OPTIMISING ARTIFICAL SEI FORMATION IN Li-S BATTERIES

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MOTIVATION

Next generation batteries with higher gravimetric energy density than Li-ion — **Li-S batteries**

Sulfur cathode and metallic Li anode; neglect of anode in literature — **Li-metal anode**

Addressing safety issues in anode (Li dendrite formation) requires looking at SEI — **SEI layer**

Li-S VS. Li-ion BATTERIES

01 STRUCTURE: Sulfur cathode & Li metal anode vs. LMO cathode & graphite anode

02 GRAVIMETRIC ENERGY DENSITY: ~2,600 Wh/kg (theoretically) vs. ~200 Wh/kg

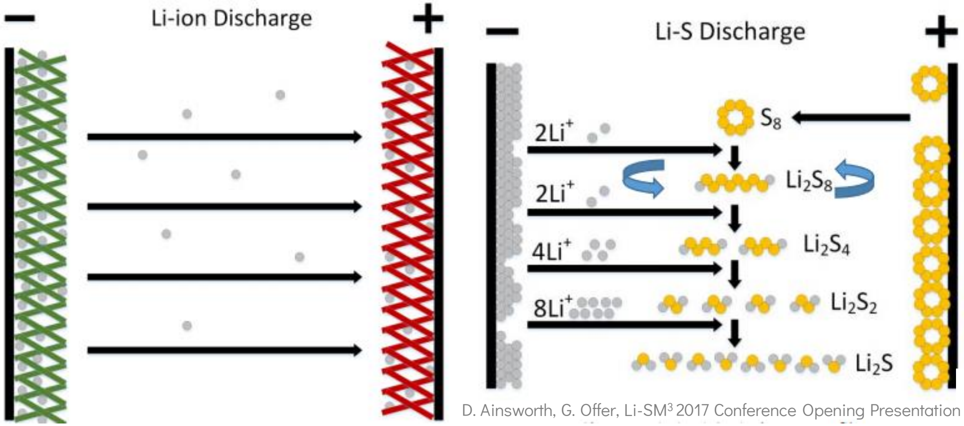
03 APPLICATIONS: Niche markets (aerospace, AUVs) vs. Widespread commercialisation

04 Li METAL ANODE (Li-S):

Advantages	Higher specific capacity (3860 mAh g^{-1})	Lower anode potential (-3.04 V)	Lower density (0.59 gcm^{-3})
Drawbacks	Li dendrite growth	Extreme volume fluctuations	Higher reactivity with electrolyte

Li-S VS. Li-ion BATTERIES

05

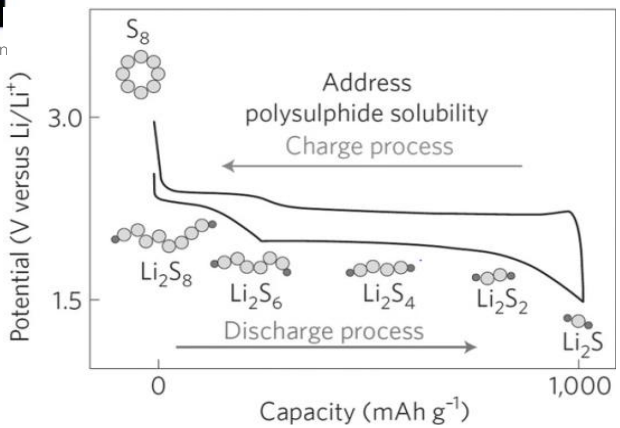


D. Ainsworth, G. Offer, Li-SM[3] 2017 Conference Opening Presentation

MECHANISM:

Li-ion Intercalation vs. Polysulfide Shuttle Effect

Discharge: surface reactions form **lithium polysulfide intermediates** via reduction at cathode, which shuttle between electrodes



A. Manthiram, S.H. Chung, C. Zu. Lithium-sulfur batteries: progress and prospects. *Adv Mater.* 2015;27(12):1980-2006. DOI:10.1002/adma.201405115

ISSUES WITH Li-S COMMERCIALISATION

01

POLYSULFIDE SHUTTLING

Insoluble polysulfides deposit on electrode surfaces, **reducing CE/cycle life** & wasting active material

02

LOW CONDUCTIVITY

S_8 active material and **Li_2S** final discharge product have poor **electrical** and **ionic** conductivity

03

VOLUMETRIC CHANGES

Virtually **infinite fluctuations** during cycling with **structural changes** at electrodes

04

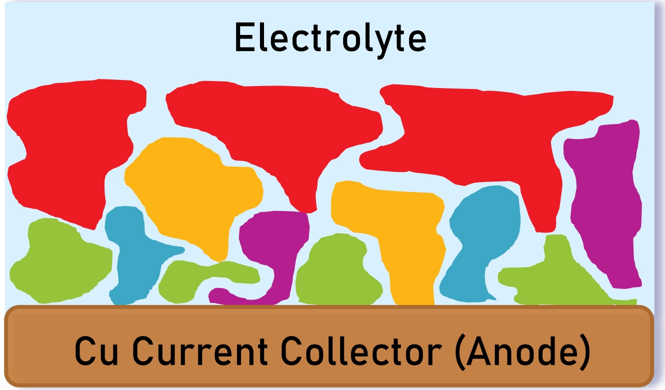
SAFETY ISSUES AT THE ANODE

High Li reactivity **consumes electrolyte** & promotes disordered deposits/**dendritic growth**

ARTIFICIAL SEI FORMATION

Electrolyte decomposition & reduction products, deposit on anode

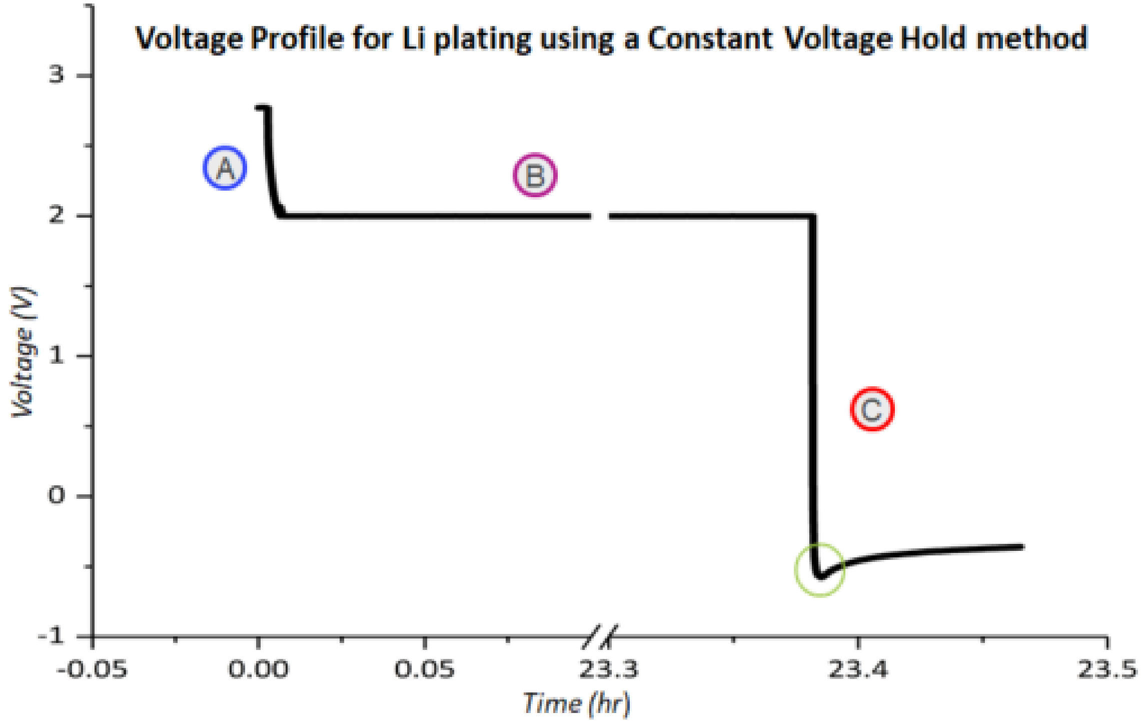
Li-metal anodes: SEI forms upon contact with electrolyte



Artificial SEI:
selectively forming specific SEI compounds

- Improves homogeneity of Li deposition
- Greater control of Li plating/stripping
- Methods involve electrolyte additives or electrode coatings
- Constant voltage hold method

THE APPROACH

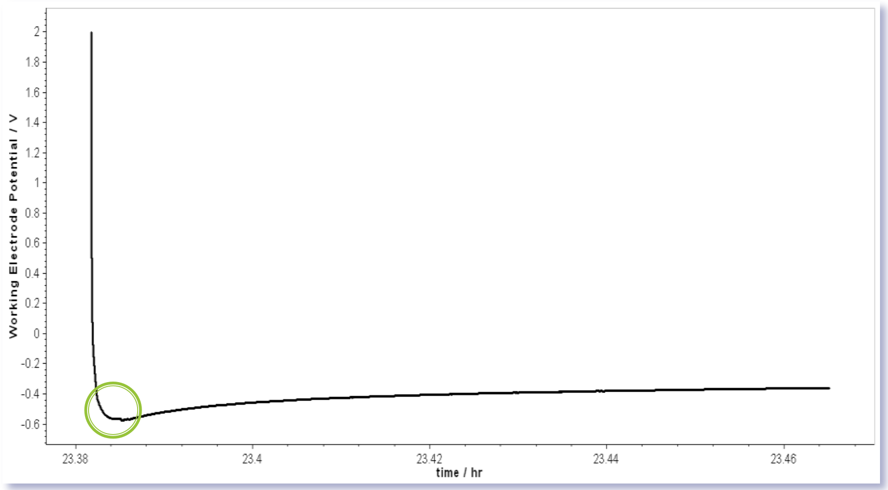


A CC until desired voltage reached

B CV over a long time to form artificial SEI

C High current during rapid plating

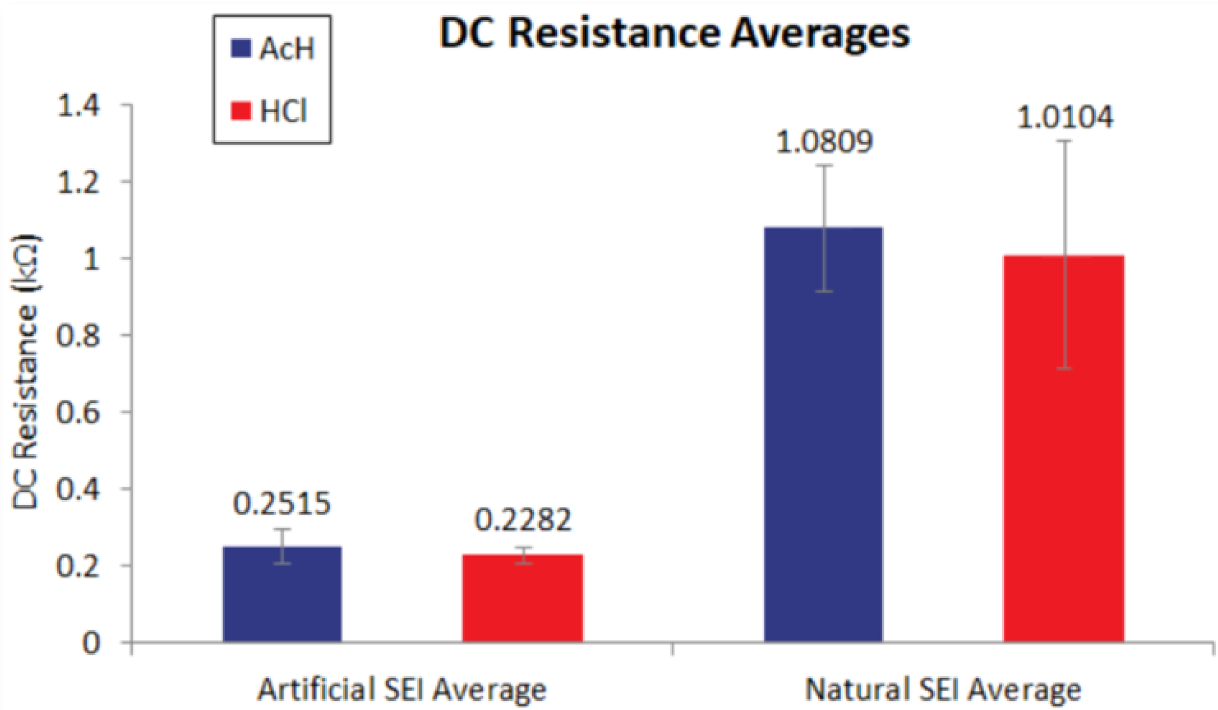
THE APPROACH (CONT.)



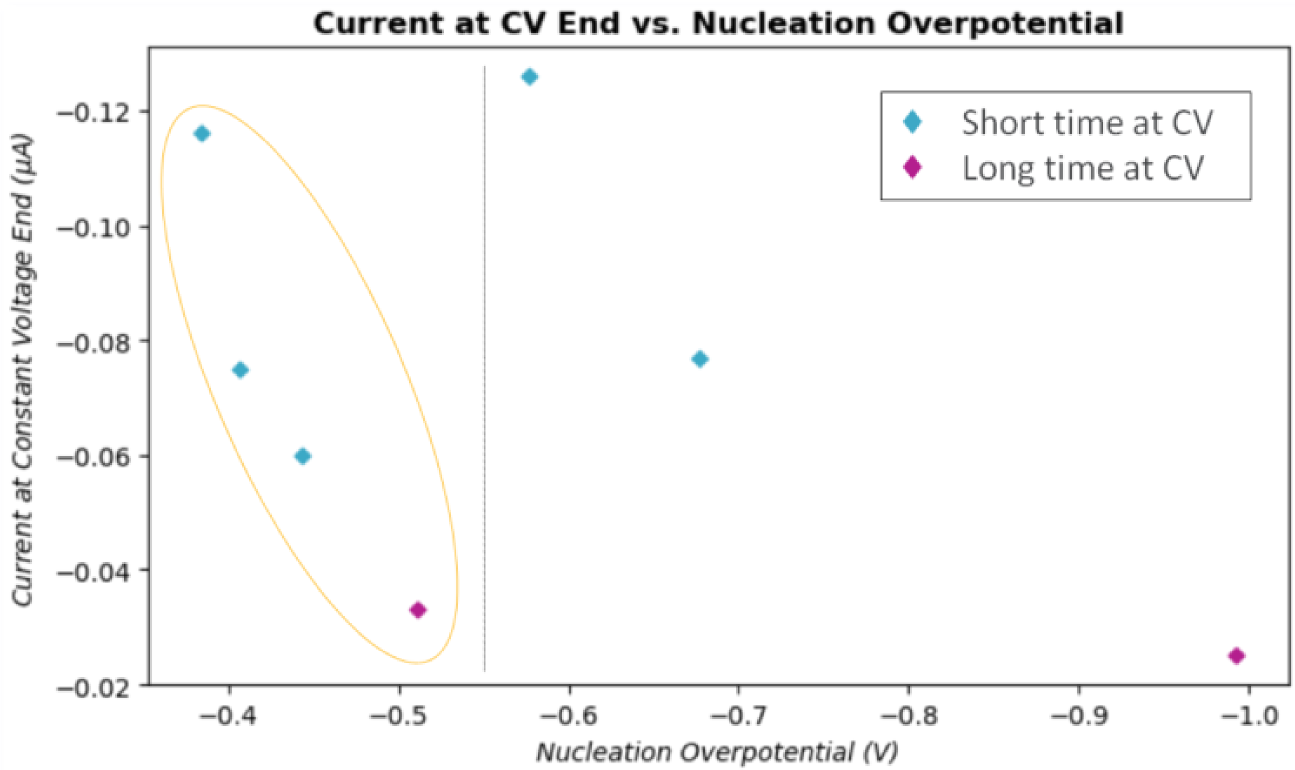
1. Find nucleation potential
2. Calculate DC resistance
3. Compare DC resistances

Artificial SEI should give a higher DC resistance

DC RESISTANCE COMPARISON

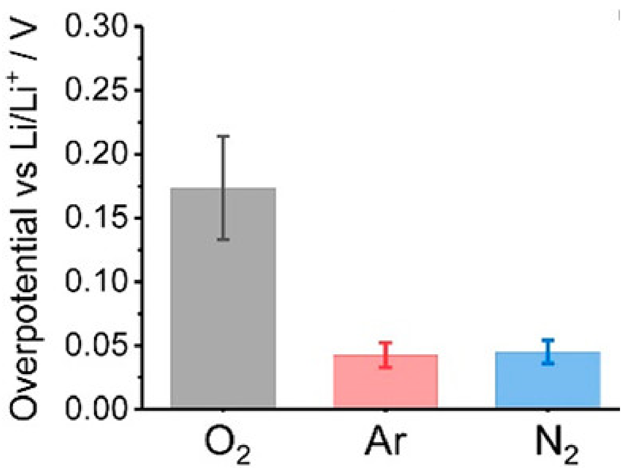


OVERPOTENTIAL VS. CURRENT/TIME AT CV

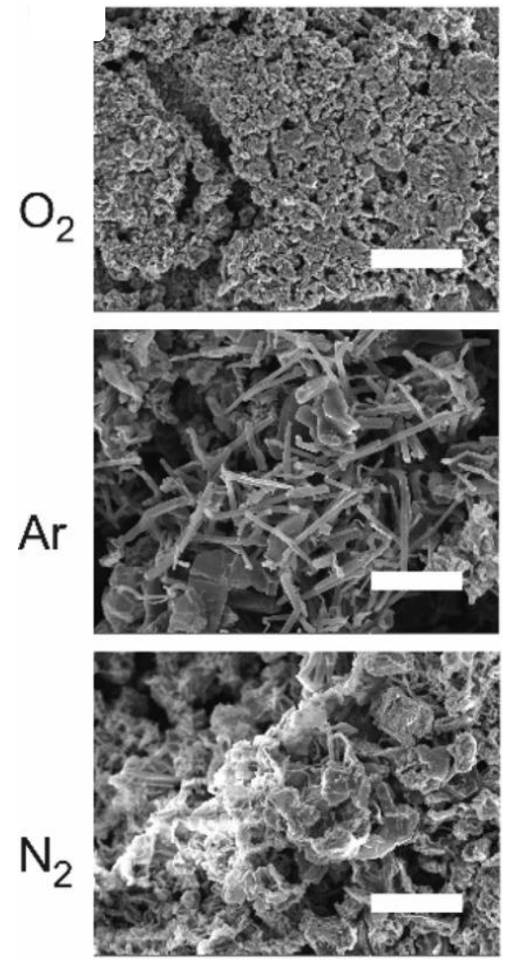


ARTIFICIAL SEI FORMATION USING GAS ATMOPSHERES

- Higher nucleation overpotentials in an O_2 atmosphere
- Improved SEI morphology -> better Li cycling CE in O_2



- Hence higher overpotential leads to a better SEI morphology



Scale bar = 10 um

E. Wang, S. Dey, T. Liu, S. Mekin, C.P. Grey, Effects of Atmospheric Gases on Li Metal Cyclability and Solid-Electrolyte Interphase Formation, *ACS Energy Letters* (2020) 5(4), 1088-1094, DOI: 10.1021/acsenergylett.0c00257

CONCLUSION & IMPACT

- **Plating current** affects DC resistance **more** than presence of an artificial SEI
- **Inverse relationship** between leakage current and overpotential
- Increased time at constant voltage **reduces** the current at the end of the period
- A **Python** program was written to automate this analysis on a range of data
- Code will be uploaded to **Github** (github.com/msychung)
- **General method** for artificial SEI analysis, applicable over a wide range of systems and experimental conditions