

Towards a microscopic model for species transport in Lithium-Sulphur cells

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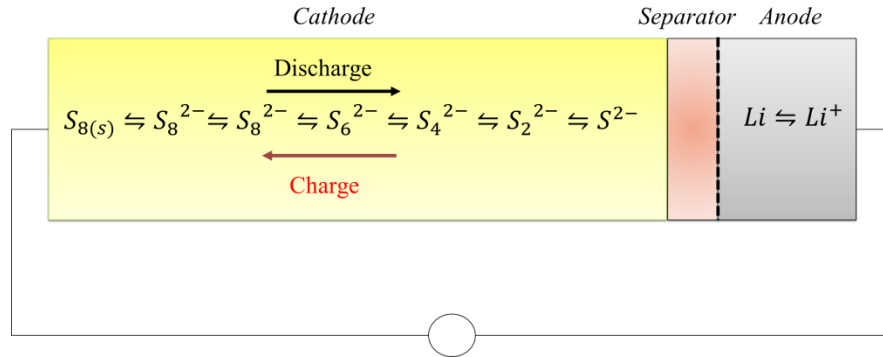


- OXIS energy have been working on Lithium Sulfur since 2005 in the Culham Science Centre (Oxfordshire, UK)
- Currently involved in the Revolutionary Electric Vehicle Battery project, in conjunction with Imperial College London, Cranfield University and Ricardo
 - Overall aim is to develop a 400Wh/kg cell
 - Also includes the development of an advanced energy system controller and the use of simulation-led R&D
- Modelling activities fall into four broad groups:
 - Battery management system (equivalent circuit)
 - Thermal behaviour
 - Homogeneous cell models
 - Microscopic models

COMSOL Multiphysics



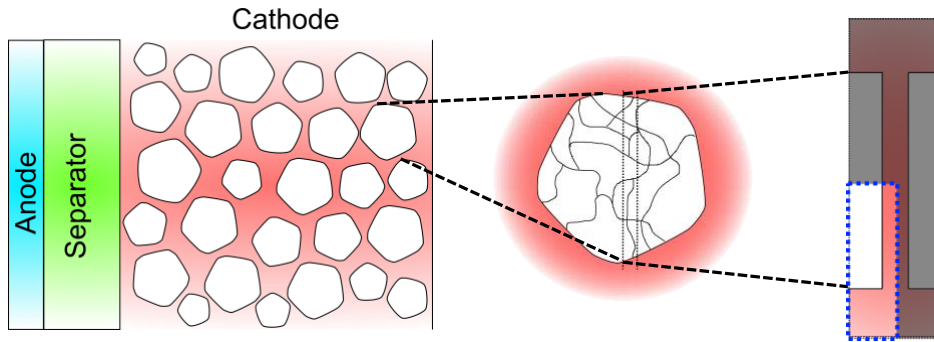
- Overall cell discharge reaction: $16 Li + S_8 \rightleftharpoons 8 Li_2S$
- Process characterised by a cascade of sulfur reduction reactions at the electrode/electrolyte interface, from S_8^{2-} to S^{2-}



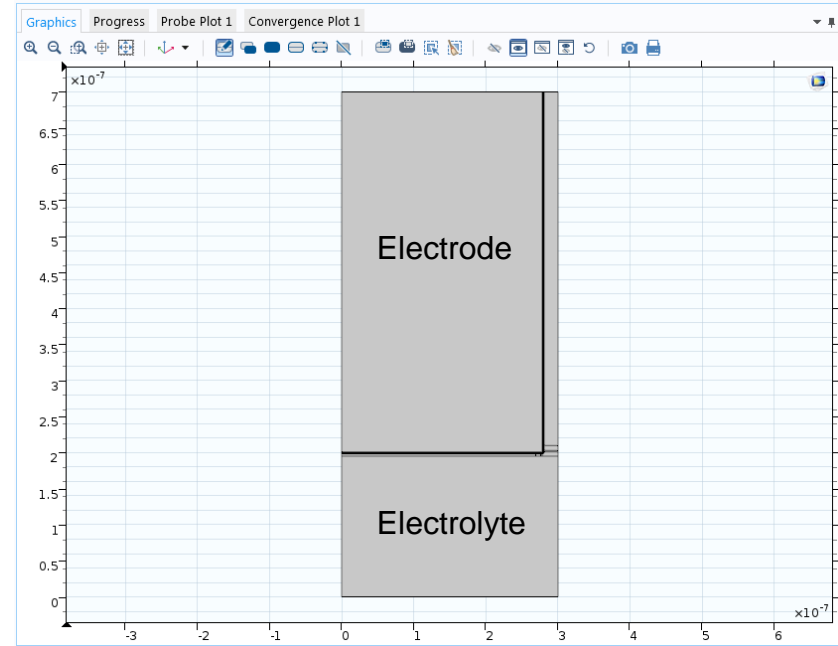
- True reaction path much more complex – multiple chemical as well as electrochemical steps¹.
- No intercalation, but porosity and reactive surface area depend on how and where S_8 and Li_2S_n precipitate at the end of charge/discharge.
- Most reactions occur in the electrolyte phase

- Cathode porosity affects cell performance:
 - Low porosity (macroporous) has low performance due to low electrochemically active surface area
 - High porosity (microporous) has low performance, despite a high active surface area
- Can we understand this in terms of species locations in the porous network?

1. M. Wild *et al*, "Lithium Sulfur Batteries, A Mechanistic Review," *Energy Environ. Sci.*, 2015, Accepted Manuscript



- Assume cathode is made from agglomerates separated by macropores
- Within each agglomerate is a meso/microporous network
- Simplify this to a slit pore geometry
- Use symmetry to simplify the model and input to COMSOL

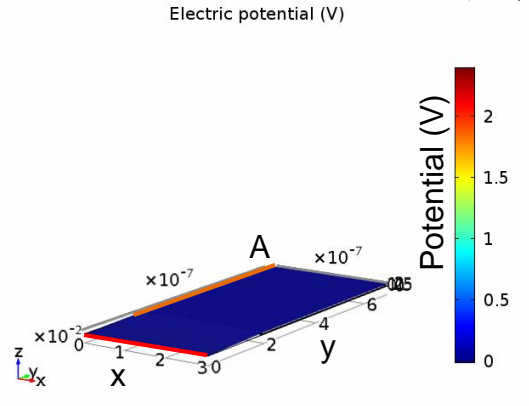
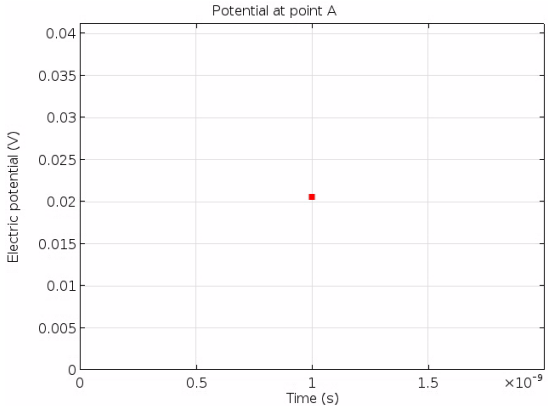
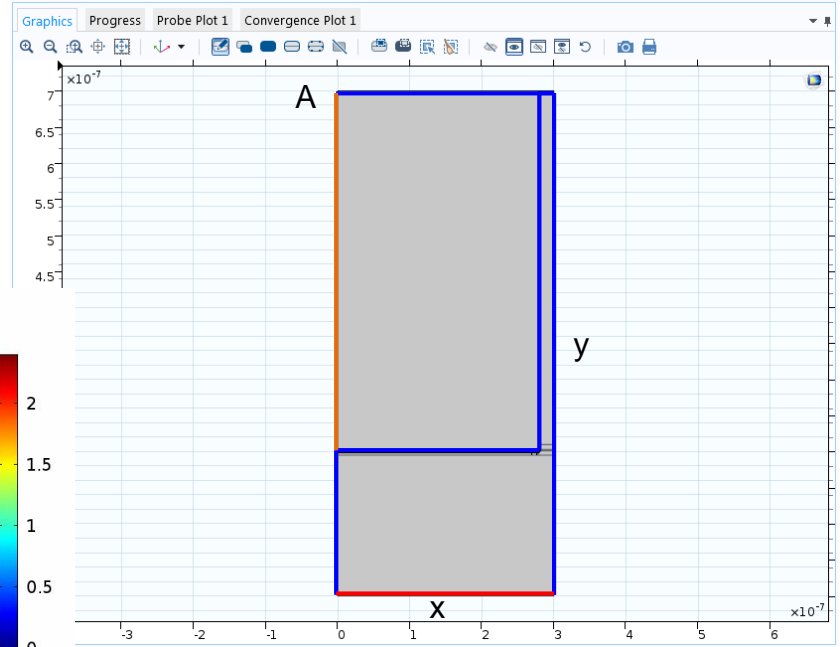


- Hard-sphere volume of electrolyte species accounted for

$$\mu_i = k_B T \ln c_i + z_i e_o \phi + \mu_i^{ex}$$

- Species transport described by modified Nernst-Planck equation

- COMSOL modules used:
 - Poisson equation module
 - Diffusion Migration Excluded volume
 - General form pde module for Nernst-Planck equation



• Applied potential
Potential at point A

Surface plot of potential across domain

Results – pore width and applied voltage

Assume four mobile species in electrolyte:

| Species | Charge | Radius (nm) |
|---------|--------|-------------|
| c_1 | -1 | 0.3 |
| c_2 | 1 | 0.3 |
| c_3 | 0 | 0.3 |
| c_4 | 0 | 0.3 |

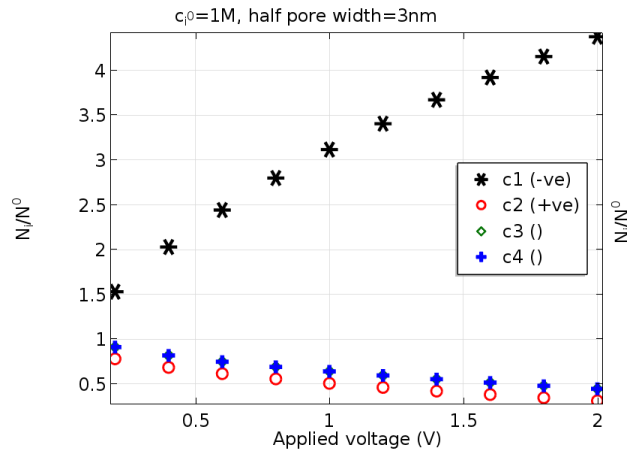
Initial concentration $c_i^0 = 1M$

Calculate the ratio of the number of ions in the charged pore to the number in an uncharged pore:

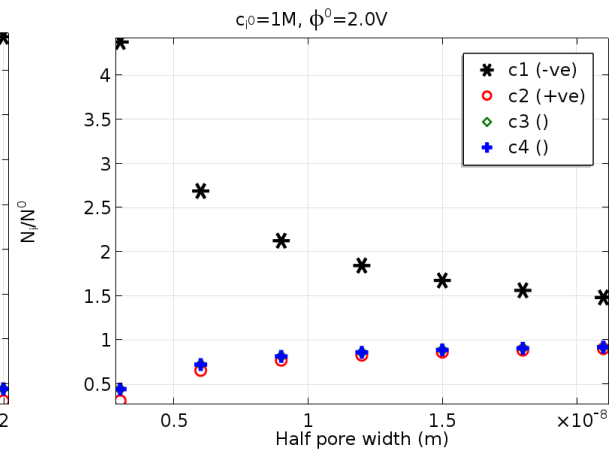
$$\frac{N_i}{N^0} = \frac{\int dA c_i}{\int dA c_i^0}$$

$\frac{N_i}{N^0} > 1$ indicates absorption of species into the pore

Voltage dependence, narrow pore



Pore width dependence, high potential



- Counter-ions (negative species) absorbed into mesopore
- Co-ions *and* neutral species pushed out into macropore/bulk
- Effect stronger as voltage increased or pore size decreased
- Purely an effect of ion crowding (i.e. accounting for the ion volume)

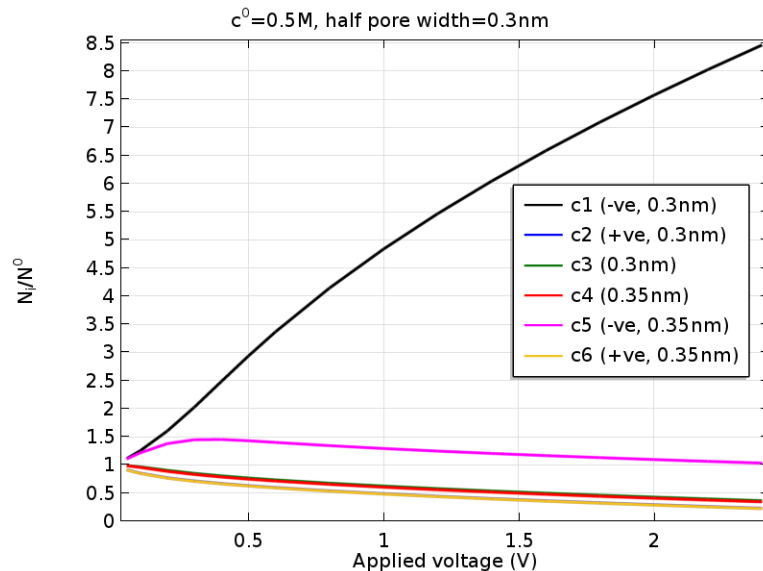
Results – ion size with more than one counter-ion species

In an Li-S cell we have more than one charge carrying species, all of different sizes.

Now we consider what happens in an electrolyte with 6 species:

| Species | Charge | Radius (nm) |
|---------|--------|-------------|
| c_1 | -1 | 0.3 |
| c_2 | +1 | 0.3 |
| c_3 | 0 | 0.3 |
| c_4 | 0 | 0.35 |
| c_5 | -1 | 0.35 |
| c_6 | +1 | 0.35 |

Initial concentration $c_i^0 = 0.5M$



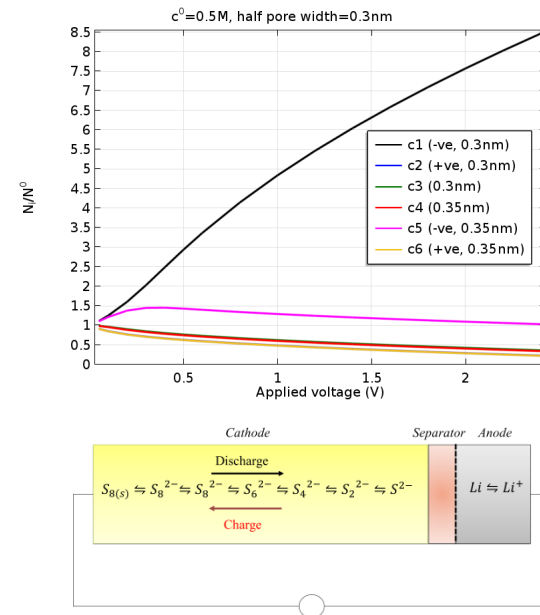
- As a counter-ion, c_5 is initially absorbed into the pore
- At higher potentials, the larger size of c_5 means that it is displaced by c_1 , excluding it from the pore, along with the co-ions and neutral species.

What does this mean for Li-S cell behaviour?

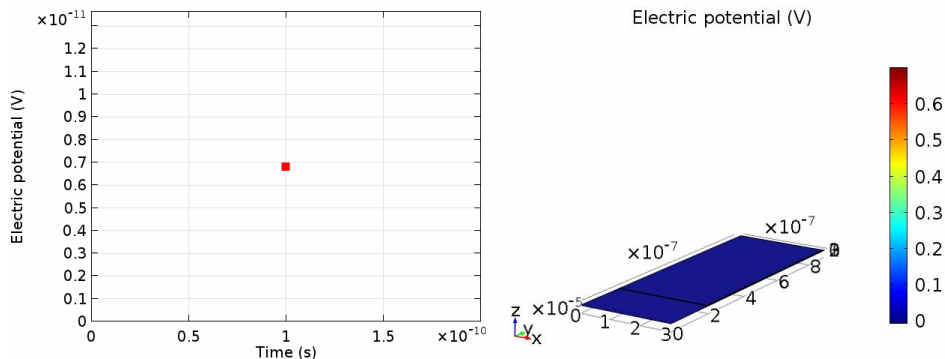
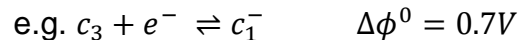
- We expect high order polysulfides to be larger than low order species.

$$r_{S_8^{2-}} > r_{S_6^{2-}} > r_{S_4^{2-}} > r_{S_2^{2-}} > r_{S^{2-}}$$

- Higher order species should tend to accumulate in larger pores.
 - Implies that different electrochemical reactions will dominate in different parts of the macro/micro-structure.
- What about precipitation?
 - This involves Li^+ and S_n^{2-} combining to form neutral Li_2S_n , which then agglomerates.
 - Increased prevalence of Li^+ and neutral species suggests that precipitation occurs in larger pores:
 - Blocking of larger pores, restricting species transport through the cell?
 - Blocking of mesopore entrances, preventing replenishment of active species?



- Addition of electrochemical reactions at the electrode/electrolyte interface:



- Plan to investigate simple combinations of chemical and electrochemical reactions.
- Inclusion of precipitation
- Introduces significant problems with convergence:
 - Meshing, element order and tolerance at electrode/electrolyte interface is crucial.
- G.Minton, L. Lue, “The influence of excluded volume and ion polarizability on the capacitance of the electric double layer”

Thanks for listening

Questions?