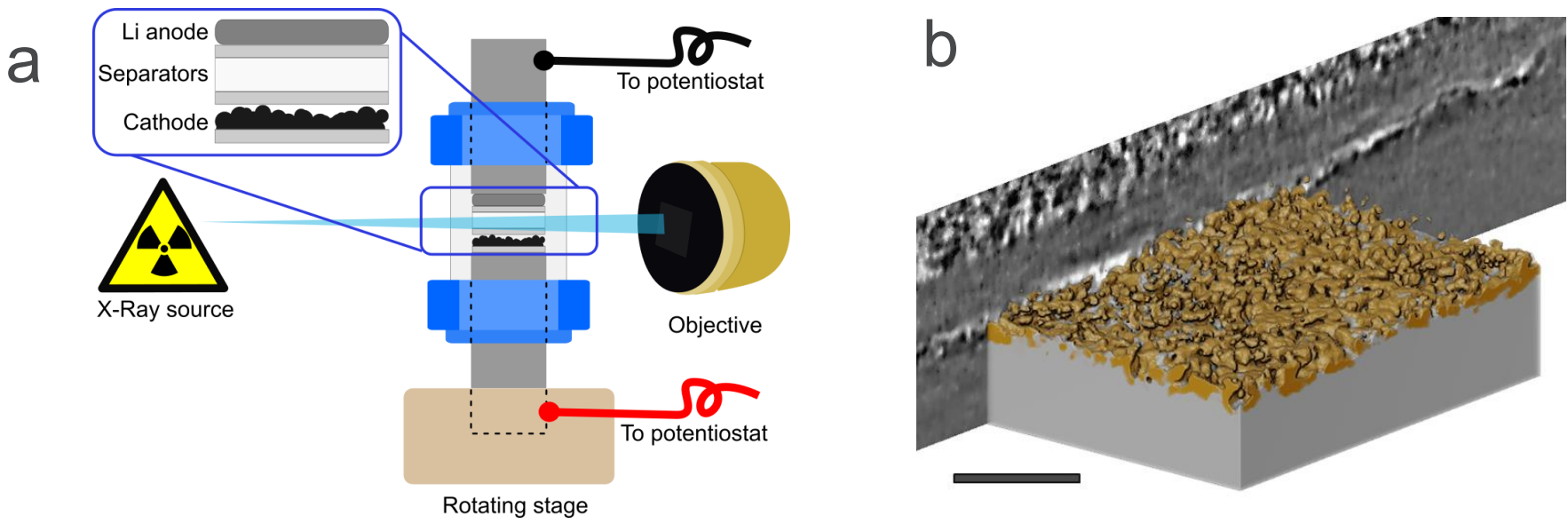


Figure 5: a) Schematic of experimental set-up using Swagelok-type in-situ cell. b) synchrotron XCT volume rendering of corrosion layer on lithium surface in liquid-electrolyte Li-S battery.

Synchrotron Characterisation Plans

- Utilising XANES at synchrotron to detect redox state changes of S and its chain length in sulfur species to understand the reaction mechanism. As many of the polysulfide transitions happen in the liquid phase, sufficient XANES signal from dissolved species while avoiding beam damage can be the main challenges.
- SAXS (small angle X-ray Scattering) at synchrotron will be utilised to detect and trace the early-stage nucleation and nanoscopic reaction intermediates inside the cathode and at the cathode interface during charging and discharging process to determine the utilisation rate of sulfur, which is related to passivation layer and the structural collapse.

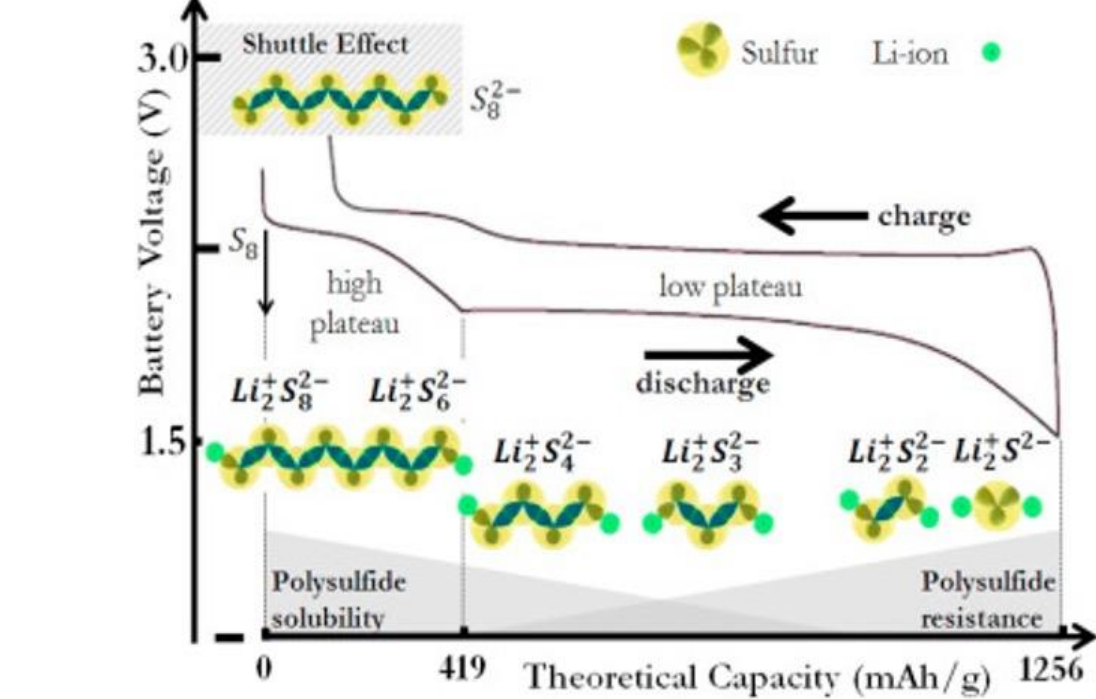


Figure 6: Schematic overview of redox state changes in S during the reactions in Li-S batteries.

- PDF (X-ray Pair Distribution Function) would provide complementary information on short-range order and amorphous solid intermediates, enabling a more detailed mechanistic distinction between solution-phase polysulfides and solid sulfur species during Li₂S oxidation.

Lab Characterisation: Raman Spectroscopy

- Ex situ: Sulfur peaks obtained in cell with LiNO₃ additive after 1 cycle, indicating the sulfur deposition.
- In situ: Redistribution and utilisation of sulfur during operando characterisation during cycling, potentially due to passivation layer on cathode surface

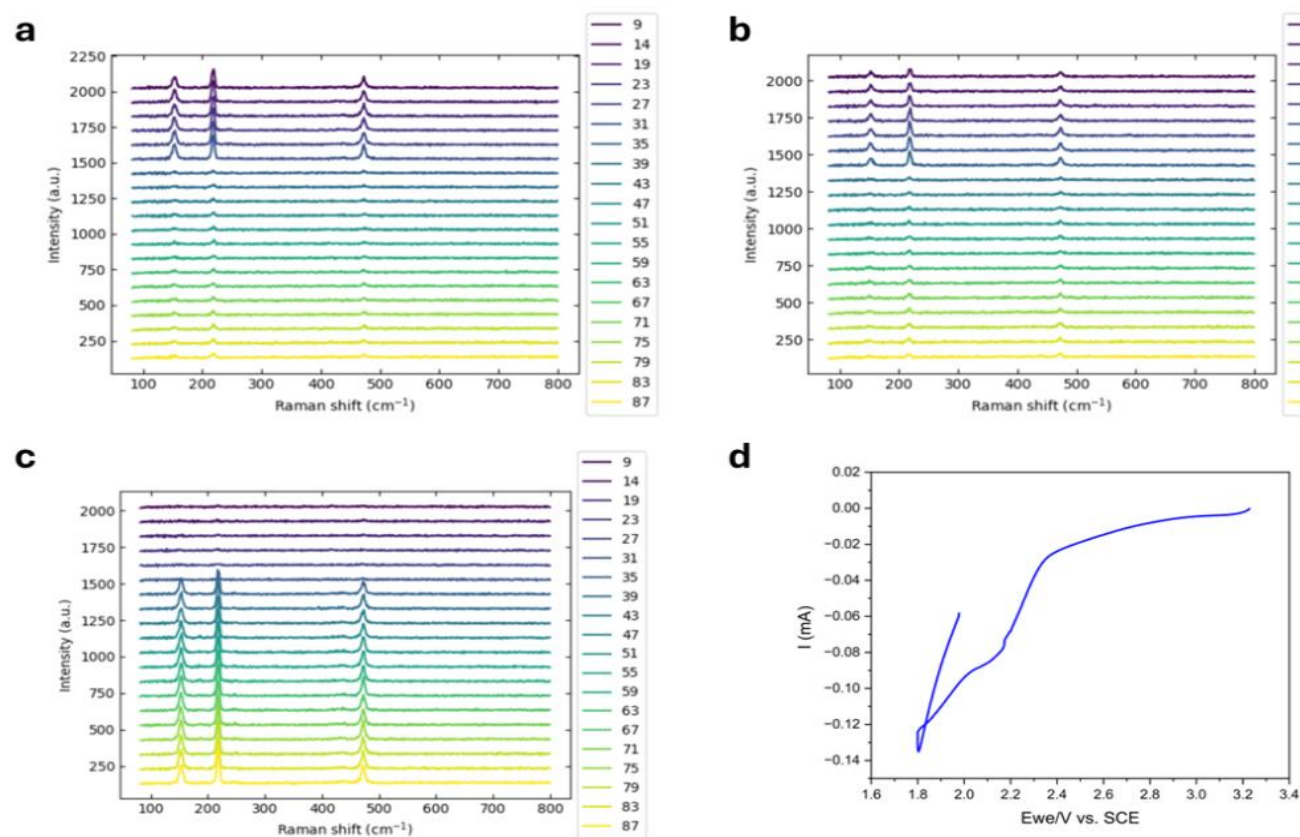


Figure 7: in-situ Raman spectra and electrochemical performance. a-c. intensity vs Raman shift graphs at different spots on the positive electrodes. d. I vs Ewe plot during in-situ Raman characterisation.

References

[1] Robinson, J.B. *et al.* (2021). 2021 roadmap on lithium sulfur batteries. *Journal of Physics: Energy*.

Yiheng Shao is a PhD researcher at University of Oxford working on in-situ and operando characterisation of Li-S batteries degradation mechanism on cathode materials and anode interface, supervised by Prof. Paul Shearing.

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