Improving the performance of LiS cells in real conditions, a model-informed approach

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Revolutionary Electric Vehicle Battery

- Target: 400Wh/kg Li-S cells
- Physics-based models & reduced-order models
- Battery pack design, drive-cycle testing
Modelling aims

Improve performance of Li-S by developing modelling tools to

- Inform cell design
  - Form factor, number vs thickness of layers
  - Identify factors limiting performance for material development
- Make better use of available cells in applications
  - Main features of charge/discharge curves
  - Charge/discharge rate capability
  - Information about SOC and SOH
Equivalent circuit model for LiS

Equivalent circuit for LiS: $R_0$, $R_1$, $R_2$, $C_1$, $C_2$, and $V_{cell}$.

$R_0$ electrolyte and electronic resistivity

$R_1 + R_2 = R_{diff}$ charge transfer reactions, formation and dissolution of solid species

$R, C = f(I, SOC, T)$

Graphs showing voltage over time for different conditions.

Graphs showing the model comparison with experiment data.
Equivalent circuit model for LiS
Constant current predictions

Charge: good for all I
Discharge: good for very low I only

What gives OCV (How to measure Em)?
- hysteresis/history effect
- role of shuttle/self discharge

More on ECM: Talk by Daniel Auger, Cranfield University
The cause and importance of $R_0$ SoC estimation possible via cell resistance

- Experiment
- Assumed concentration-dependent conductivity
- 1D model with constant conductivity
- OD model with IRs drop
A zero-dimensional model for LiS

\[ S_8^0 + 4e^- \leftrightarrow 2S_4^{2-} \]
\[ S_4^{2-} + 4e^- \leftrightarrow 2S^{2-} \downarrow + S_2^{2-} \]

- Two-step electrochemical reaction and shuttle
- Nernst equations for equilibrium potentials
- Butler-Volmer for reaction currents
- Simple Li$_2$S precipitation/dissolution model

Charge/discharge a constant current
Predictions from the 0D model

- Charge/discharge curves retrieved with the same chemical and electrochemical mechanism
- Tracks battery ‘SOC’
  - V-plateau => V-reading
  - Shuttle => Coulomb counting

Discharge characteristics
Flat voltage plateau is caused by precipitation

\[ E_L = E^0_L + \frac{RT}{4F} \ln \left( c_L \frac{S^2_{4-}}{(S^{2-})^2 S^2_{2-}} \right) \]

Charging characteristics
Rate is limited by dissolution and shuttle rates

Capacity fade
Study by partial cycling

- 0.3C charge/0.3C discharge => 30% SoC
- Voltage/SoC drift, capacity fade & apparent cell death
- Poster by Teng Zhang, Imperial College
Partial cycling
Model predictions

- SOC drift caused by incomplete dissolution during charge
  - Driving force for precipitation can be much stronger than for dissolution
- Only retrieves stage 1 of partial cycling

Partial cycling
Model predictions including loss by shuttle

- The 3 stages are retrieved with the inclusion of shuttle loss
- Active sulfur mass: decreased by shuttle loss and precipitate accumulation
- Fixed current rate effectively increases as cell capacity decreases
  - higher voltage during charge

Partial cycling
Is partial recovery possible?

Capacity fade: Irreversible (shuttle) + Reversible (slow dissolution)

- Periodic slow charges extend cycling by dissolving accumulated Li$_2$S

Model predictions

- Model overestimates degradation from shuttle during recovery cycle
  => fine-tuning of degradation model needed

Limitations of the 0D model
No mass transport

=> Introduce mass transport via 1D model
1D model formulation

- PDE’s for species concentration (vs ODE’s)
- Flux equation of species mass
- Diffusion and migration

1D model predictions
Discharge rate is limited by slow diffusion

![Experiment vs model](image1)

Polysulfides temporarily trapped in cathode pores and/or the separator (mass transport limitation)
- Improve conductivity to improve power during discharge
- Can this capacity be recovered?

1D model predictions
Recovery of lost capacity upon discharge

- Extra capacity can be recovered after rest
- The higher the rate of the previous discharge, and the longer the rest, the more capacity is recovered
- Effect is similar to *charge redistribution* in supercapacitors

Discharge limitation: mass transfer or charge transfer?

- Li$_2$S surface coverage apparently increases with current.
- Discharge capacity may be reduced by increased charge transfer resistance.
- Voltage-dependent Li$_2$S nucleation rate proposed.

Mass transfer vs charge transfer

- Stepwise discharge: resistance & capacity are unaffected by current history
- Charge kink: Dependent on discharge SoC but NOT on discharge current

=> Surface passivation by Li$_2$S is independent of current
=> Discharge is limited by mass transfer

Zhang, T., Marinescu, M., Walus, S., Kovacik, P., Offer, G. What limits the rate capability of Li-S batteries: charge transfer or mass transfer, JECS, 2017 (accepted).
0D model with transport limitation

- Transport-limited reaction kinetics by Butler-Volmer equation
- Retrieved the correct stepwise discharge behaviour
- Also captured the kink at the beginning of charge

Zhang, T., Marinescu, M., Walus, S., Kovacik, P., Offer, G. What limits the rate capability of Li-S batteries: charge transfer or mass transfer, JECS, 2017 (accepted).
What we learnt from models

- Designing a sufficiently accurate ECM for LiS is not easy
  - Precipitation/dissolution occurs at time lengths similar to current rate for measuring OCV
  - For estimation/control use ECM based on understanding from physical models
  - Talk by Daniel Auger, Cranfield University

- A lot can be understood and optimised without knowing the exact charge/discharge reaction paths
  - Dissolution limits charging power
  - Mass transport limits discharge rate – slow diffusion
  - Precipitation/dissolution gives memory effect

- Developing tools to get the best out of cells in applications is equally important to improving cell performance
  - SOC estimation based on physical models is possible ($R_0$ for concentrated electrolyte)
  - Intelligent cycling strategies can improve performance
  - Thermal and electrical effects when going from one cell to a battery pack (Poster by Ian Hunt, ICL)
Next steps

• Nucleation/precipitation/dissolution must be understood to improve reversibility and charging rate
  • Chemical versus electrochemical
  • Dependence on current or potential
  • Evolution of active surface area

• Shuttle
  • During discharge versus rest versus charge

• Capacity fade
  • How much does the anode contribute (Poster by Sylwia Waluś, Oxis Energy)
  • Effect of electrolyte

• The effect of heat generation on the performance and ageing
LiS in use