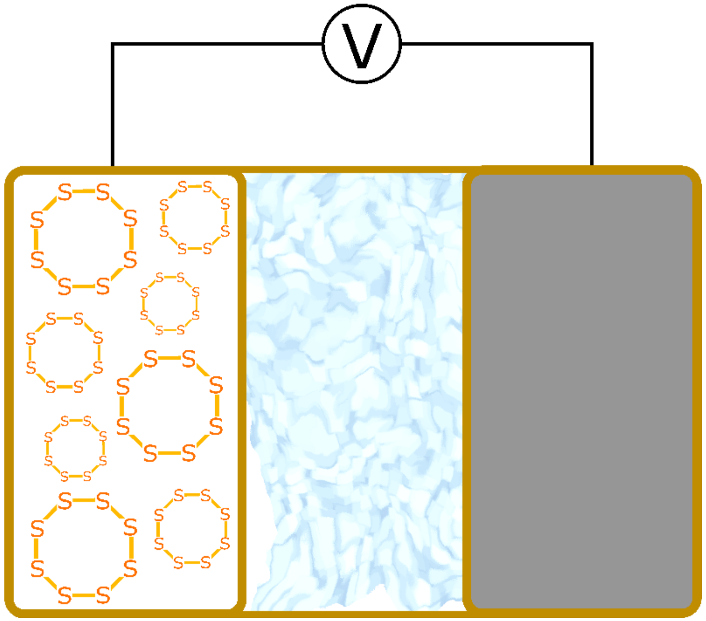
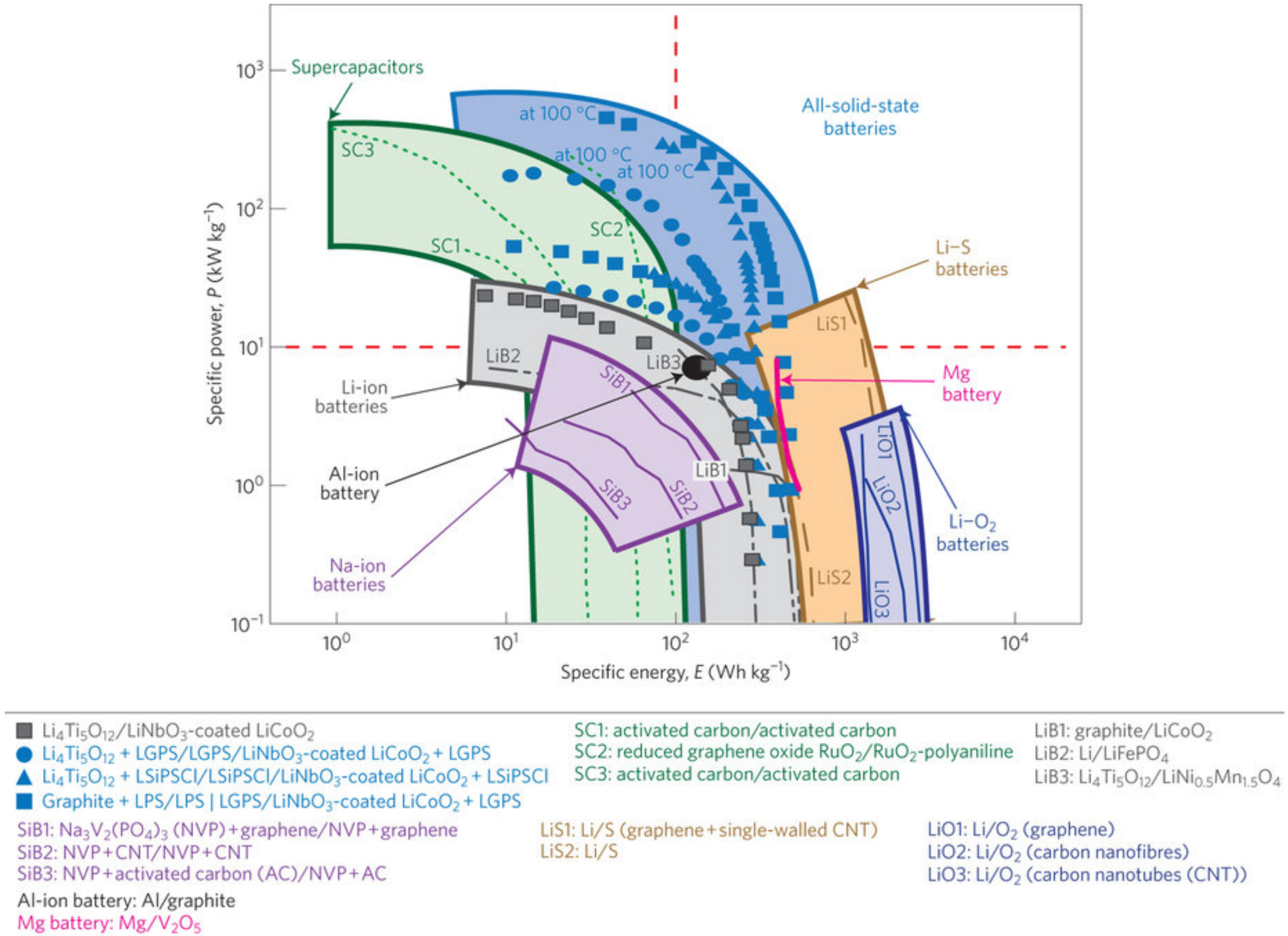
Lithium–Sulfur batteries and discharge products from cycling



Molleigh Preefer
MTRL 286G, Spring 2016

See, K. A.; Leskes, M.; Griffin, J. M.; Britto, S.; Matthews, P. D.; Emly, A.; Van der Ven, A.; Wright, D.S.; Morris, A.J.; Grey, C.P.; Seshadri, R. **Ab Initio Structure Search and in Situ ^{7}Li NMR Studies of Discharge Products in the Li–S Battery System.** *Journal of the American Chemical Society*, 2014, *136*(46), 16368-16377.

Why Li–S batteries?



Kato, Y.; Hori, S.; Saito, T.; Suzuki, K.; Hirayama, M.; Mitsui, A.; Yonemura, M.; Iba, H.; Kanno, R. High-power all-solid-state batteries using sulfide superionic conductors. *Nature Energy*, 2016, *1*, 16030.

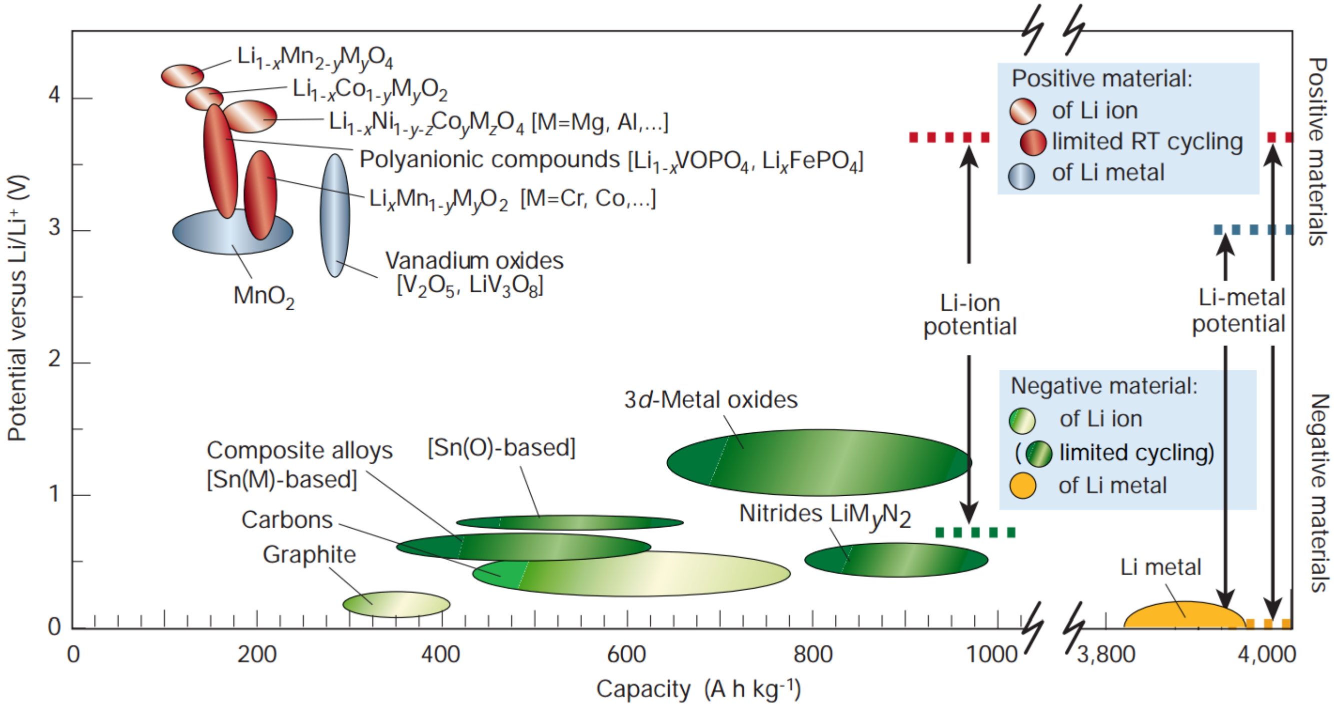
Cathode: why sulfur?

Recovered sulfur as an industrial side product of oil refining in British Columbia

- Inexpensive
- Abundant
- Non-toxic
- High theoretical capacity (1672 $mAhg^{-1}$)

Wikimedia commons

Anode: why lithium?

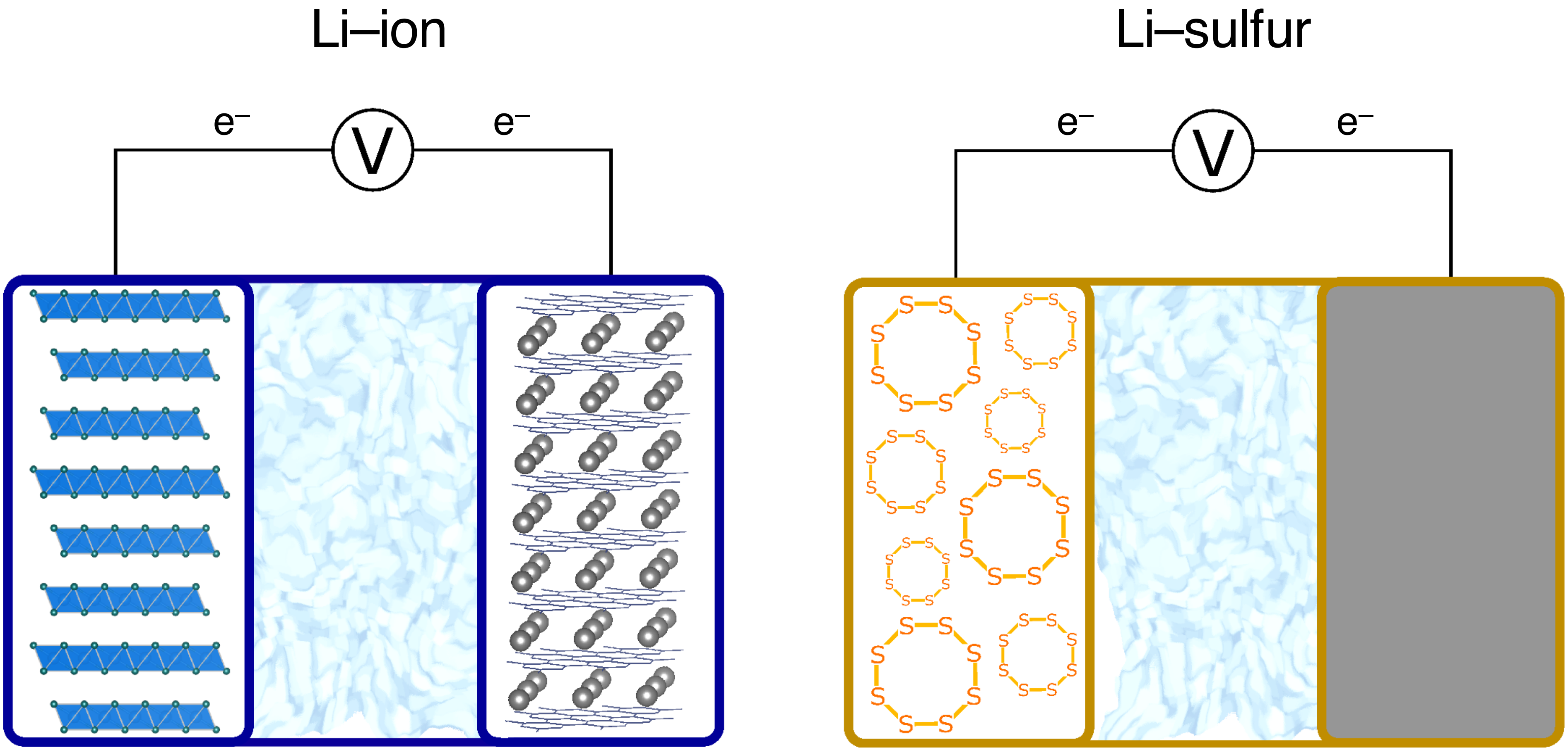


Graphite (typically used in Li–ion batteries) has a theoretical specific capacity of 372 $mAhg^{-1}$ (operating capacity of ~350 $mAhg^{-1}$) which is incompatible with a sulfur cathode

Li metal has a theoretical specific capacity of 3860 $mAhg^{-1}$

Tarascon, J-M., and Armand, M. Issues and challenges facing rechargeable lithium batteries. *Nature,* 2001, *414*(6861), 359-367.

The difference between Li–S and Li–ion



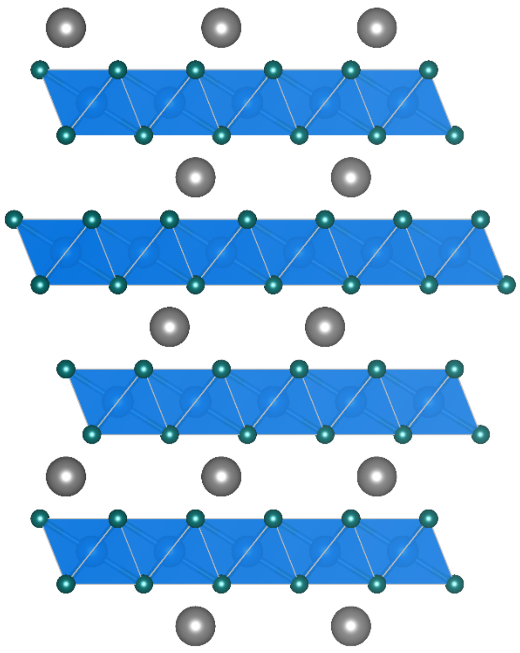
Cathode: $Li_{1-x}CoO_2$
Anode: Li_xC_6

Cathode: Sulfur
Anode: Lithium metal

Charged cathode structures

Li–ion cathode

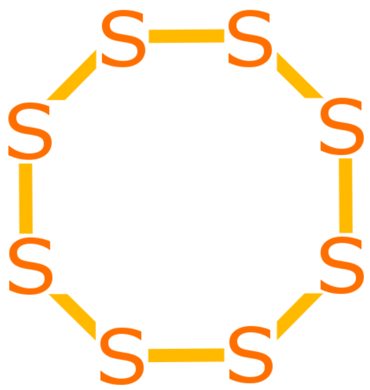
Li–sulfur cathode



charge

delithiate

oxidize



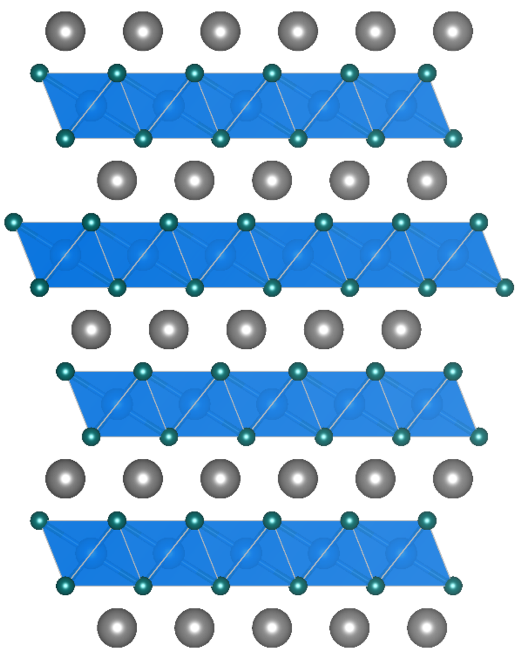
Cathode: $Li_{1-x}CoO_2$
Anode: Li_xC_6

Cathode: Sulfur
Anode: Lithium metal

Discharged cathode structures

Li–ion cathode

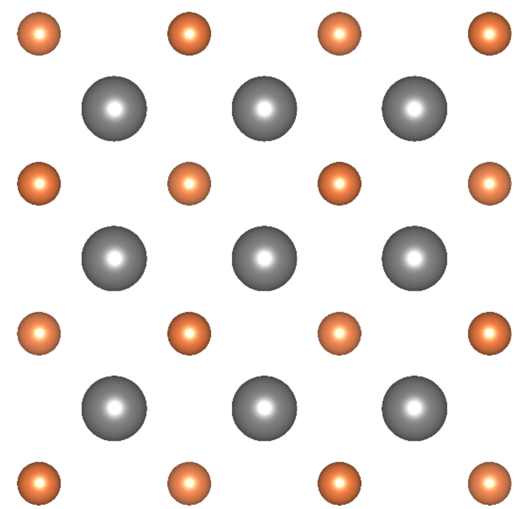
Li–sulfur cathode



discharge

lithiate

reduce



Cathode: $Li_{1-x}CoO_2$

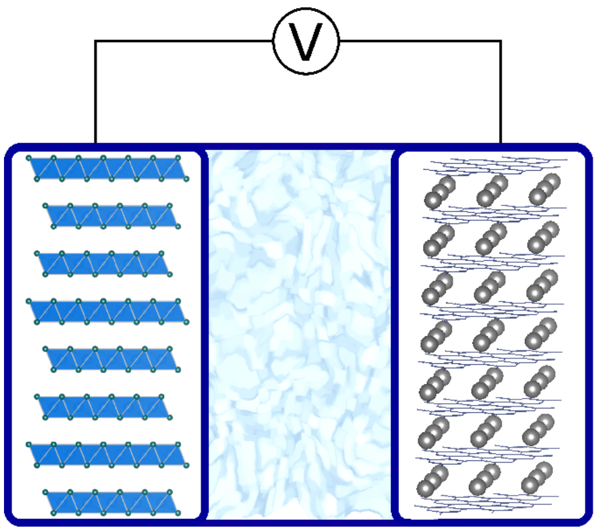
Anode: Li_xC_6

Cathode: Sulfur

Anode: Lithium metal

Capacity of Li–S vs Li–ion

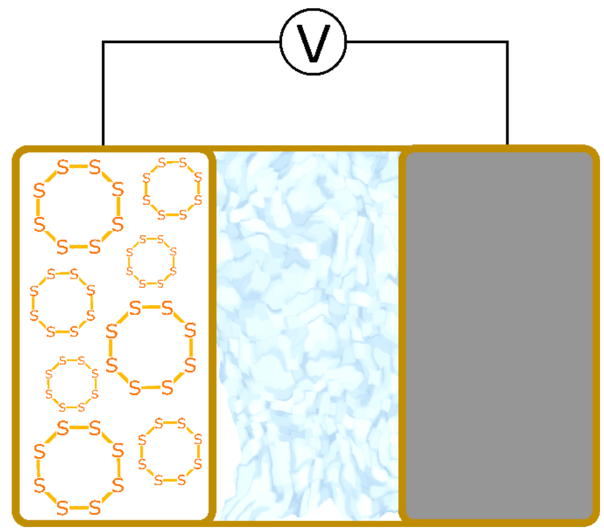
Li–ion



Theoretical capacity $LiCoO_2$:
274 mAhg^{-1}

Structural limitation of capacity:
~150 mAhg^{-1}

Li–sulfur



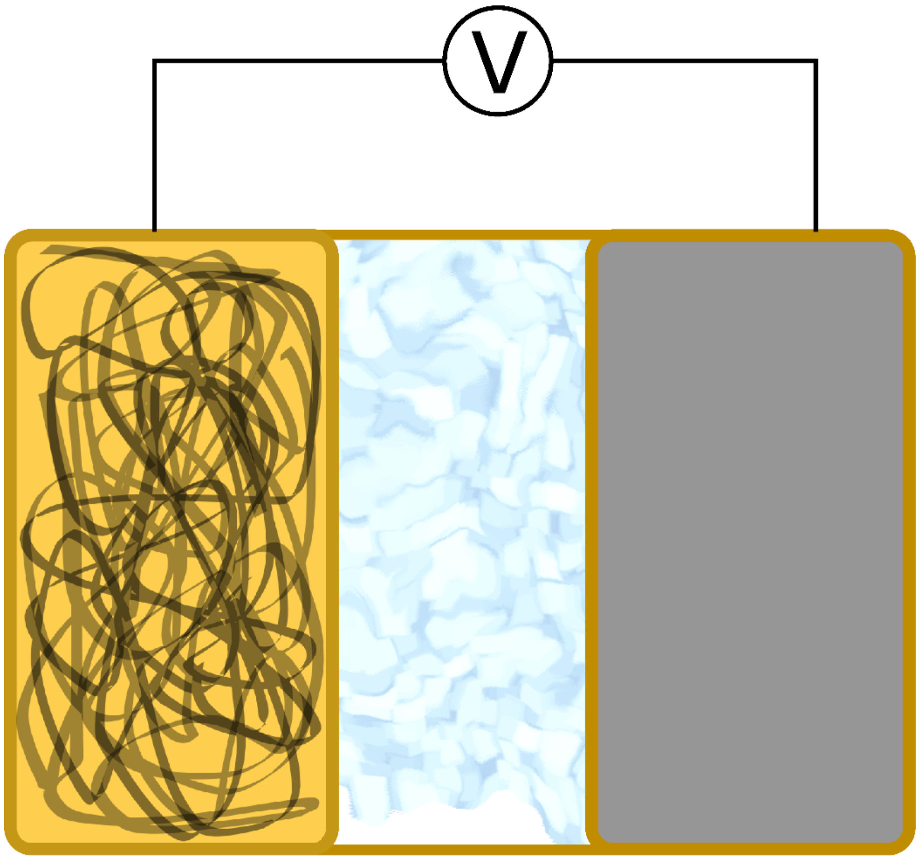
Theoretical capacity:

$$\frac{2\ \text{mol e}^-}{1\ \text{mol S}} \cdot \frac{96485\,\frac{\text{C}}{\text{mol e}^-}}{32.06\,\frac{\text{g}}{\text{mol S}}} \cdot \frac{1\ \text{mAh}}{3.6\ \text{C}}$$

=1672 mAhg^{-1}

Li–S challenges

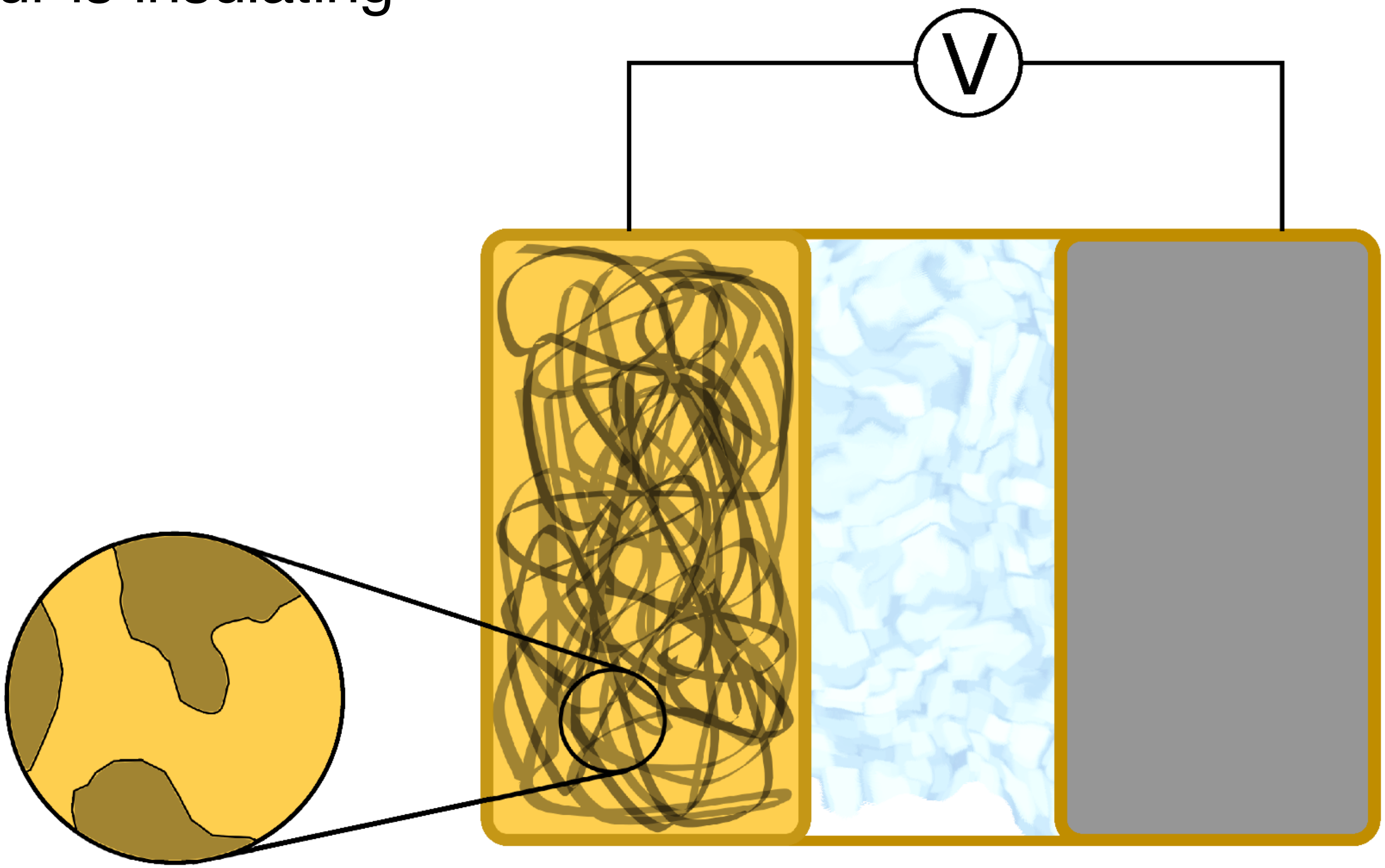
1. Sulfur is insulating



The cathode must include a mixture of conducting carbon and sulfur to get sufficient charge and ion mobility needed for battery cycling

Li–S challenges

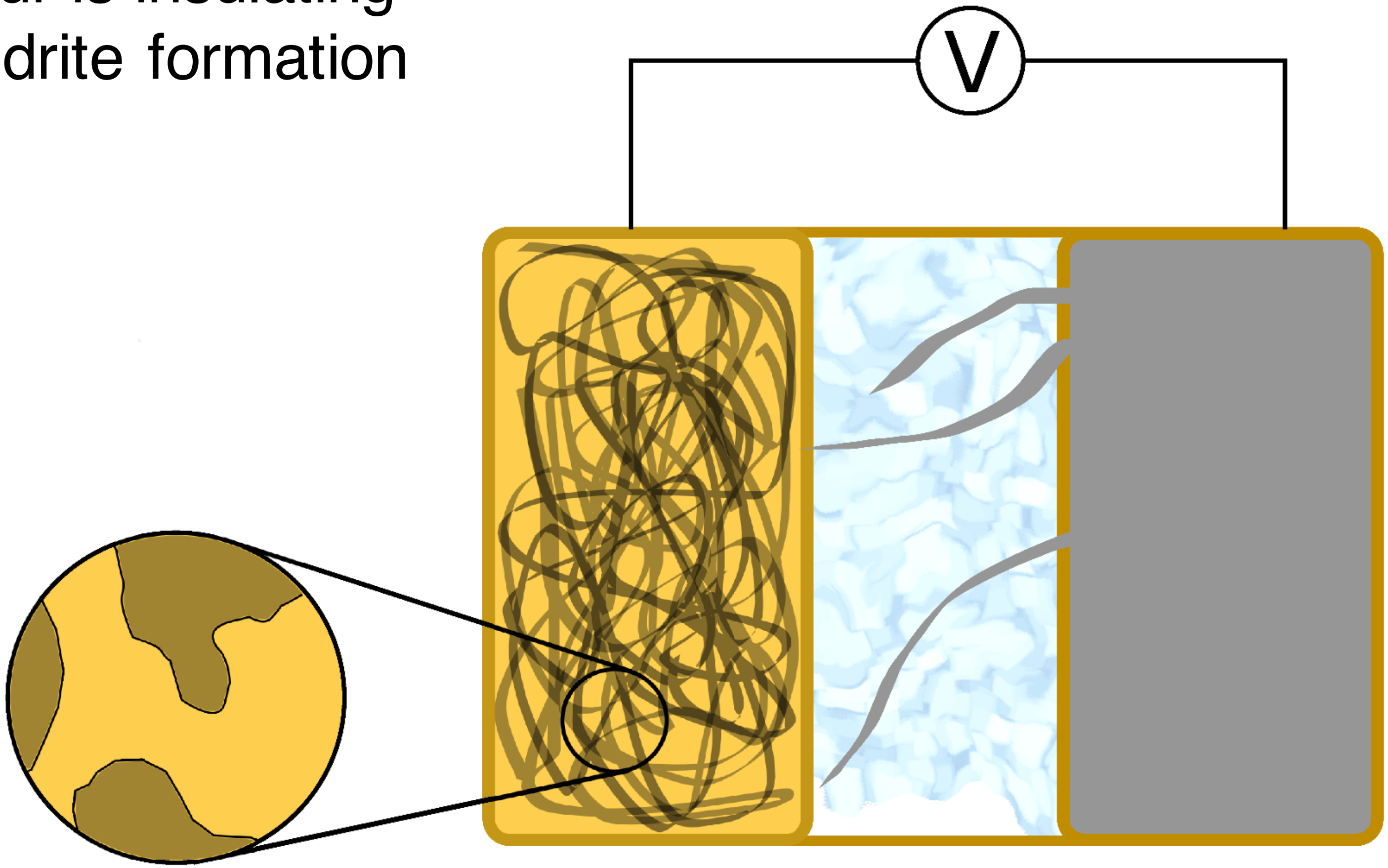
1. Sulfur is insulating



Adding conducting carbon presents an engineering problem to get around the issue of having distinct domains of carbon and sulfur

Li–S challenges

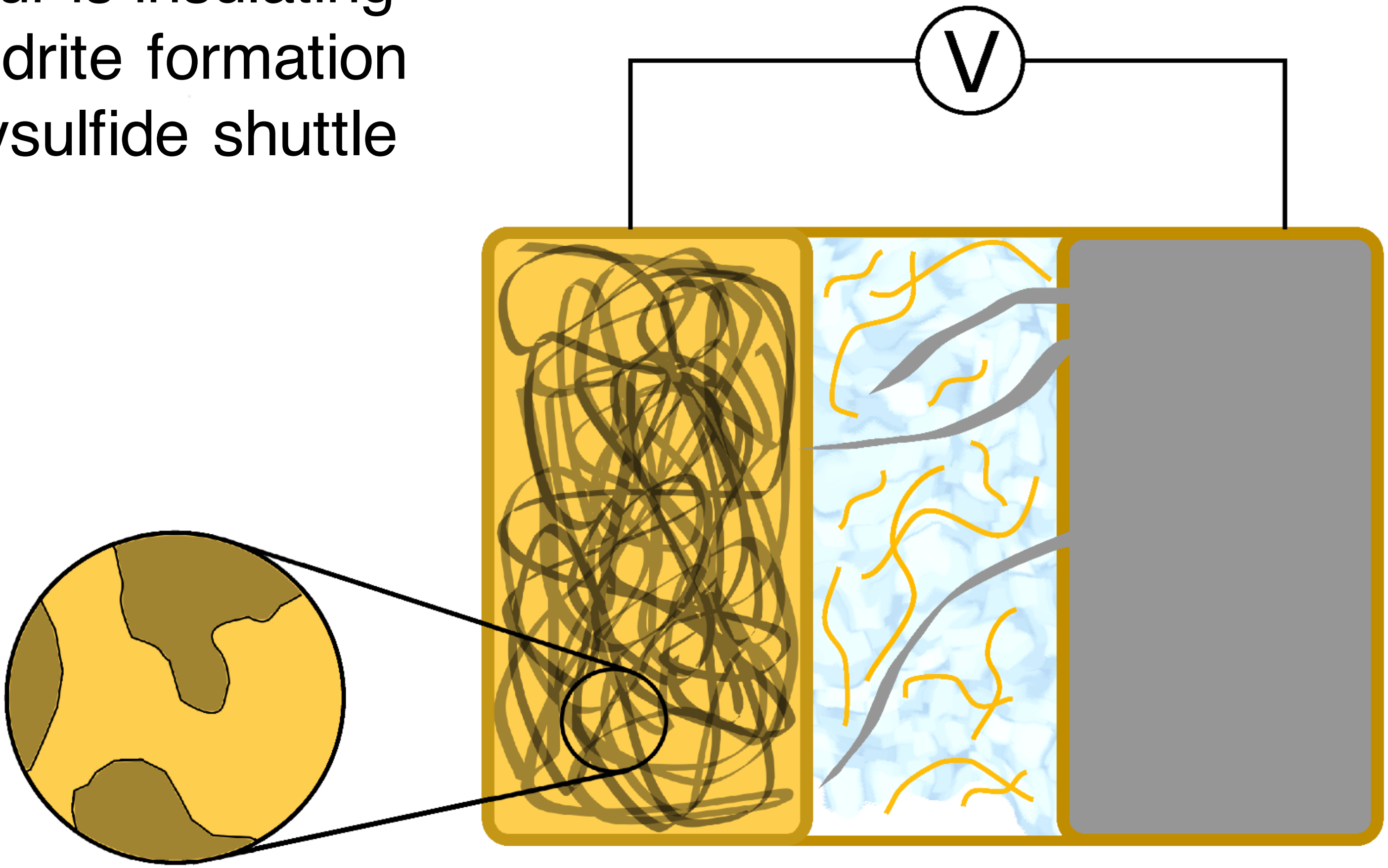
1. Sulfur is insulating
2. Dendrite formation



Dendrites can be atomically thin fibers of Li that extend from the anode to the cathode over many cycles and cause short-circuiting + safety concerns

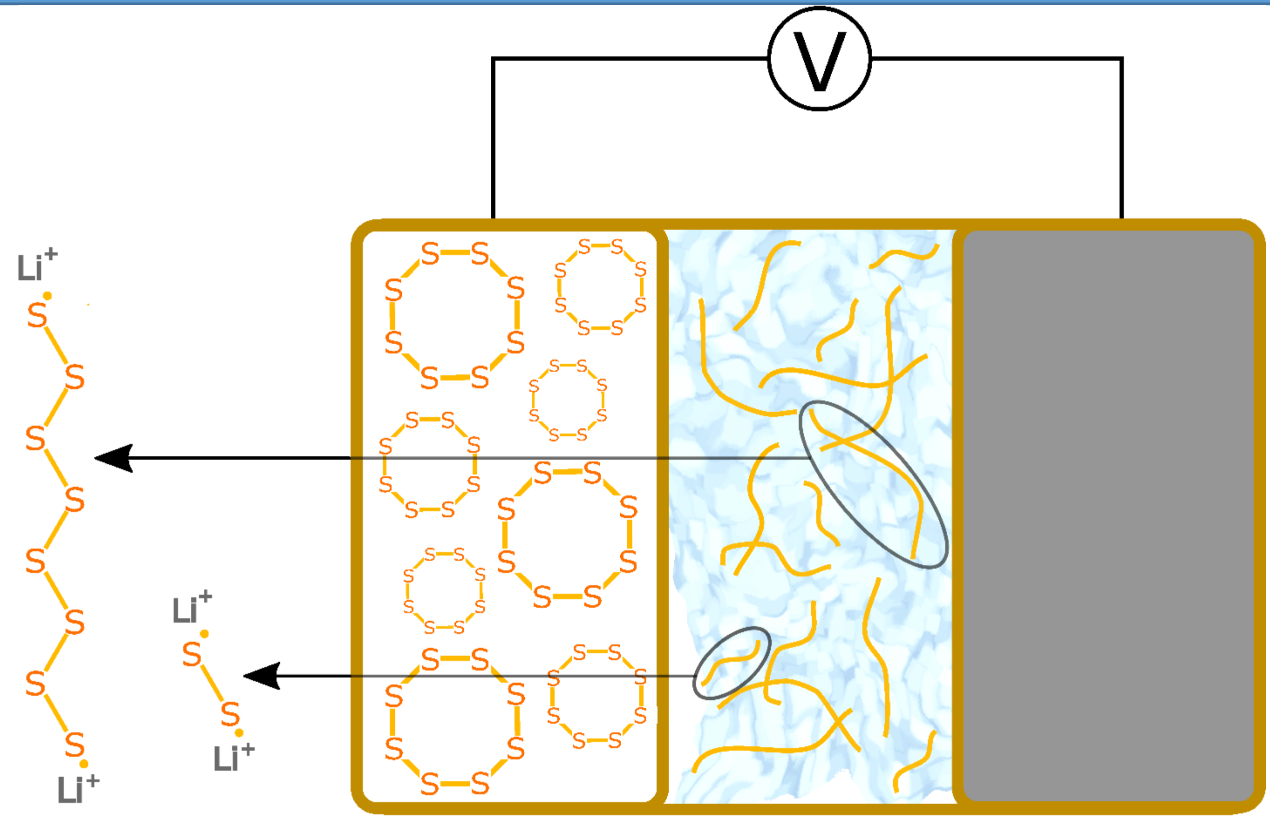
Li–S challenges

1. Sulfur is insulating
2. Dendrite formation
3. Polysulfide shuttle



Chains of diradical sulfur and their counter lithium cations solubilize in the liquid electrolyte during discharge, causing capacity fade

Polysulfide chains participate in redox and contribute to capacity fade



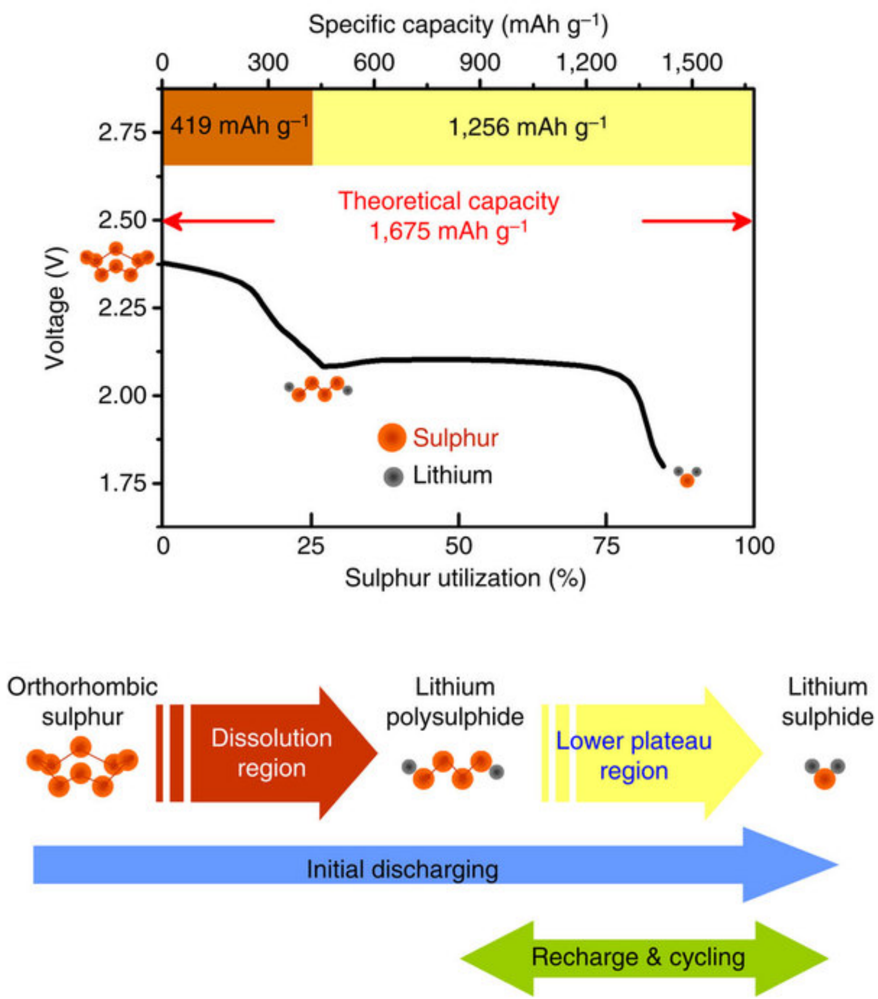
S_2^{2-} near the cathode can further reduce to create Li_2S, adding to the capacity

Long-chain polysulfides shuttle to the anode and become reduced, creating short-chain polysulfides

Short-chain polysulfides shuttle back to the cathode and form long-chain polysulfides again, leading to loss of active material (capacity fade)

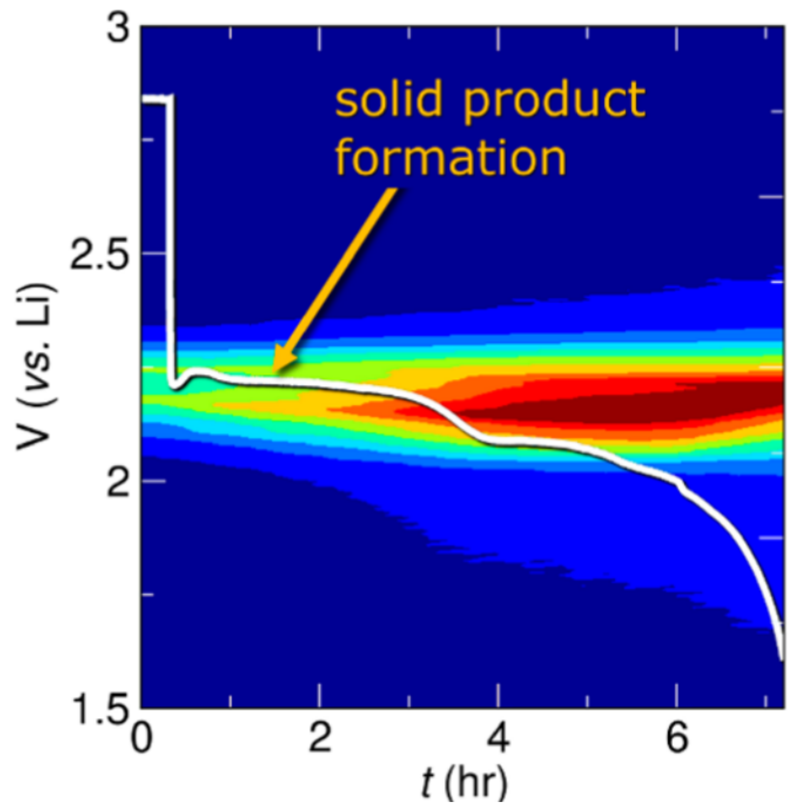
Debate of proposed discharge pathways

Series of solution reactions to form Li_2S



Su, Y. S., Fu, Y., Cochell, T., Manthiram, A. A strategic approach to recharging lithium-sulphur batteries for long cycle life. *Nature communications*, 2013, *4*(2985).

Li_2S forms from the beginning



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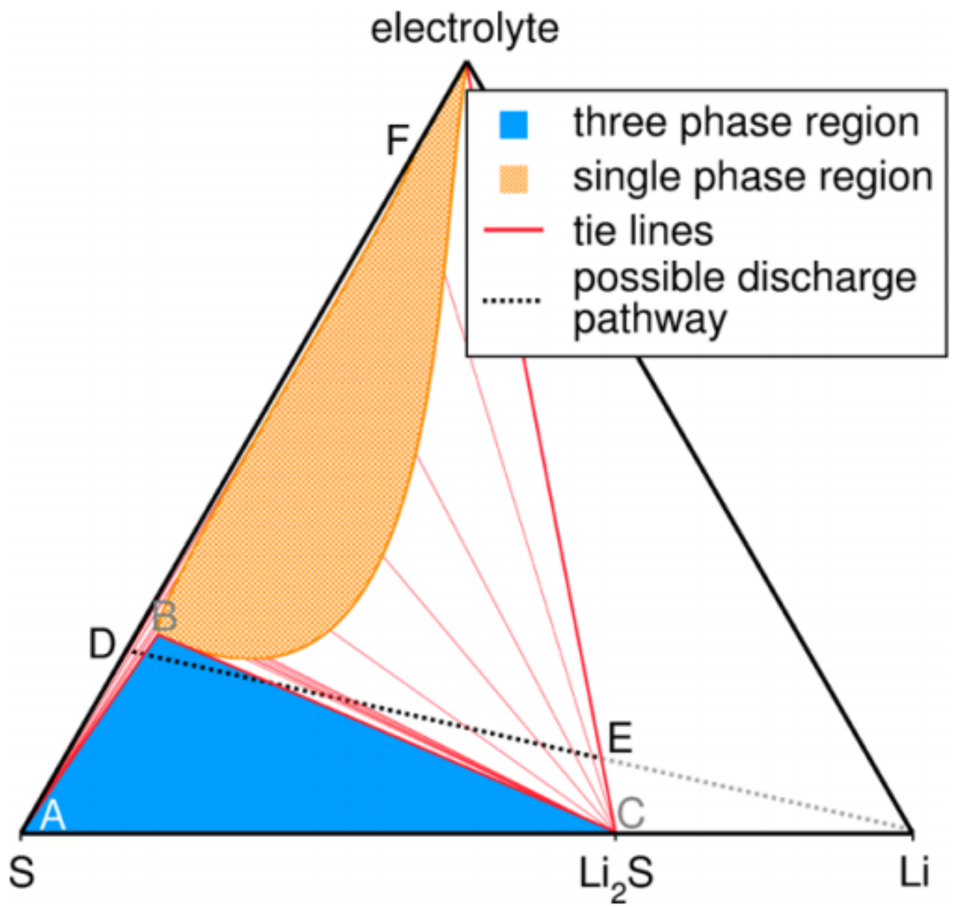
Ab Initio Structure Search and in situ ^{7}Li NMR Studies of Discharge Products in the Li–S Battery System



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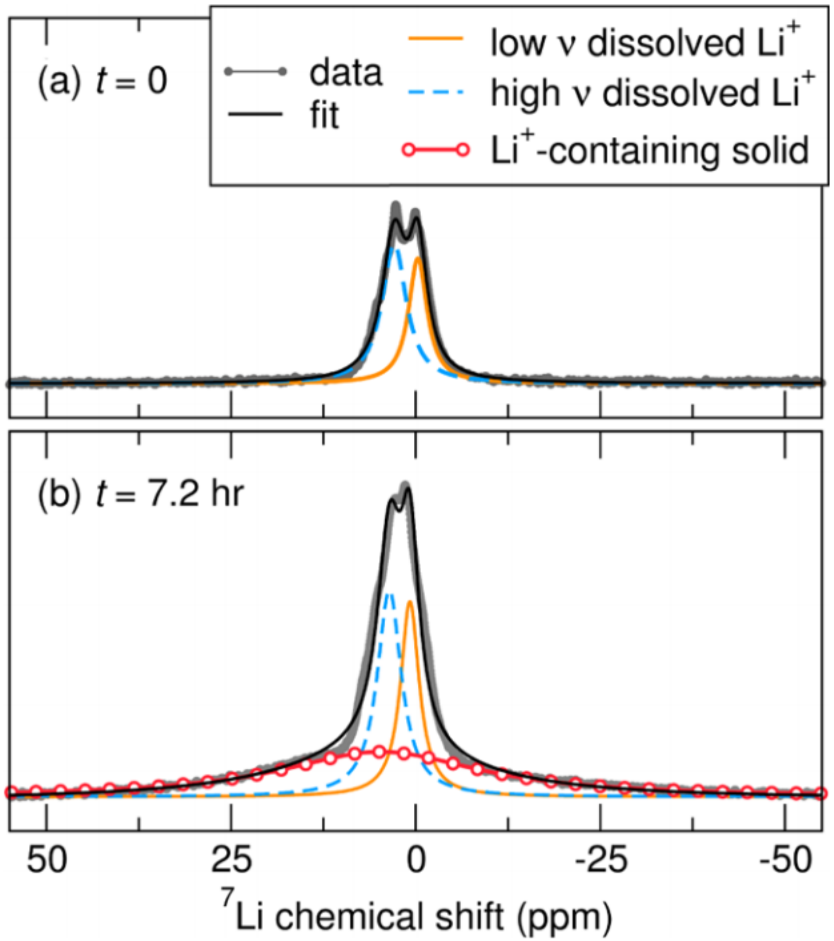
Benefit of in situ ^{7}Li NMR is the ability to characterize solids without crystallinity and dissolved species



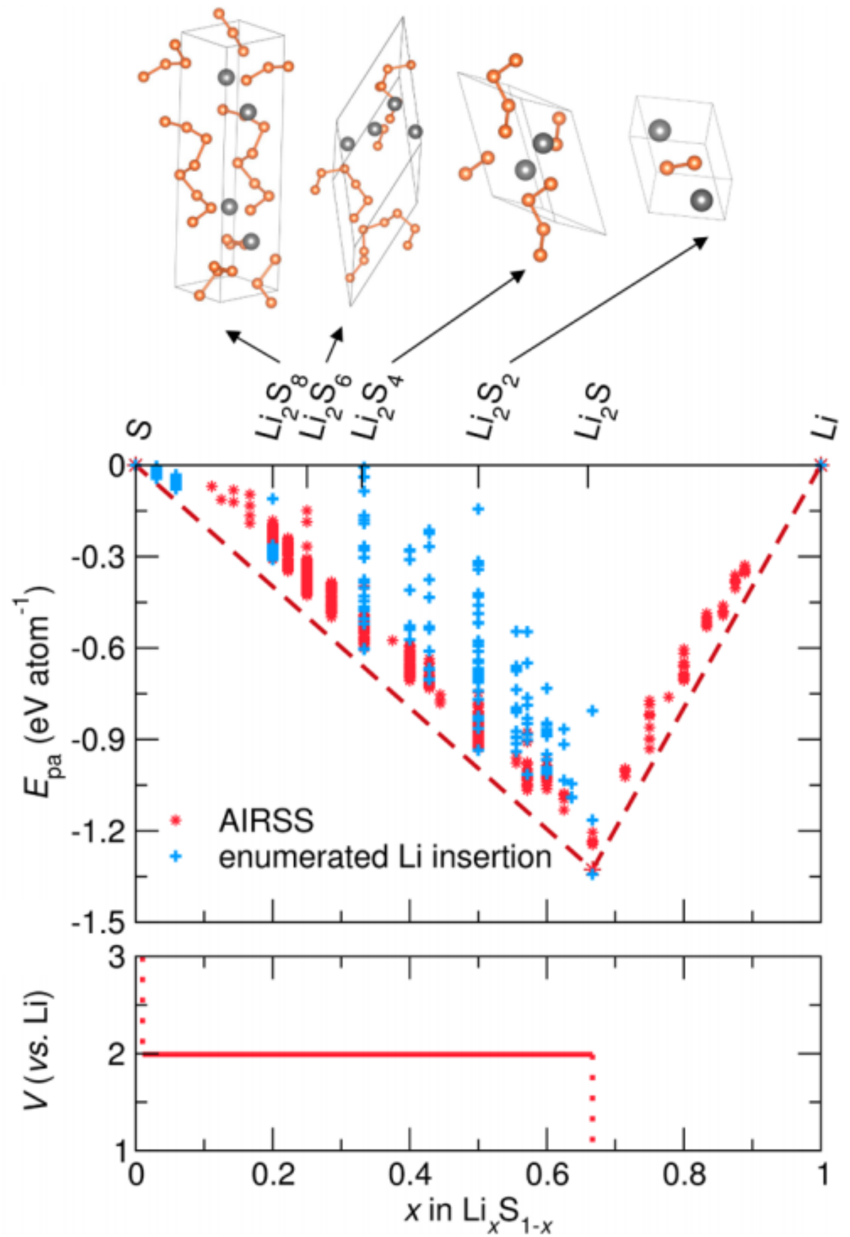
Monitor formation of Li_2S (red, broad peak)
Distinguish between solid and dissolved products
Low X-ray scattering powers of Li and S

DFT calculations of the convex hull show Li_2S is the only favored solid-state phase in this system

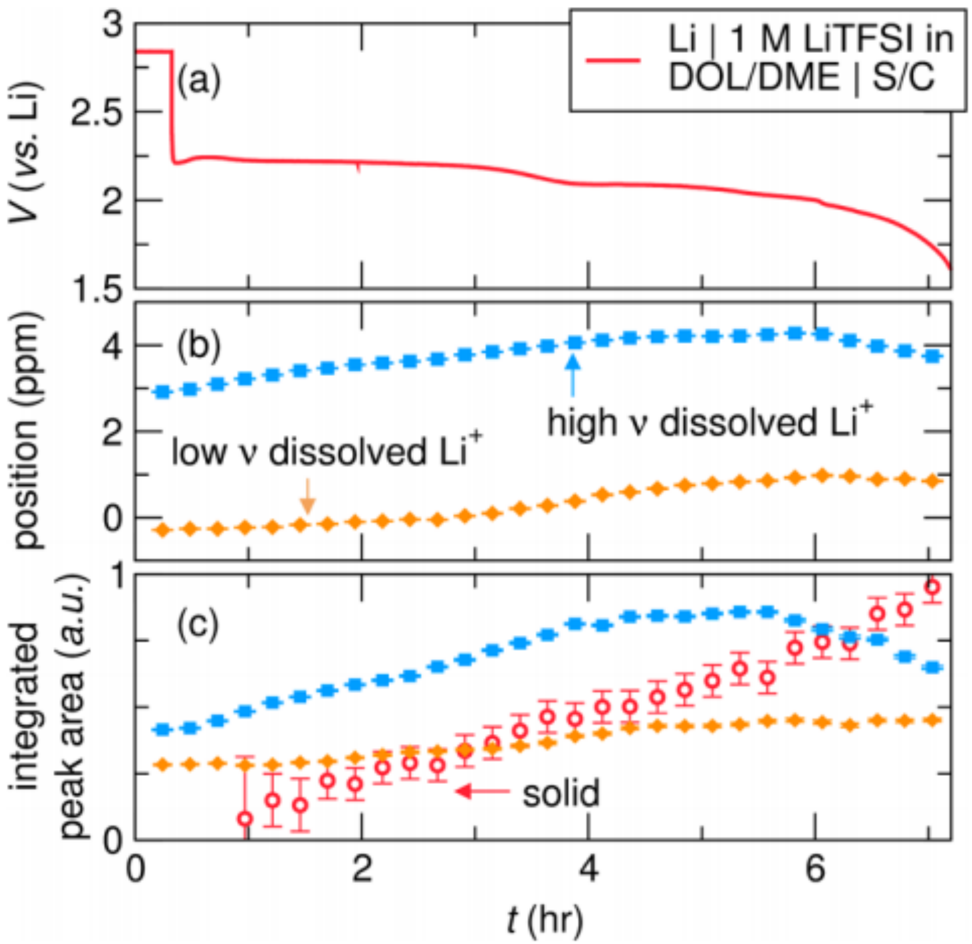
Lowest energy solid-state structures for Li_2S_8, Li_2S_6, Li_2S_4, and Li_2S_2

Formation energies of possible stoichiometries of Li and S: all lie above the convex hull except Li, S, and Li_2S

Discharge of an all-solid state battery would have one plateau corresponding to direct conversion to Li_2S



^{7}Li NMR shows formation of Li_2S forms from the beginning



High frequency Li+ = closer to cathode

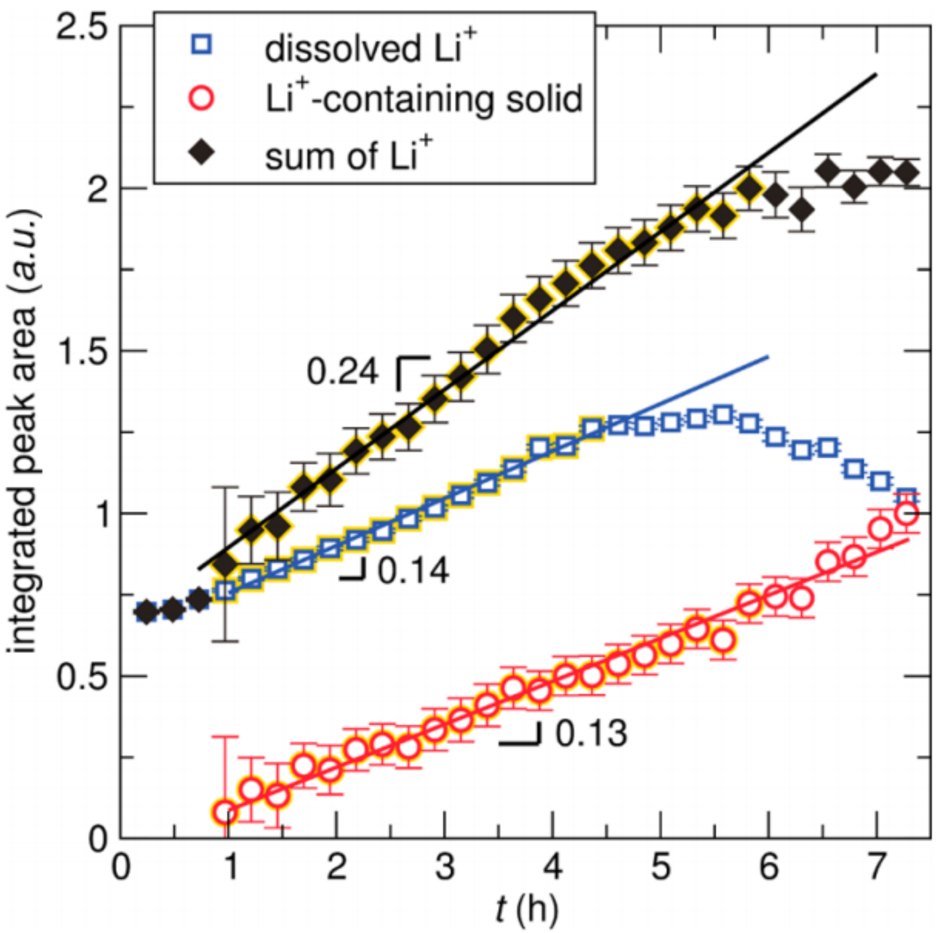
High concentrations of Li+ cause a positive shift in resonance

Low frequency Li+ = closer to anode

Dissolution of polysulfides is relatively localized to the electrolyte near the cathode

Solid forms from beginning of discharge cycle

^{7}Li NMR confirms formation of Li_2S is from electrochemical processes

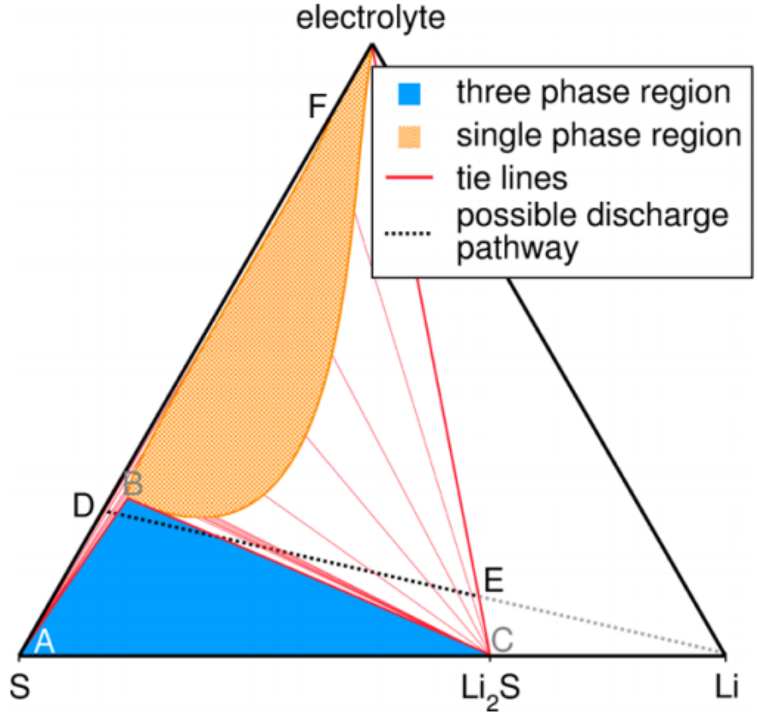


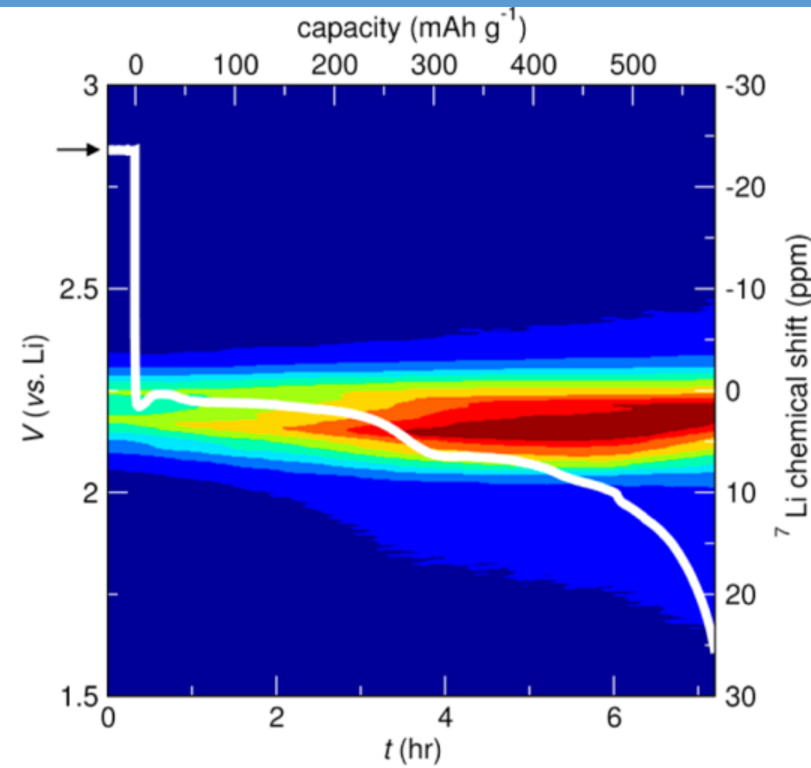
Integrated area of solid increases linearly with discharge

Suggests Li^+-containing solid is formed via electrochemical processes

For 1 e^- pulled from the anode to produce 1 Li^+ ion, current and rate of formation of Li^+ should be equal

Discharge mechanism best explained by ternary diagram





Single phase region: Li^+ and polysulfide species in solution

Two phase region: Li_2S and electrolyte solvent

Three phase region: S (point A), dissolved polysulfides (point B), and Li_2S (point C)

First plateau: discharge pathway passes through three phase region (form Li_2S)

Drop in voltage: passage through set of dense tie lines between Li_2S and stable dissolved polysulfide

Second plateau: S_x^{2-} reduction from solution (incomplete) through two phase region