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Self-discharge and cycling stability in the Li-S battery…

…where every component plays a role!

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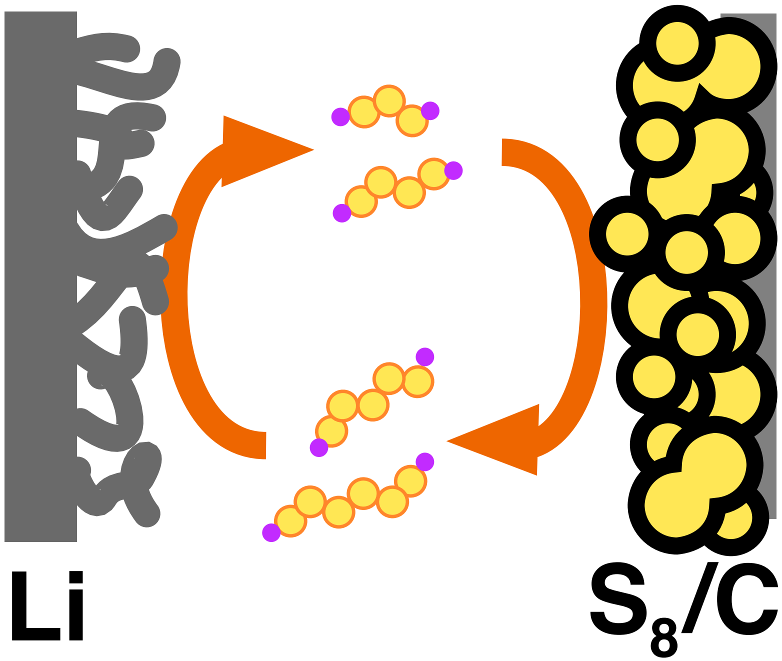
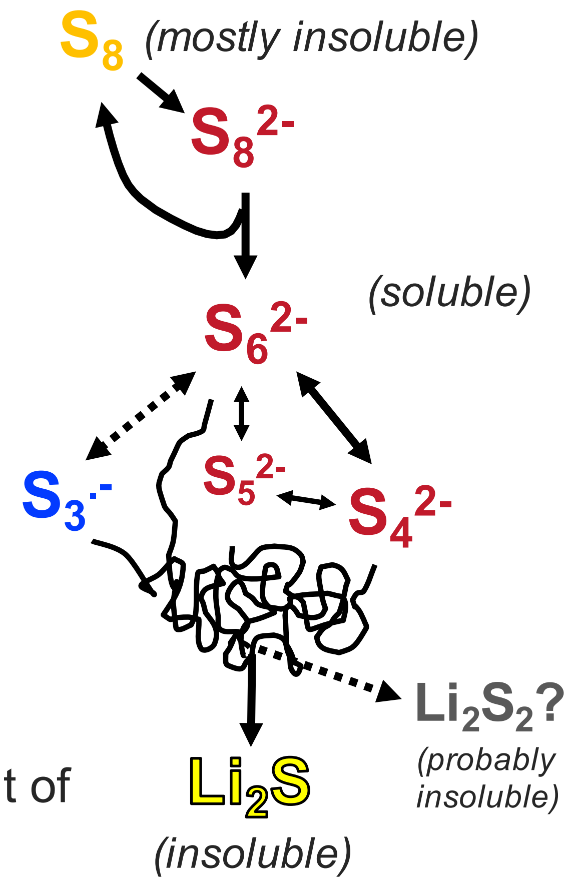
A brief overview…

- Electrolyte volume
- Self-discharge over extended periods
- Mechanism
  - [Li_2S_x] changes in cell
  - Changes in negative electrode surface
- Interfacial stability of anode
- Positive electrode binders (PEO:PVP)

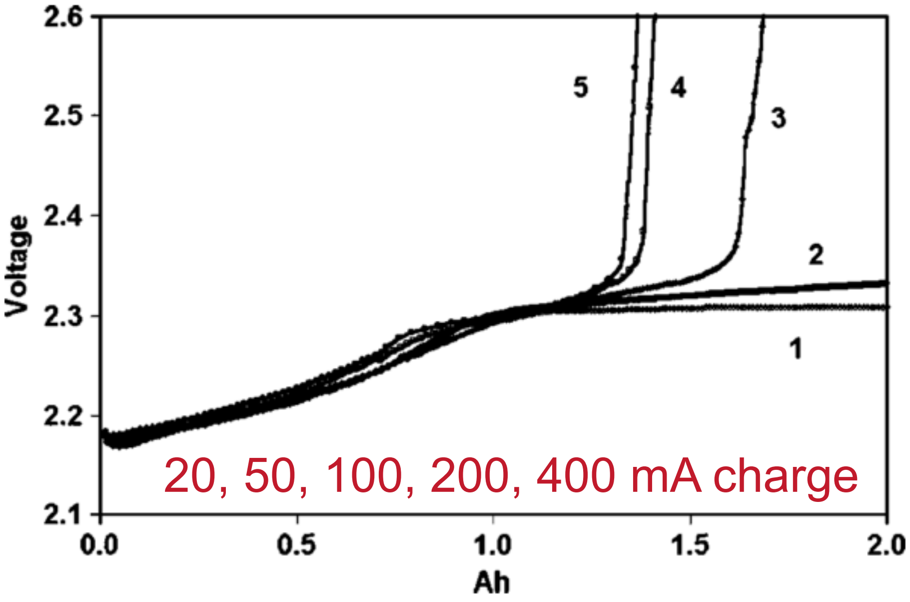
“Catholyte-type” Li-S batteries





- Sulfur species dissolve into a relatively large amount of electrolyte
- Can reach good S utilisation at high sulfur loadings
- Reactions at anode (redox shuttle, etc) a huge problem

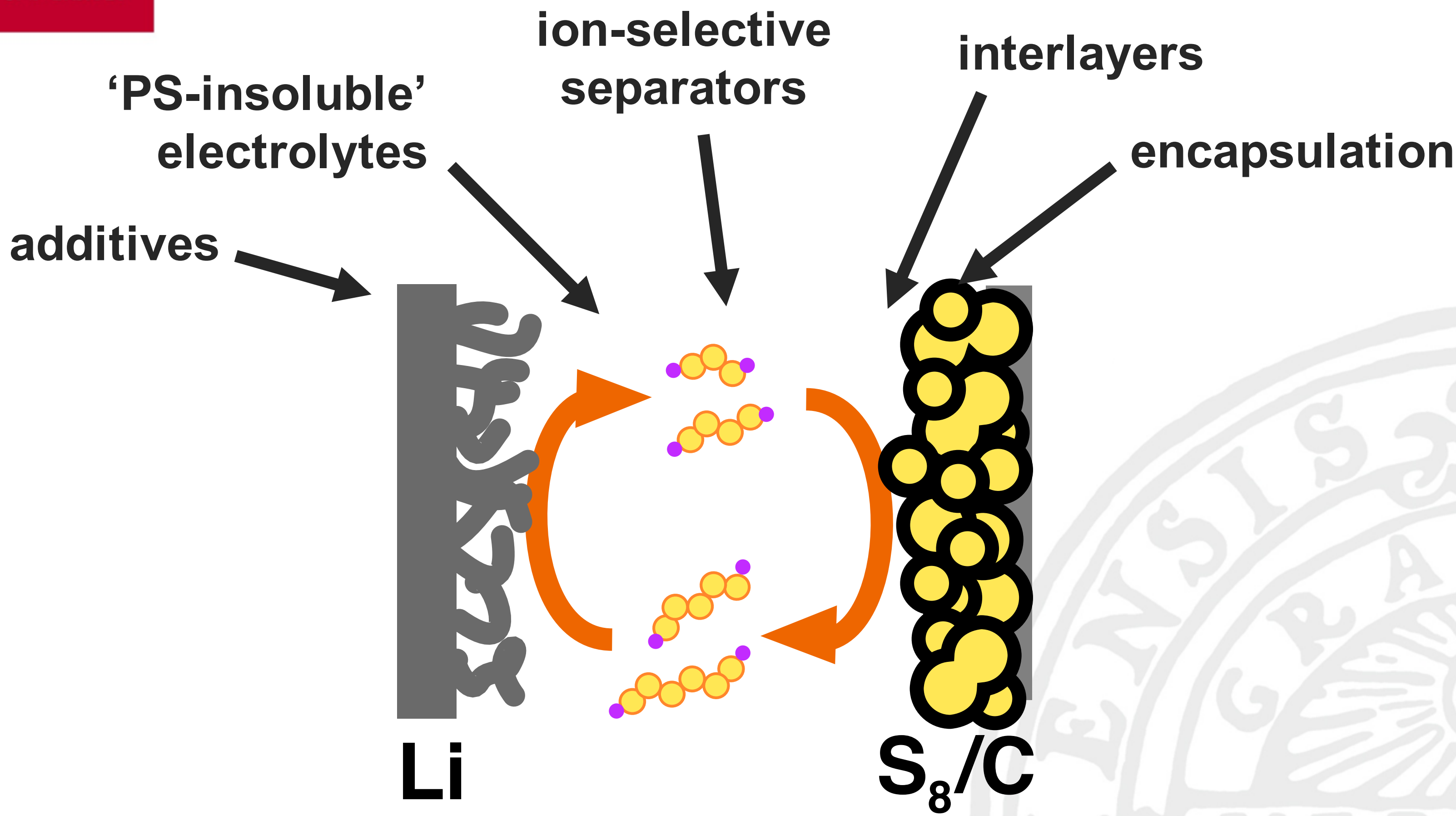
The polysulfide redox shuttle



- "Higher order" PS are formed during charge but diffuse back to negative electrode where they are reduced
- Not like in nickel batteries where a separate process competes with the charge – it counteracts it!
- Implicated in anode corrosion, loss of active sulfur mass, etc.

Mikhaylik et al, J. Electrochem. Soc. ***151,*** *A1969 (2004)*

Research strategies

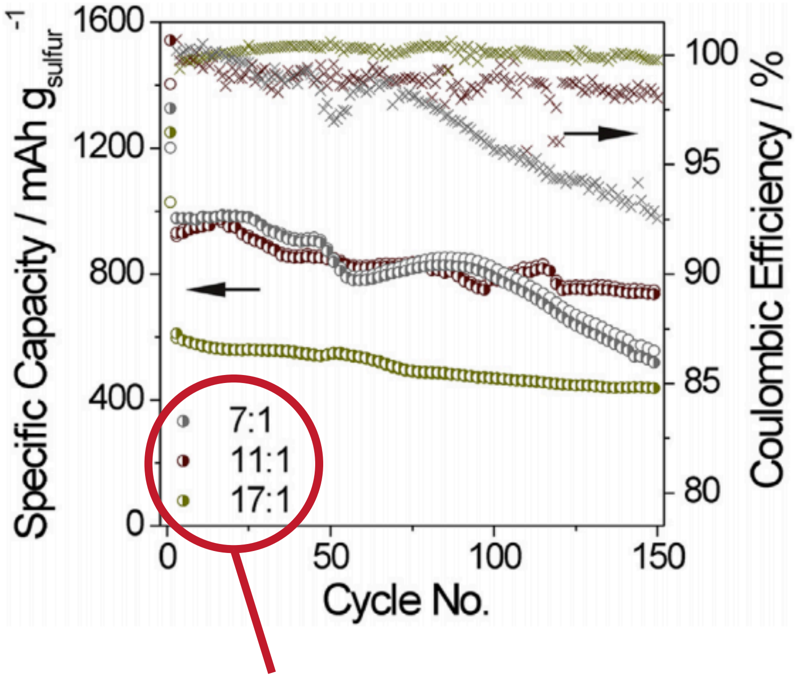


Should expect better capacity retention and closer to 100% efficiency

but is that a good measure of success?

Beware the effect of excess electrolyte!

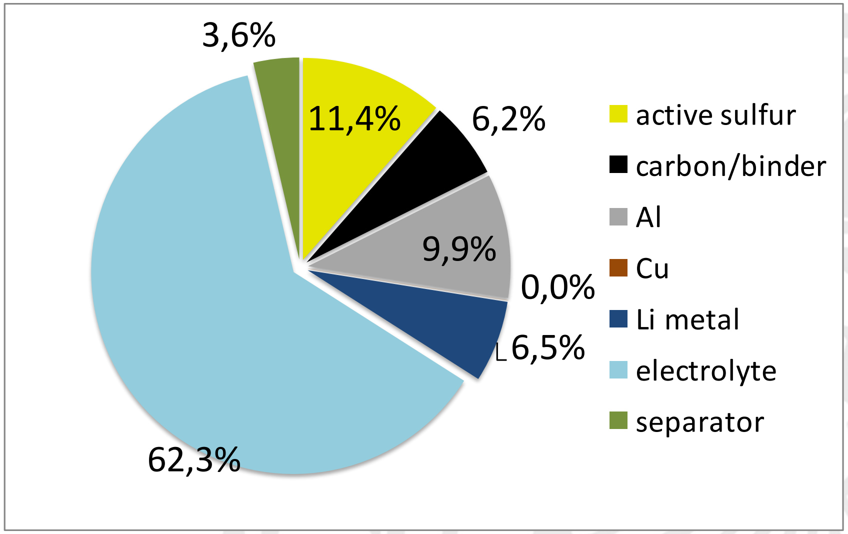
Electrolyte volume is a huge barrier to energy density.



electrolyte/sulfur ratio
(µL/mg_S)

Typical electrolyte mass fraction in 18650 Li-ion cells: **~10% w/w**

Optimistic scenario for our best cells (est. 240 Wh/kg scaled up): **~62% w/w**



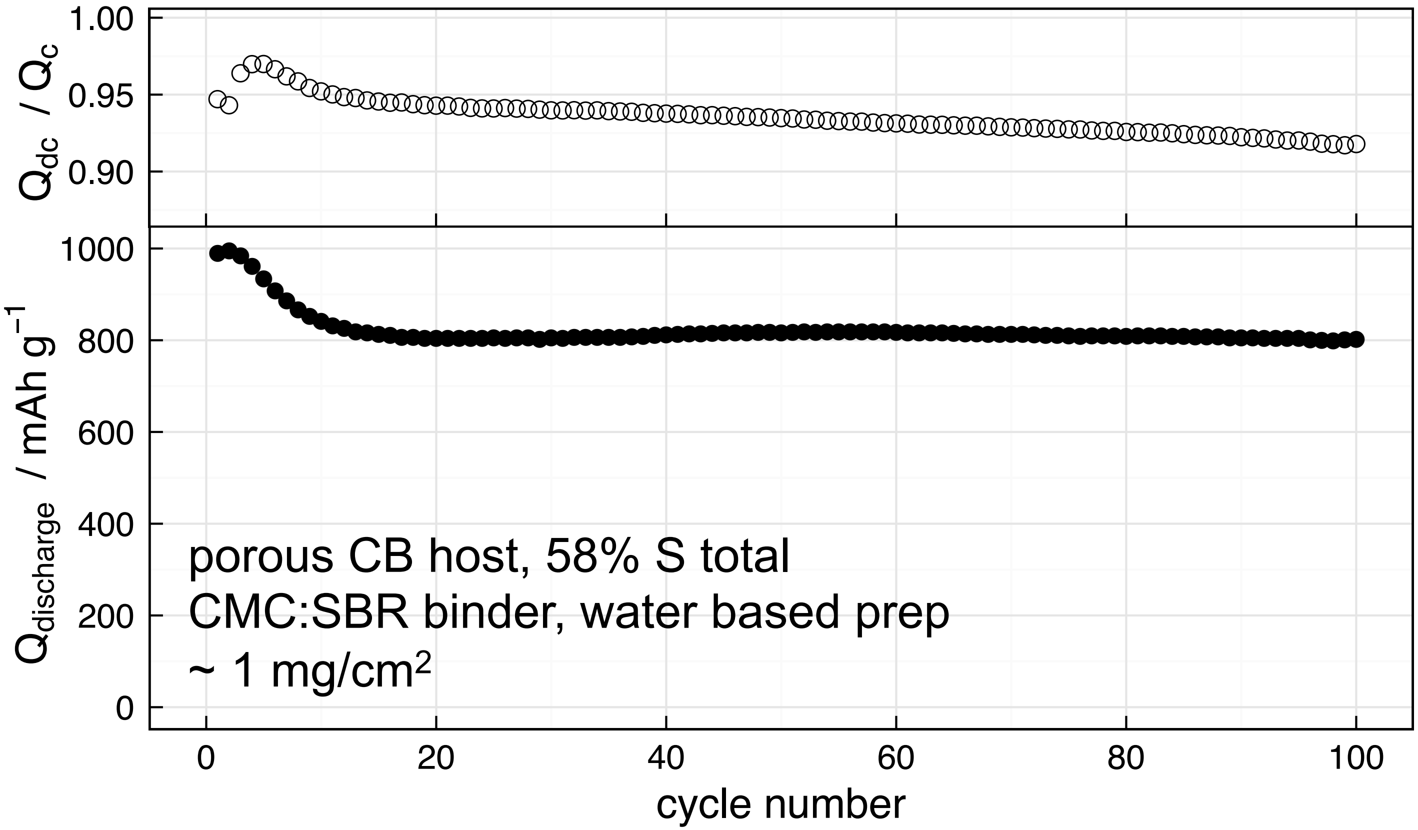
5 µL/mg, 100% excess Li, no Cu c.c., ~3 mAh/cm^2

On the occasions when optimum electrolyte volume is reported, it is often reported to be in the range 10 – 20 µL/mg_S!

Jozwiuk et al, J. Power Sources 296, 454 (2015)

Good capacity retention **does not** imply good control of polysulfides

Our typical point of reference for the last couple of years:



Electrolyte: 6 µL/mg 1 M LiTFSI, 0.25 M $LiNO_3$, DME:DOL

Lacey et al, submitted.

Despite $LiNO_3$, self-discharge is still significant

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Mostly reversible capacity loss
~275-280 mAh/g … in < 3 days

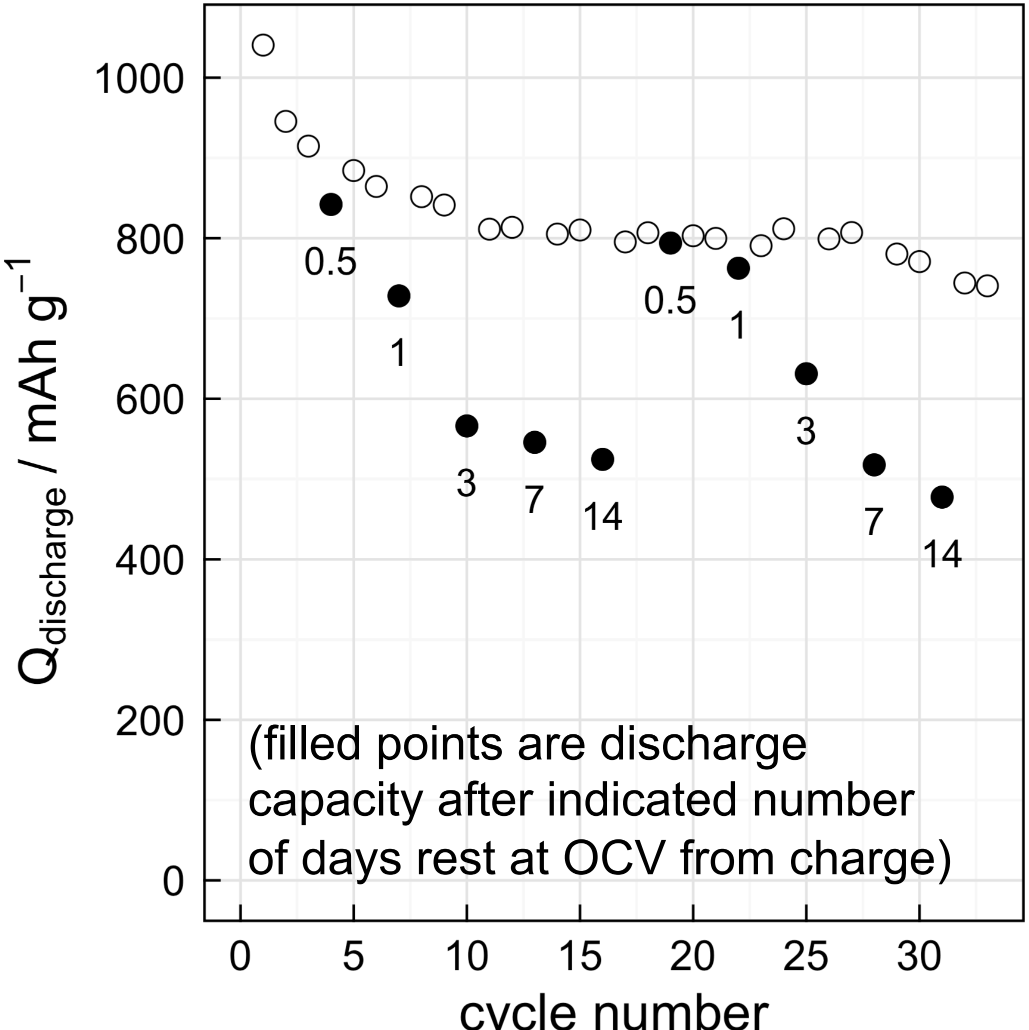
Equivalent C-rate:

$$C/n = \frac{\text{capacity loss}}{t_{\text{relax}}}$$

~C/200 – C/300, upper plateau
(first couple of days)

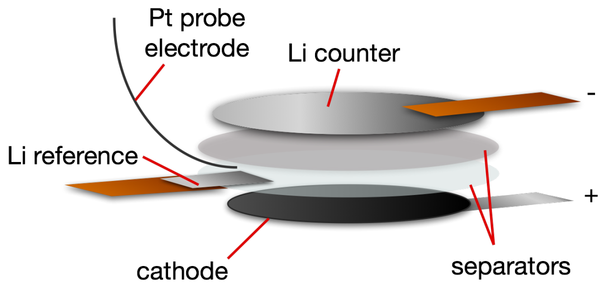
Slows dramatically after 3 days
<< C/10000

C/10, 1.8 – 2.6 V

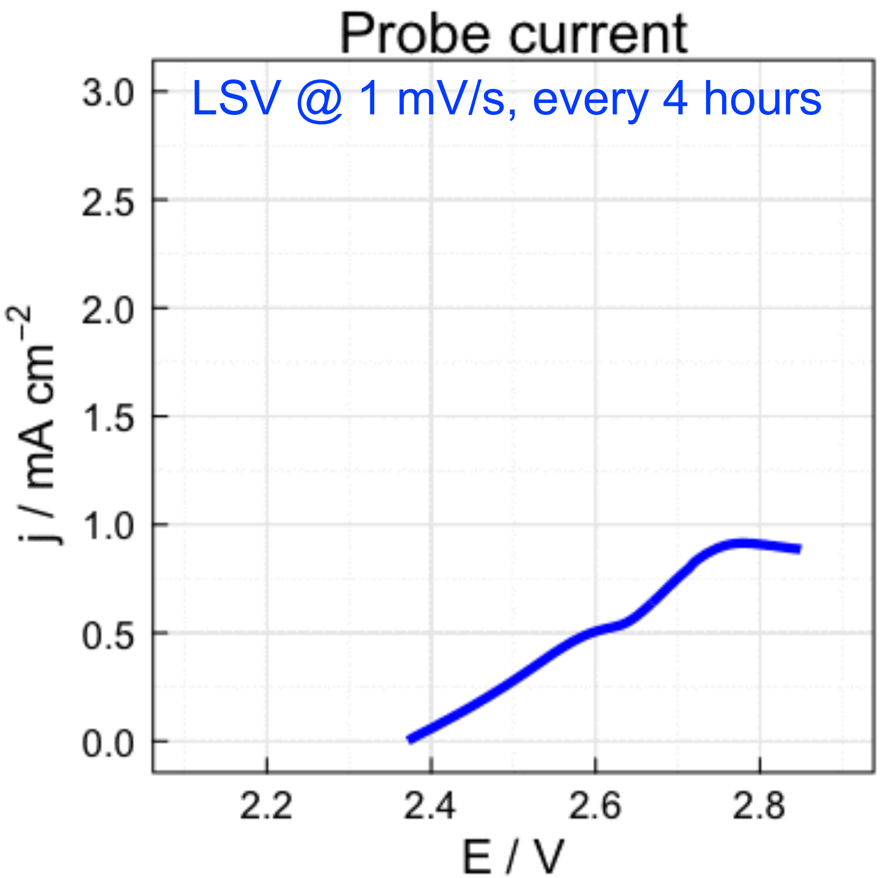


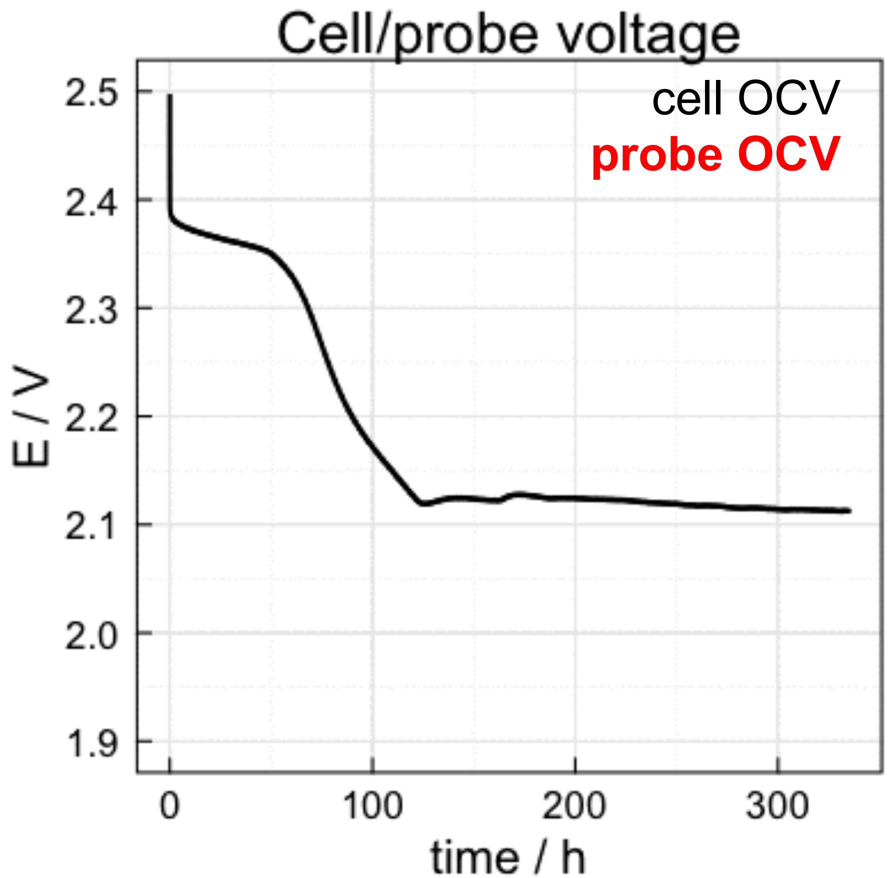
Lacey et al, submitted.

2 weeks of self-discharge…
…in 8 seconds

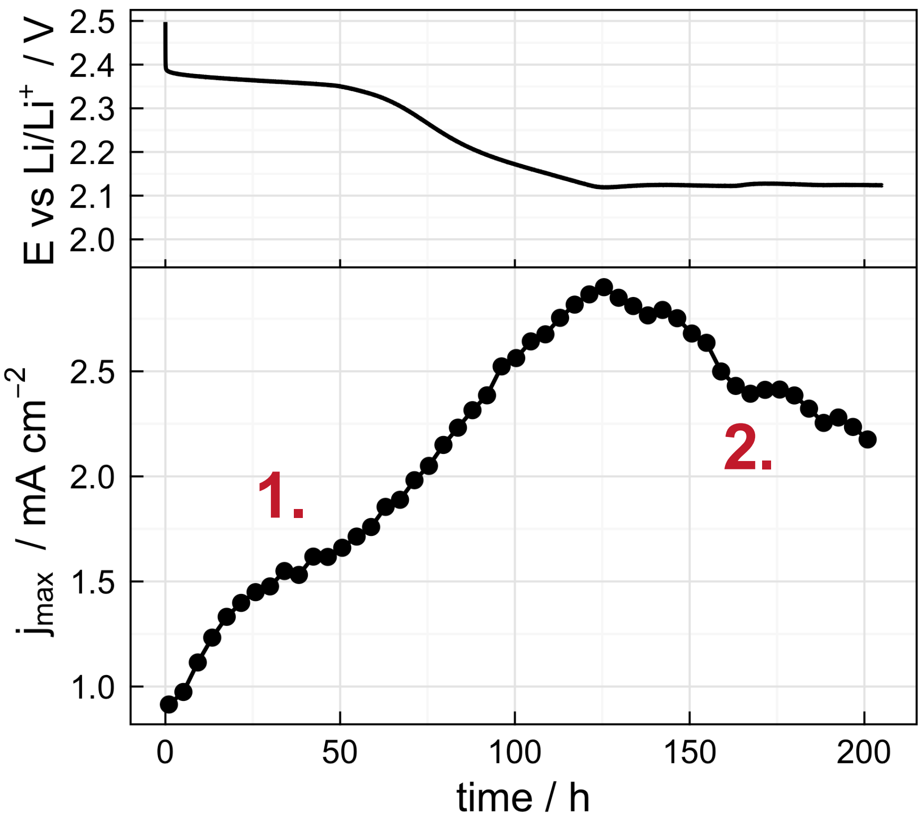


Lacey et al, Electrochem. Comm. 46, 91 (2014)
Lacey et al, submitted.

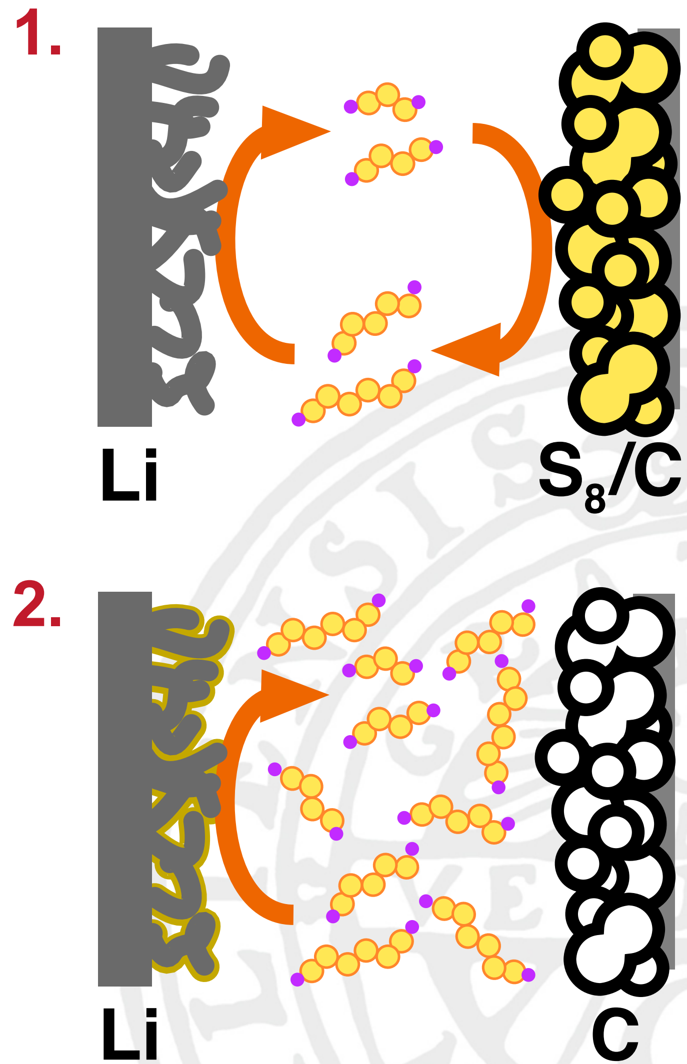




Redox shuttle at open circuit



Redox shuttle drives S dissolution out of positive electrode.



Lacey et al, submitted.

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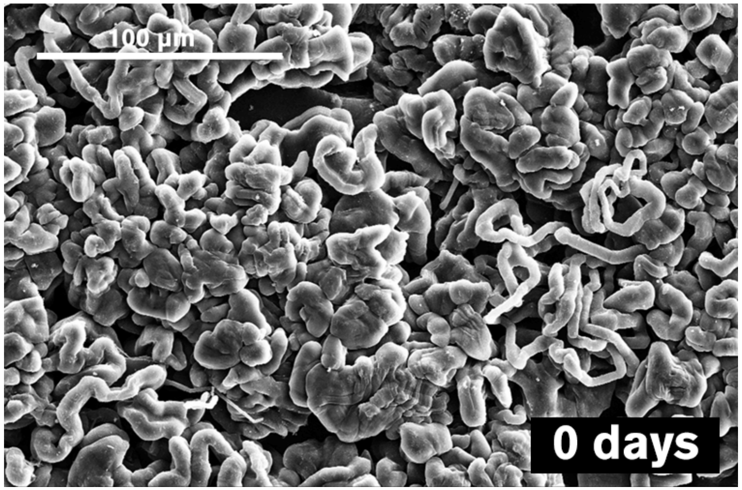
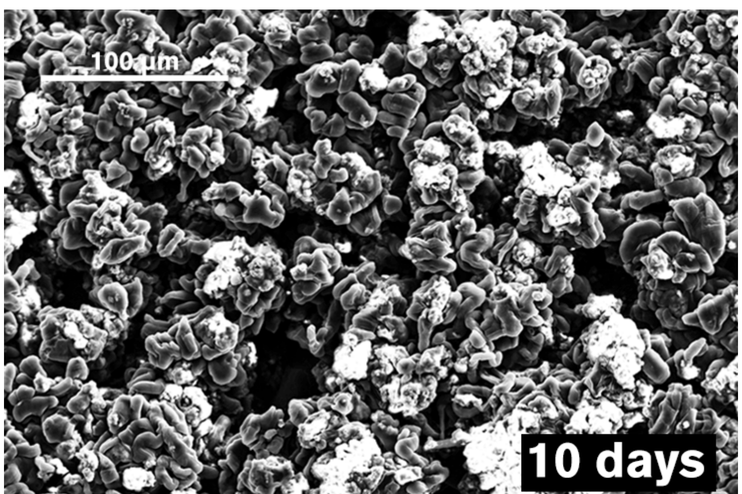
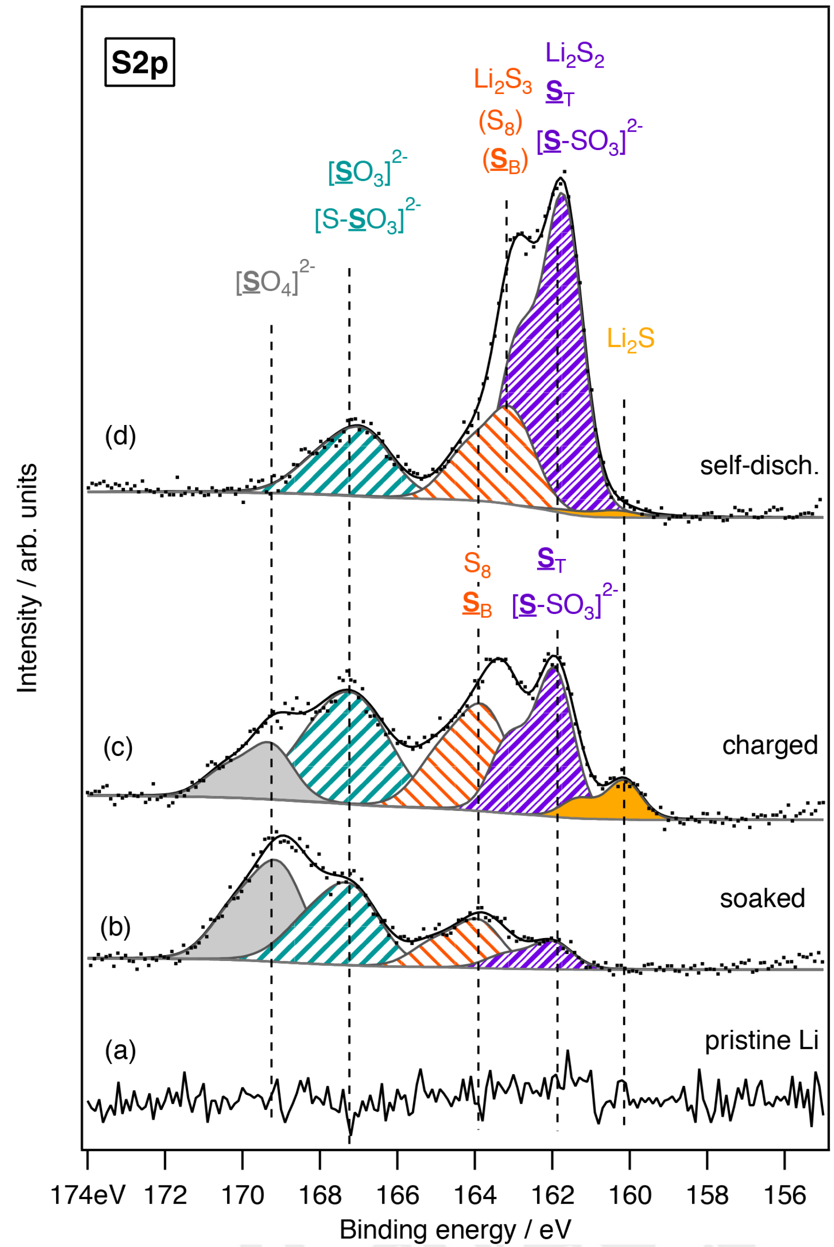
On the –ve electrode…

Lacey et al, submitted.

(Li||Li cell, LiTFSI replaced by $LiClO_4$)







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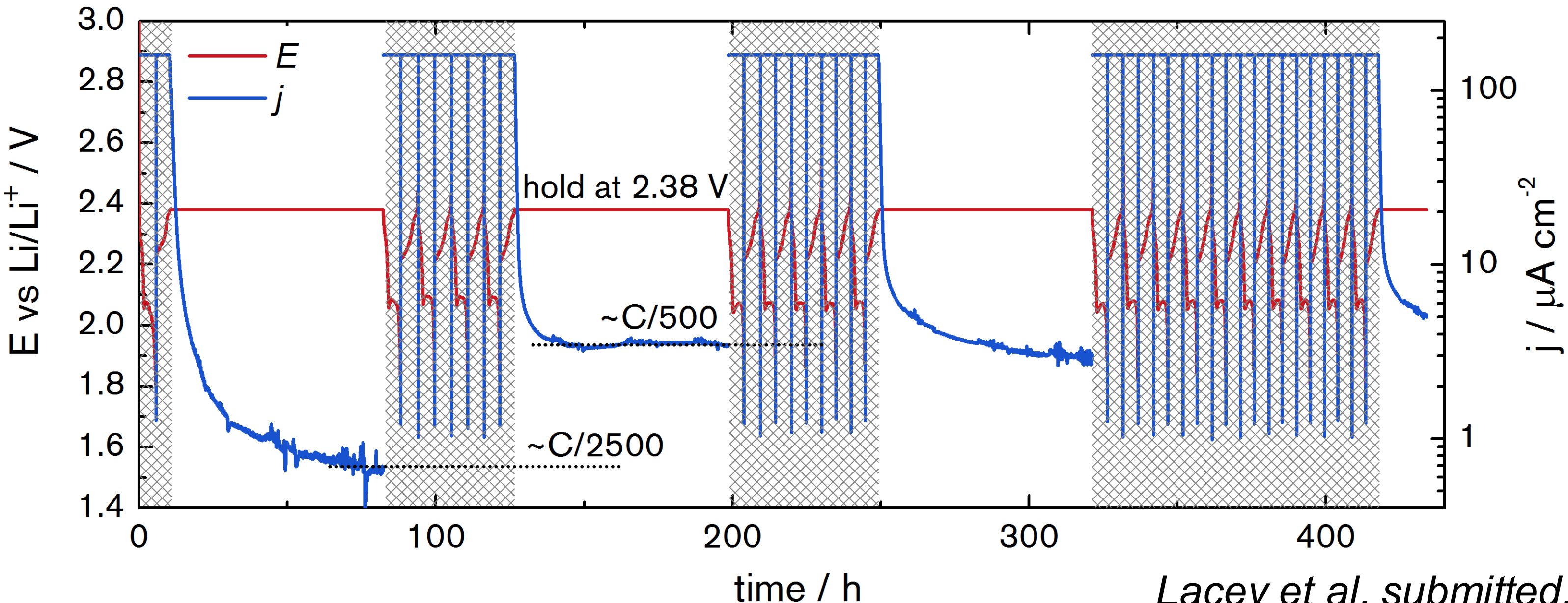
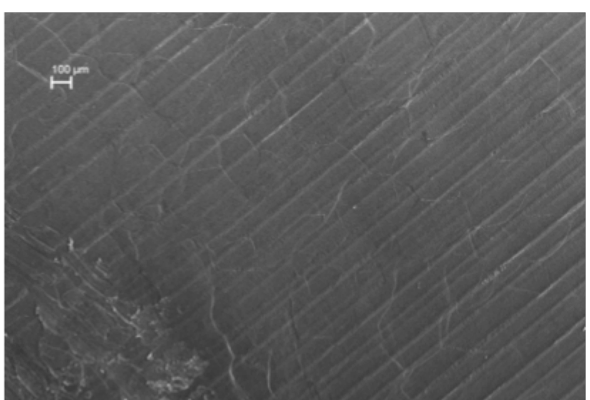
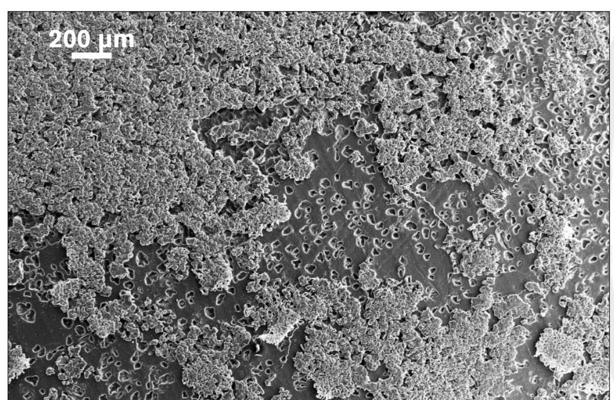
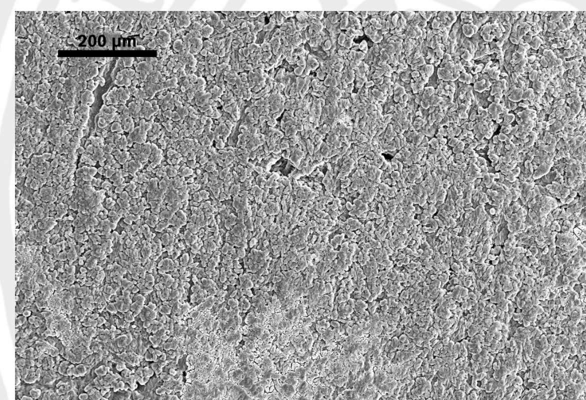
Negative electrode morphology



Lacey et al, submitted.







Longer-term changes in self-discharge

7 day rest every 10 cycles (C/10 rate)

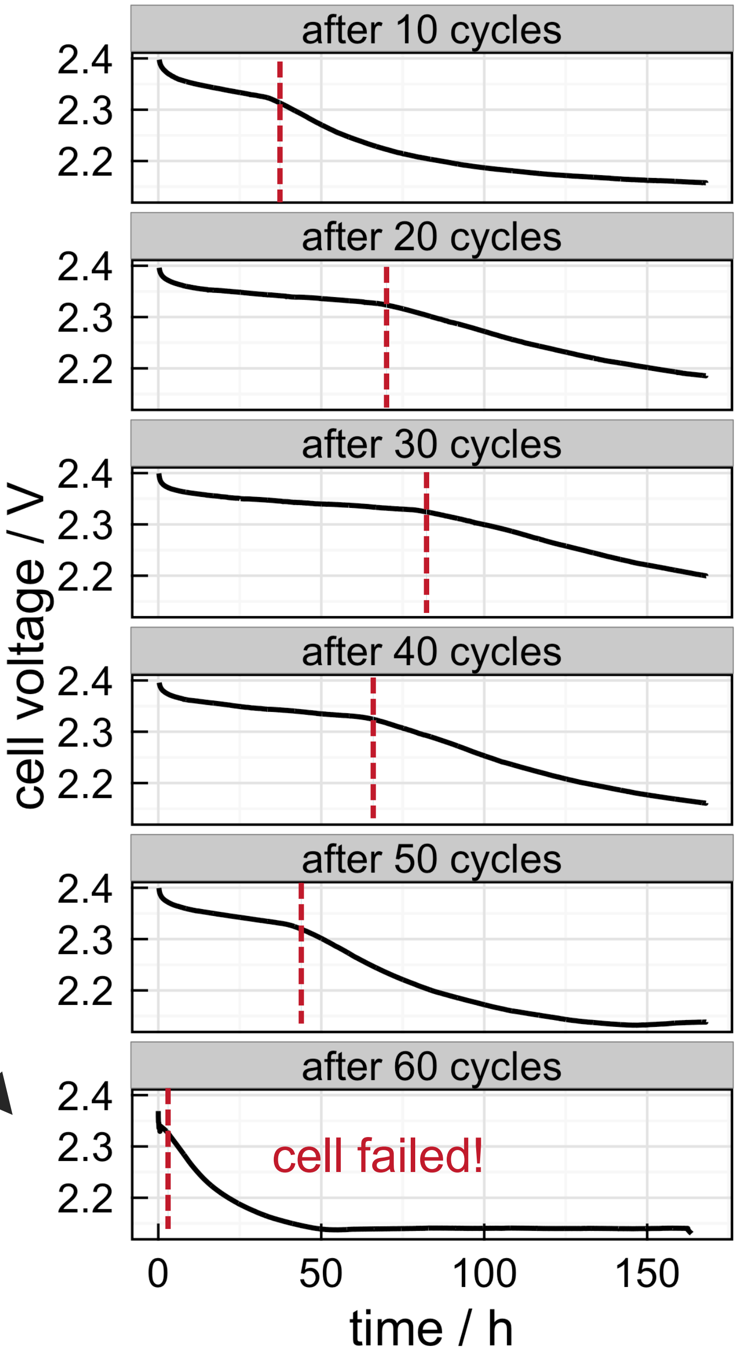
SEI growth?

Consumption of $LiNO_3$?

Electrolyte decomposition and eventual cell failure

(What is the effect of +ve electrode morphology?)

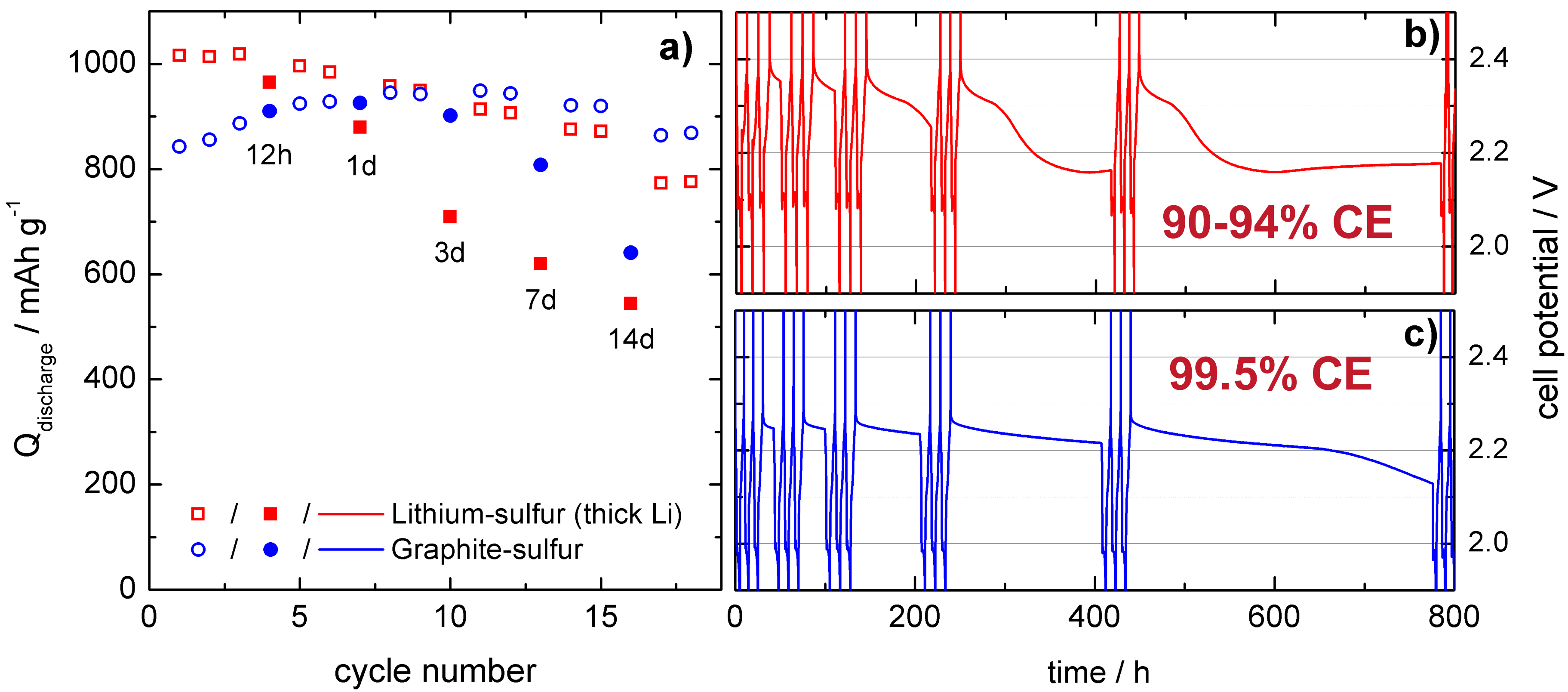
Cell failure after 60 cycles is much sooner than normal for continuous C/10 cycling.



Lithiated graphite vs lithium metal

Graphite cycling in DME:DOL enabled by protective binder

See presentation by Fabian Jeschull **tomorrow, 09:50** in here!



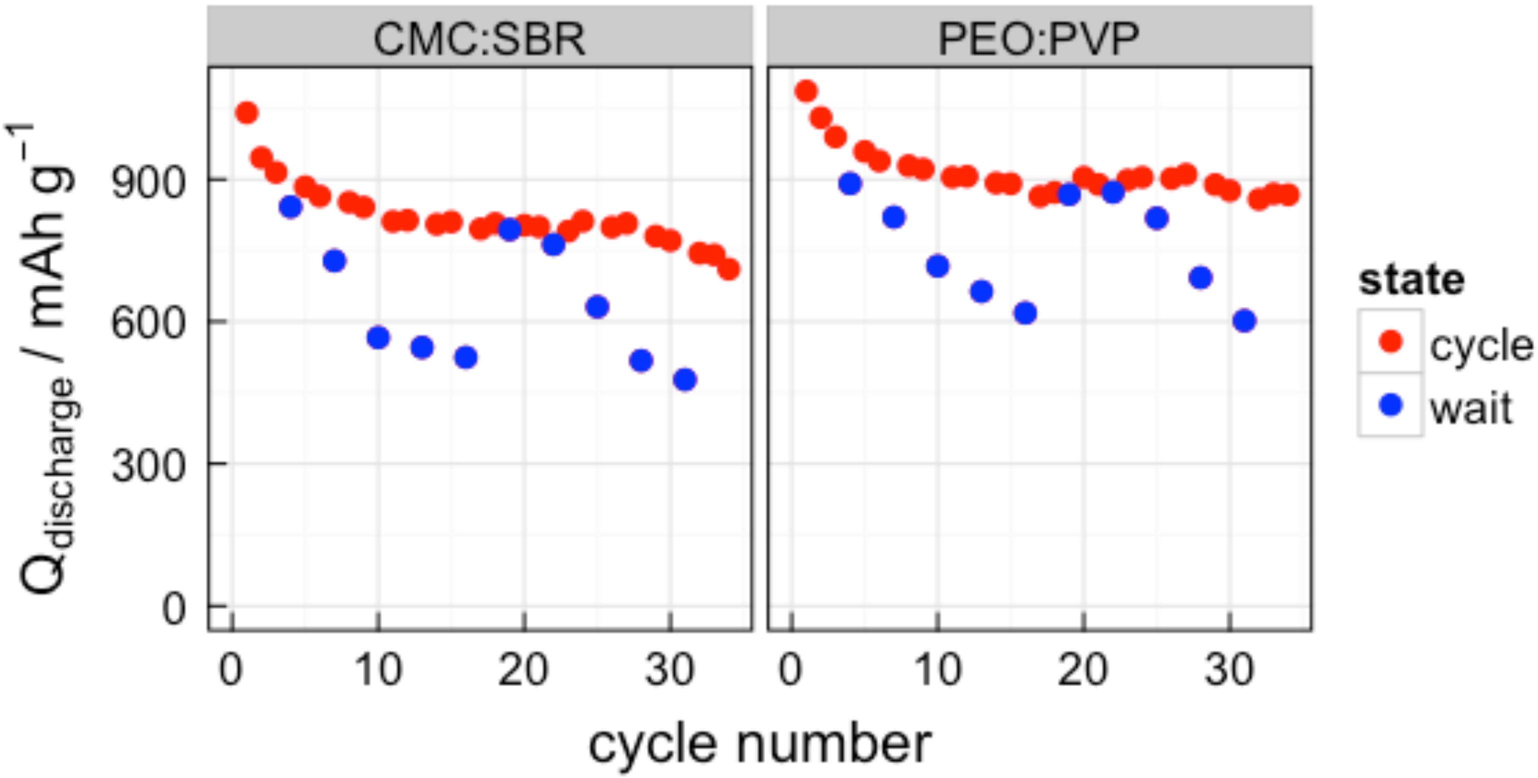
Higher interfacial stability → 5 or 6x slower self-discharge!

Jeschull et al, submitted

Functional binders

More recent results: 65% S (total), Ketjen Black, 2 – 3 mAh/cm²

C.E. @ C/10: **90-94%** **97-98%**



Self-discharge rate is roughly halved compared to CMC:SBR

Lacey et al, J. Power Sources 264, 8 (2014)
Lacey et al, manuscript in preparation

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Summary

1. **Beware the effect of excess electrolyte!**
   – Electrolyte/sulfur ratio is important for fair comparison, and further research into reducing this value is crucial

2. **Good capacity retention does not imply good control of polysulfides**
   – Coulombic efficiency can be a useful guide, but see point 1…

3. **Despite $LiNO_3$, self-discharge is still significant**

4. **Good reversibility of self discharge (in the short term) likely derives from the very slow conversion of PS to Li_2S at the anode**

5. **Alternative anodes and functional binders are among the many approaches which can mitigate self-discharge**

Acknowledgements

Experimental work:

Fabian Jeschull
Viking Österlund
Anurag Yalamanchili
Julia Maibach
Carl Tengstedt *(Scania CV AB)*

Collaboration and discussion:

Sören Thieme, Holger Althues
(Fraunhofer IWS)

Finance:

Era Net Transport project "MaLiSu"
Vinnova

For more information:

Presentation by Fabian Jeschull
tomorrow, **09:50**, in here

Functional binders:
M. J. Lacey *et al*, *J. Power Sources* **264C**, 8-14 (2014)

Graphite-sulfur:
F. Jeschull *et al*, *in submission*

Self-discharge
M. J. Lacey *et al*, *in submission*