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
  – $[\text{Li}_2\text{S}_x]$ 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.

20, 50, 100, 200, 400 mA charge

Research strategies

- ‘PS-insoluble’ electrolytes
- Ion-selective separators
- Interlayers
- Encapsulation
- Additives

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.

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

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

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

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

(filled points are discharge capacity after indicated number of days rest at OCV from charge)

Lacey et al, submitted.
2 weeks of self-discharge…
…in 8 seconds

Lacey et al, submitted.

Probe current

LSV @ 1 mV/s, every 4 hours

Cell/probe voltage

cell OCV
probe OCV
Redox shuttle drives S dissolution out of positive electrode.

Lacey et al, submitted.
On the -ve electrode...

(Li||Li cell, LiTFSI replaced by LiClO₄)

Lacey et al, submitted.
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 $\rightarrow$ 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
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 LiNO₃, 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 Li₂S at the anode**

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