Modelling Migration-Diffusion-Reaction Processes in an Idealised Lithium-Sulfur Cell

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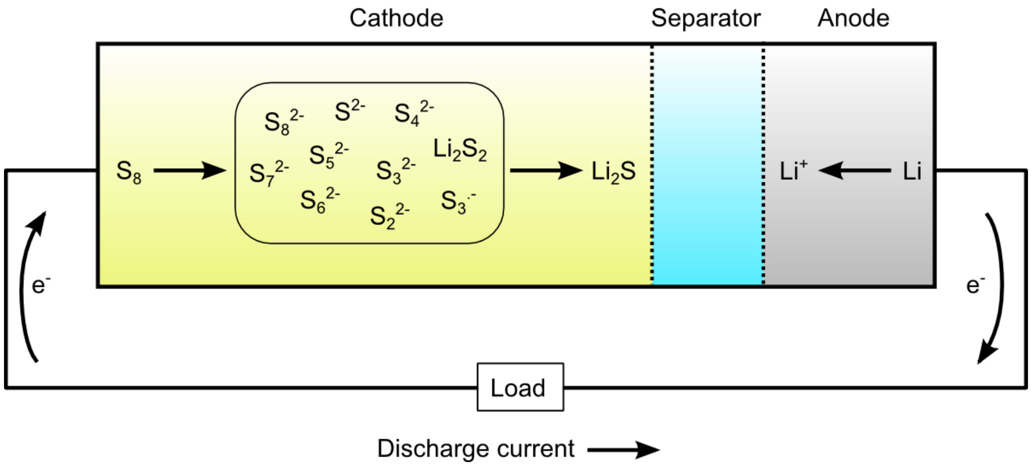
OXIS Energy

- Developing Lithium Sulfur since 2005 in the Culham Science Centre (Oxfordshire, UK)
- Currently undertaking a number of projects, including the Revolutionary Electric Vehicle Battery project 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

(Thermal behaviour, Homogeneous cell models, Microscopic models → COMSOL Multiphysics)

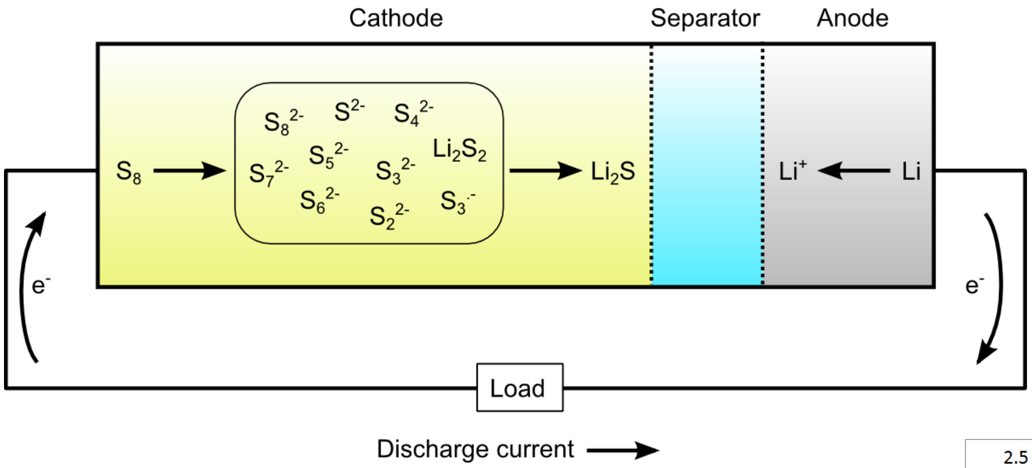
Lithium Sulfur overview



- Electrochemical surface processes
- Surface and bulk phase chemical processes
- Probable feedback loops/non-linear reaction pathway

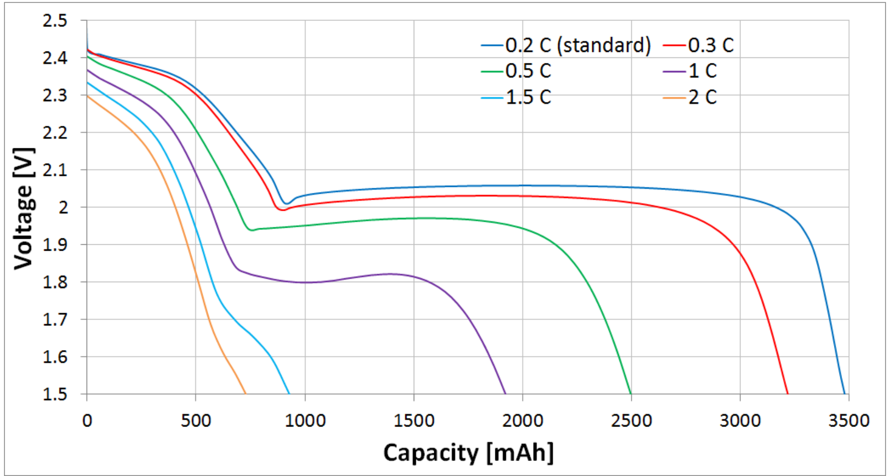
- Maximum capacity realised when all solid S_8 is reduced to solid Li_2S.
- Reaction mechanism by which this occurs is not clear, but most electrochemistry occurs in the liquid phase (i.e. this is not Li-ion).
- We want a tool to help understand how these complex mechanisms may interact to lead to LiS-like behaviour.

Lithium Sulfur overview

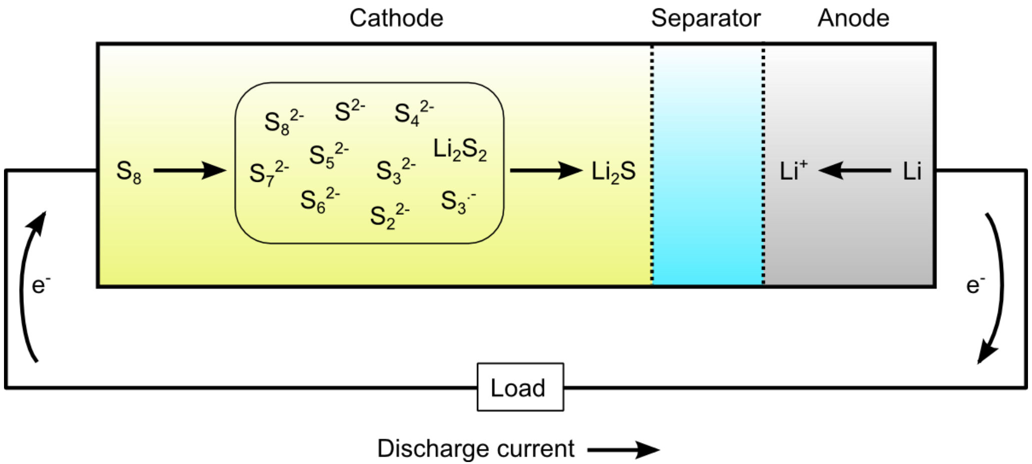


- Electrochemical surface processes
- Surface and bulk phase chemical processes
- Probable feedback loops/non-linear reaction pathway

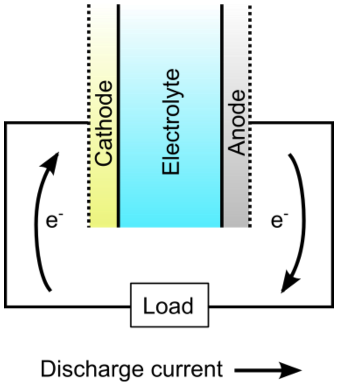
- Two step discharge process
- Variation in curve shape and capacity with applied current



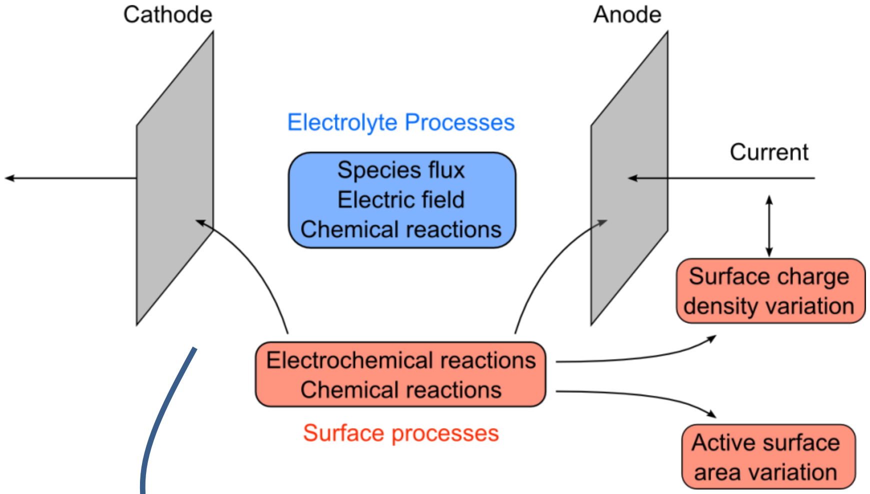
Lithium Sulfur modelling approach



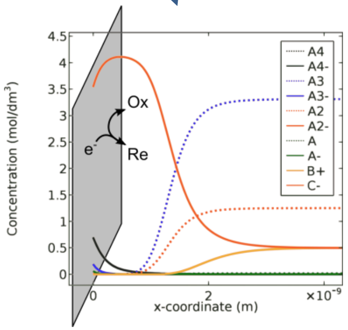
- Standard modelling approach: homogenisation, electroneutrality and Butler-Volmer kinetics.
- We collapse both cathode and anode into layers either side of an electrolyte: slit-pore geometry.
- Allows electrode-electrolyte interface to be modelled.
- Removes geometrical properties of cathode.



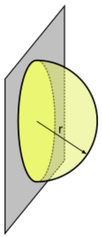
Model structure: 1D planar electrode/slit pore



- Species fluxes and electric field described by modified Poisson-Nernst-Planck model
- Generalised Frumkin-Butler-Volmer type electrochemical reaction kinetics



- Resolves double layer
- Includes ionic hard sphere volume
- Redox reactions depend on double layer structure



- Hemispherical growth model
- Dependent on surface activity
- Homogenised surface

A mixed reaction system

Cathode

$A(s)$

$\downarrow$ Dissolution

$A(l)$

$\downarrow$ Electrochemical

A^{2-}

$\downarrow$ Bulk phase dissociation

$2B^{-}$

Anode

$C(s)$

$\downarrow$ Electrochemical Dissolution

C^{+}

Species sizes:

$r_{A(l)} = 0.30\text{nm}$

$r_{A^{2-}} = 0.32\text{nm}$

$r_{B^{-}} = 0.30\text{nm}$

A mixed reaction system

Cathode

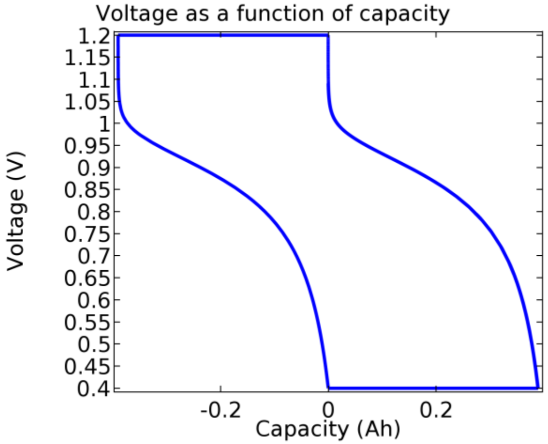
$$A(s) \downarrow A(l) \downarrow A^{2-} \downarrow 2B^-$$

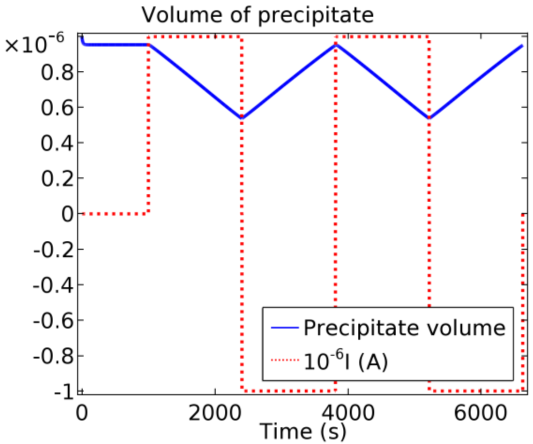
$$\Delta\phi = 0.5V$$

Anode

$$C(s) \downarrow C^+$$

$$\Delta\phi = -0.5V$$





- Initial voltage > 1V
- Reversible charge/discharge process
- Reversible precipitation/dissolution process

A mixed reaction system

Cathode

$$A(s) \downarrow A(l) \downarrow A^{2-} \downarrow 2B^-$$

$$\Delta\phi = 0.5V$$

Anode

$$C(s) \downarrow C^+$$

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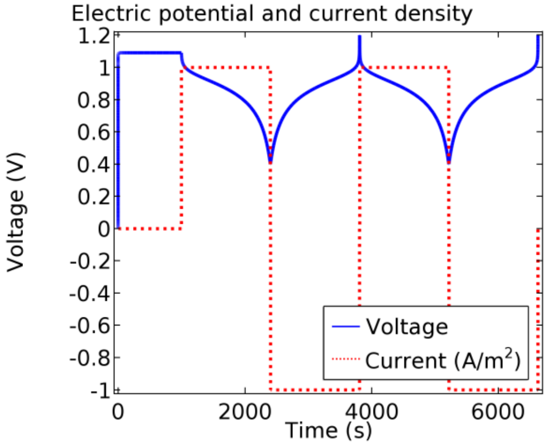
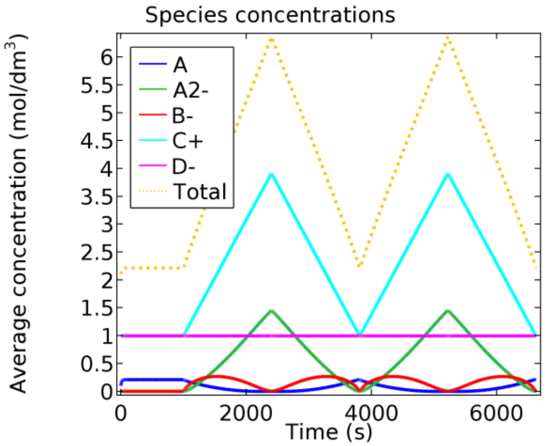
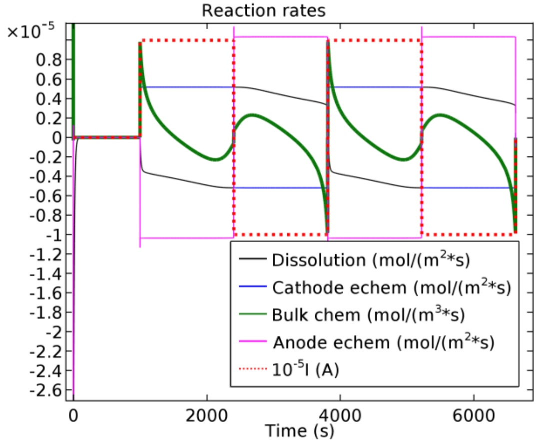


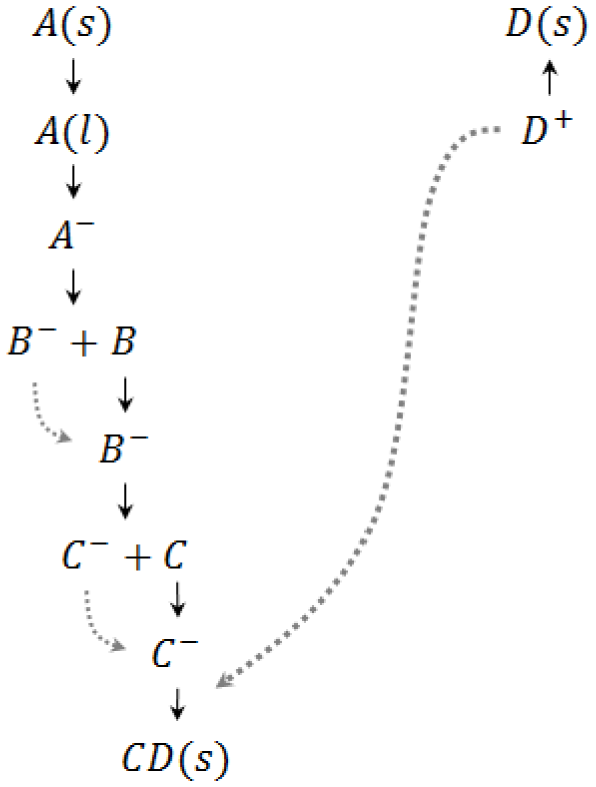


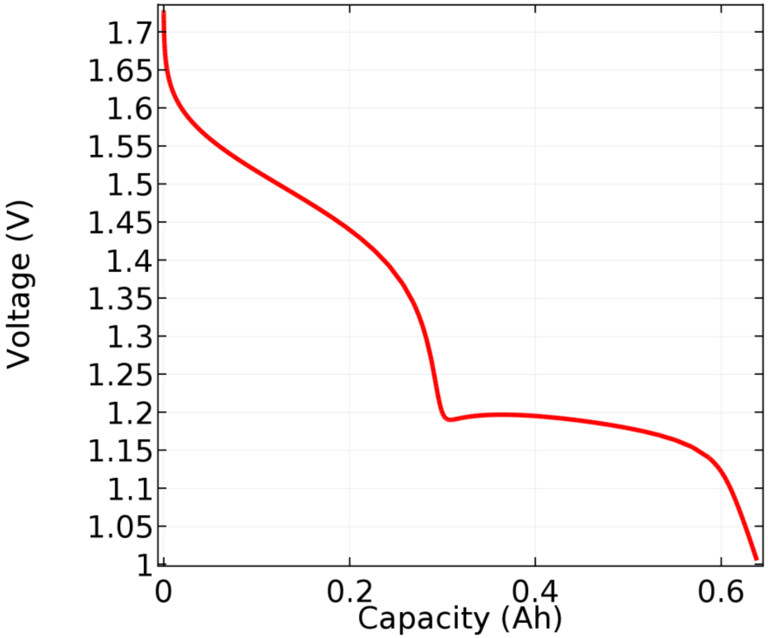
- Divalent ion dominant throughout discharge
- Monovalent ion consumed during second half part of discharge



LiS-like behaviour

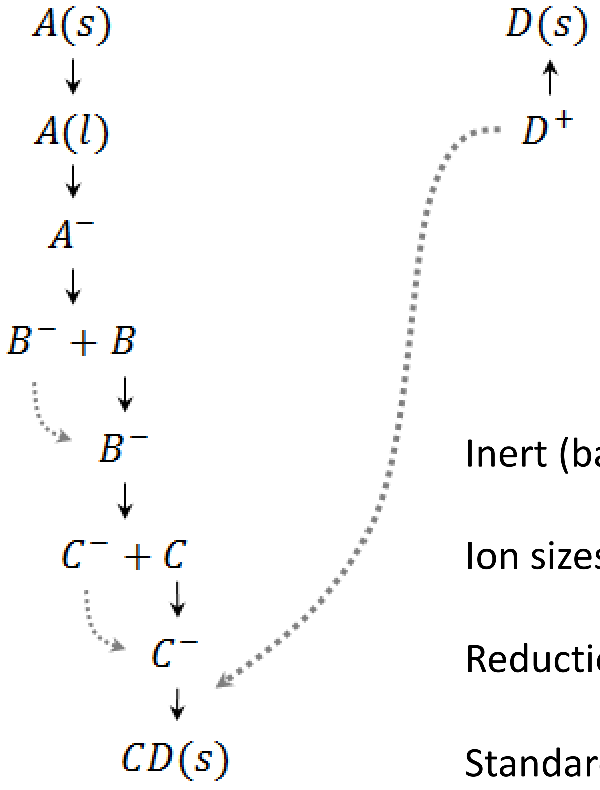
- Simplest reaction-map for a LiS-type discharge



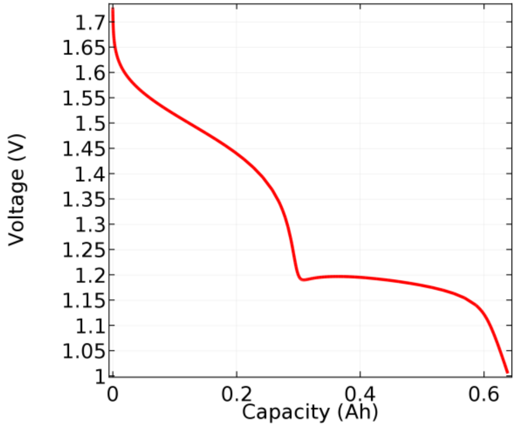


- Simplest reaction-map for a LiS-type discharge

Chemical dissolution
Electrochemical reduction
Chemical dissociation
Electrochemical reduction
Chemical dissociation
Electrochemical reduction
Chemical precipitation



Electrochemical dissolution



Inert (base salt) species E^- also present

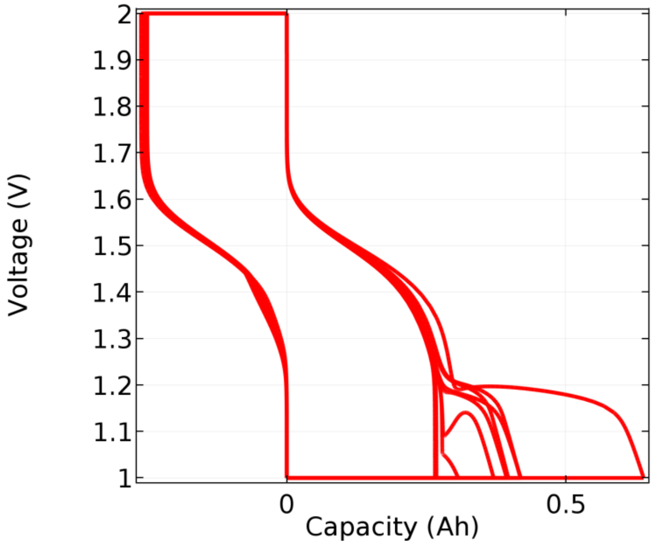
Ion sizes: $\mathrm{r}_{\mathrm{E}^-} > r_{A^-} > r_{B^-} > r_{C^-}$

Reduction potentials: $\Delta\phi^{A\rightarrow A^-} > \Delta\phi^{C\rightarrow C^-} > \Delta\phi^{B\rightarrow B^-}$

Standard state rate constants: $k^{\ominus,A\rightarrow A^-} > k^{\ominus,B\rightarrow B^-} > k^{\ominus,C\rightarrow C^-}$

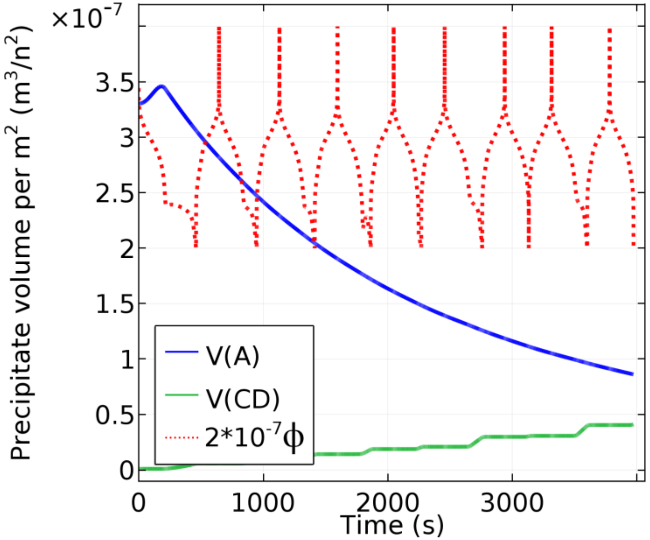
LiS-like behaviour

- Leads to two-step discharge process:



- There remains a problem with the precipitation
- Better understanding of dissolution required

- Subsequent cycles behave oddly
- Charge and discharge capacities differ significantly



Summary

Conclusions

- Developed a model for general complex reaction-diffusion processes in a geometrically simple electrochemical cell.
- The introduction of chemical reaction processes leads to emergent behaviour of the cell.
- Promising for being able to probe more complex reaction mechanisms.

Future work

- Understand what restricts the dissolution of the final solid phase.
- Investigate how reaction map complexity affects predicted behaviour.
- Investigate the so-called shuttle effect, which significantly affects LiS Coulombic efficiency.

- Acknowledgements:

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- Thanks for listening

- Questions?