

OPTIMISING ARTIFICIAL SEI FORMATION IN LITHIUM-SULFUR BATTERIES

A Data-Driven Approach towards Stabilising the Li Metal Anode Interface



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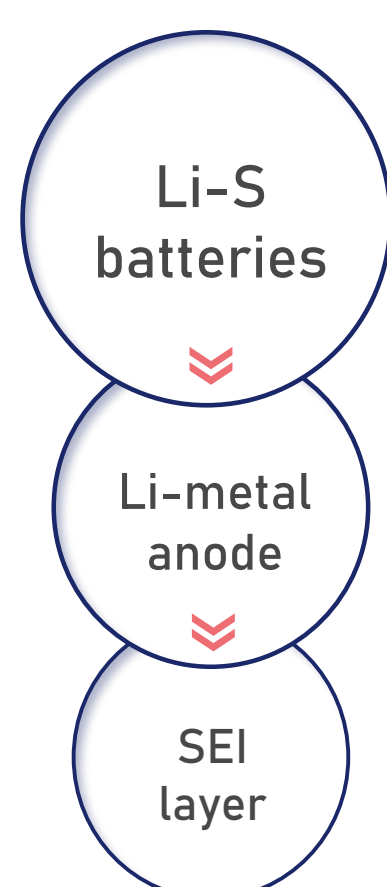
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ABSTRACT

In our energy-driven world, more efficient energy storage solutions are presently required, both to meet increasing societal energy demand and to tackle the intensifying climate crisis. This has necessitated searching beyond the Li-ion batteries which have thus far dominated the energy storage landscape, and towards the commercialisation of more lightweight, compact and long-lasting batteries.

An attractive candidate is the Lithium-Sulfur (Li-S) battery, which boasts an improved theoretical specific energy of 2600 Wh/kg¹. Wide-scale commercialisation has been limited by various technical issues, including Li dendrite growth from the anode, leading to eventual shorting of the battery. Herein, a data-driven approach is proposed to prevent such dendrite growth via the promotion of a stable, homogeneous SEI (Solid Electrolyte Interphase).

MOTIVATION



Rechargeable Li-S batteries consist of a **sulfur** cathode and **lithium metal** anode.

The Li-S literature distribution demonstrates neglect of the Li-metal anode², resulting in a need to address **safety** problems due to **Li dendrite formation**.

One strategy involves altering anode surface chemistry through modification of the **SEI**, which is a somewhat poorly understood area³.

BACKGROUND

- SEI consists of **electrolyte** reduction/decomposition products, which deposit in **mosaic** structures

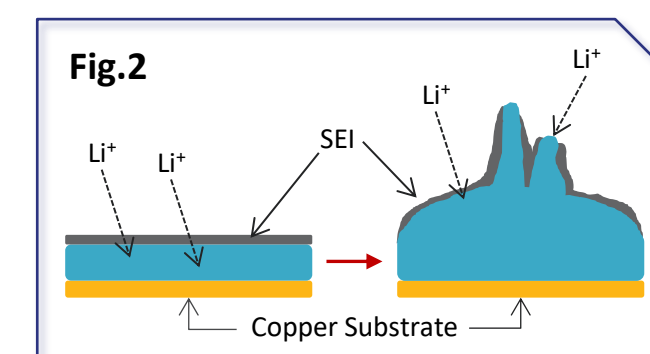
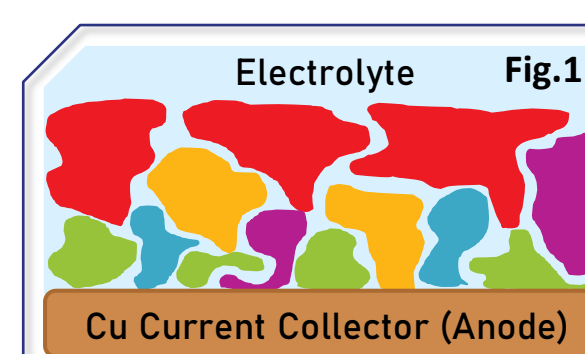


Fig.1: Li deposition under the SEI and dendrite formation

- Li plating morphology depends on SEI **homogeneity**, which determines severity of **dendrite** formation during cycling (Fig.2)

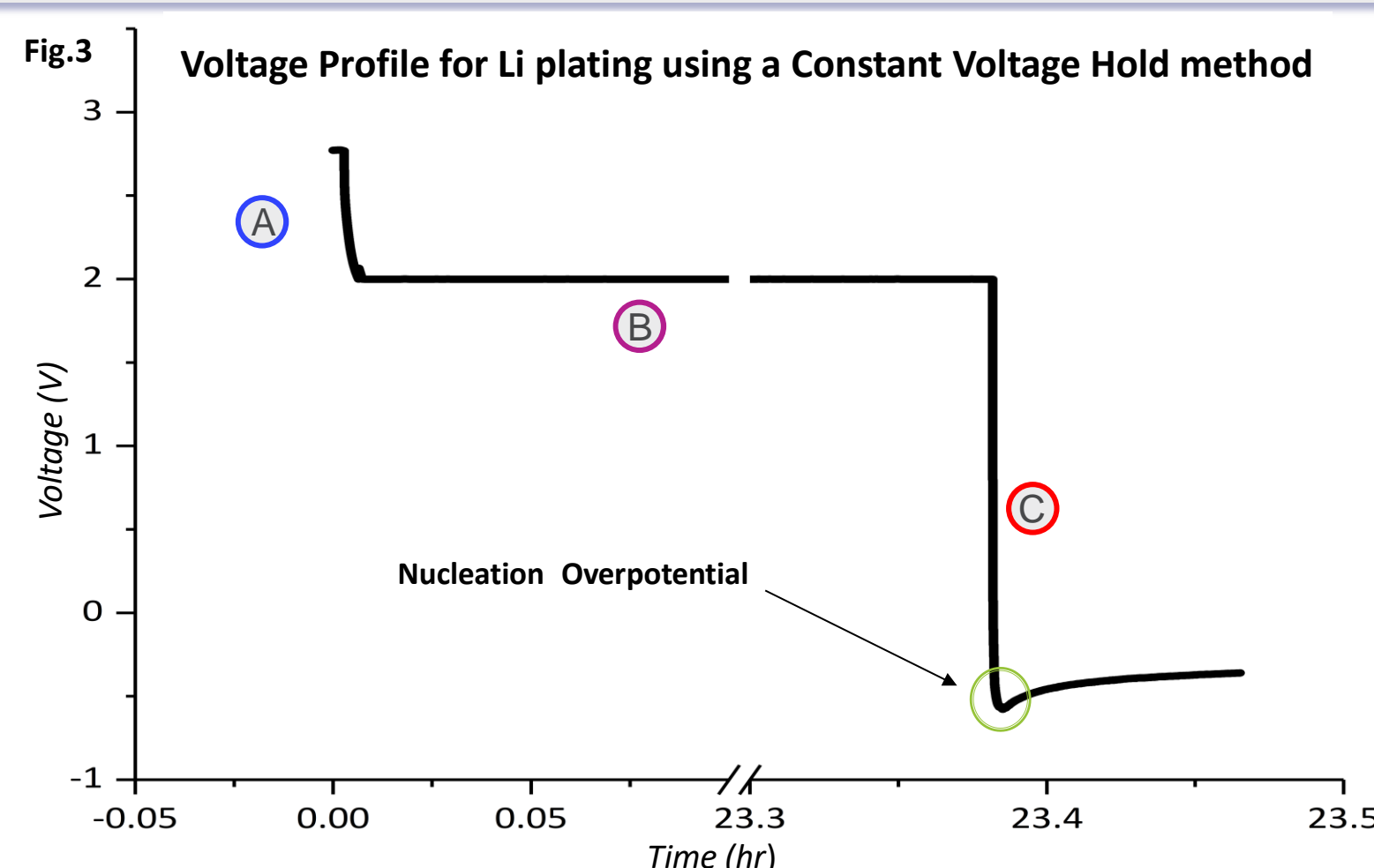
- Artificial SEI**: modifications used to form specific SEI compounds, improving SEI homogeneity and hence cell efficiency, cycle life and durability

METHOD

Of the various strategies to form artificial SEIs, a **constant voltage hold** method is one of the easiest to implement. The stages of this procedure are outlined in a voltage profile (Fig.3)

- Apply **constant current** for a short time period until desired voltage reached
- Hold cell at **constant voltage (CV)** over a large time period to form artificial SEI
- Allow Li **plating** to occur rapidly at high current

Li plating only occurs at **negative** potentials, and the lowest potential reached is the **nucleation overpotential**, when Li nucleation first occurs.

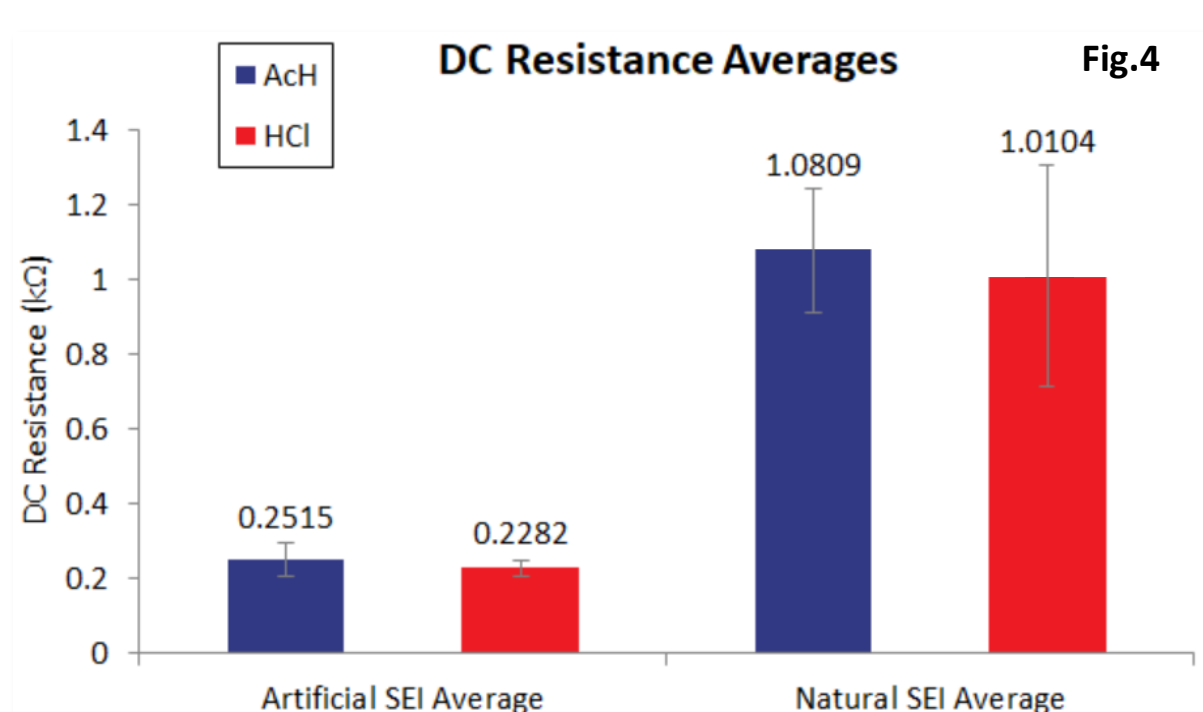


The artificial SEI should have a **higher resistance** than a natural SEI formed under the same conditions. This is due to increased layer **thickness** and more **resistive** compounds formed.

A method to verify this involves:

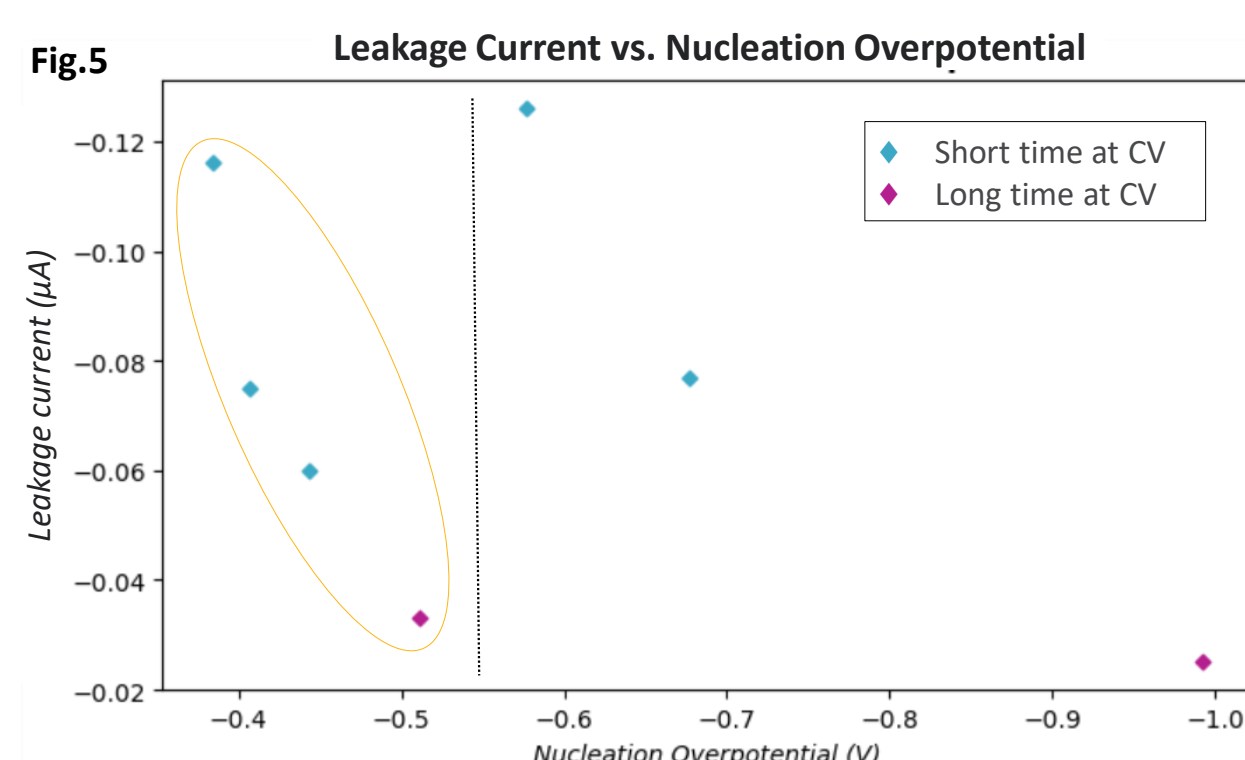
- Finding **nucleation overpotential** (as in Fig.3)
- Calculating **DC resistance** ($R = V/I$ assuming Ohm's law) using plating current at overpotential
- Comparing** DC resistances between artificial and natural SEIs, indicating whether there is an additional resistance due to the artificial SEI

RESULTS



- Dependence of nucleation overpotential with leakage current (current at end of CV period) investigated
- Non-linear inverse** relationship between magnitude of current and overpotential, at **lower** overpotentials
- Unclear** trend at very high overpotentials (> 0.6 V)
- Cells held at constant voltage for a **long time** (> 1 day) demonstrate a **lower** end current at constant voltage

- DC resistances calculated for cells pre-treated with either dilute **HCl** or concentrated acetic acid **AcH**, for surface oxide removal (see Fig.4)
- Average artificial SEI resistances much **lower** than in natural SEI, due to **higher plating current**
- Leads to increased plating and surface area, **reducing** overall resistance which negates any resistance gain due to artificial SEI



CONCLUSION & IMPACT

- Magnitude of **plating current** affects DC resistance **more** than the presence of an artificial SEI
- Inverse relationship** between leakage current and overpotential, due to **less resistive** SEI giving rise to higher leakage current.
- Dependencies difficult to determine at **high** overpotentials due to formation of a very **thick and resistive** SEI
- Increased time at constant voltage **reduces** the leakage current at the end of the period
- A **Python** program was written to automate this analysis on a range of voltage profile shapes, including identifying and removing data.
- Code can be found on **Github** (see below)
- Produced a **general method** for artificial SEI analysis, applicable over a wide range of systems and experimental conditions

NEXT STEPS

- Obtaining further data to **verify** expected trends and characterise impacts of artificial SEI, e.g. data over a range of CVs to determine ideal SEI formation voltage
- Investigating **SEI formation kinetics** using current relaxation curves over the CV period (**stage B**)
- Investigating **feasibility** of technique implementation in Li-S batteries for commercial use:
 - Effects of a constant voltage hold method on other **cell components**
 - Feasibility of an **anode-free** application in Li-S, using a Cu current collector and lithiated sulfur cathode to provide a source of Li⁺ ions

REFERENCES & ACKNOWLEDGEMENTS

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- I offer my deepest gratitude to Dr Svetlana Menkin⁴ for her excellent supervision, ideas, patience and guidance. My appreciation extends also to Evelyn Wang for her provision of additional data, and the wider Grey group at the University of Cambridge for their kind welcome and collective knowledge. Lastly, I would like to thank the LiSTAR group and the Faraday Institution for the opportunity to engage in exciting research.

INTERN BIO & CONTACT INFO

Melissa is entering her final year of studying a BSc (Hons) Physics at Lancaster University. Propelled by a desire to tackle the rising energy challenges we face, she is looking towards completing a Masters in Energy Technologies, from where she hopes to apply her skills in the energy industry. In future, she would particularly enjoy immersing herself in interdisciplinary projects, since she finds great value in innovative collaboration.

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