IMPERIAL

Scan me:

1D Numerical Modelling for Lithium-Sulfur Batteries

Dharshannan Sugunan,
Dr. Monica Marinescu,
Dr. Michael Cornish

INTRODUCTION

Li-S batteries offer high theoretical energy density & cost-effectiveness but face challenges like the shuttle effect & capacity fade. Numerical modelling is essential to better understand and tackle these challenges to maximize the potential of Li-S batteries.

Using a 1D Li-S model developed by Kumaresan [1], with the simplified precipitation/dissolution dynamics proposed by Zhang [2], a bespoke solver tailored for 0D Li-S models was overhauled and optimized to account for the complexity of spatial resolution in 1D models. The Li-S model was tested with error metrics like mass & charge conservation, as well as partial currents, & consecutive charge tests as explored by Ghaznavi & Chen [3,4,5].

NOVEL SOLVER LOGIC

The solver logic that was used to code the algorithms, including the optimized numerical methods, are described in the flow chart below:

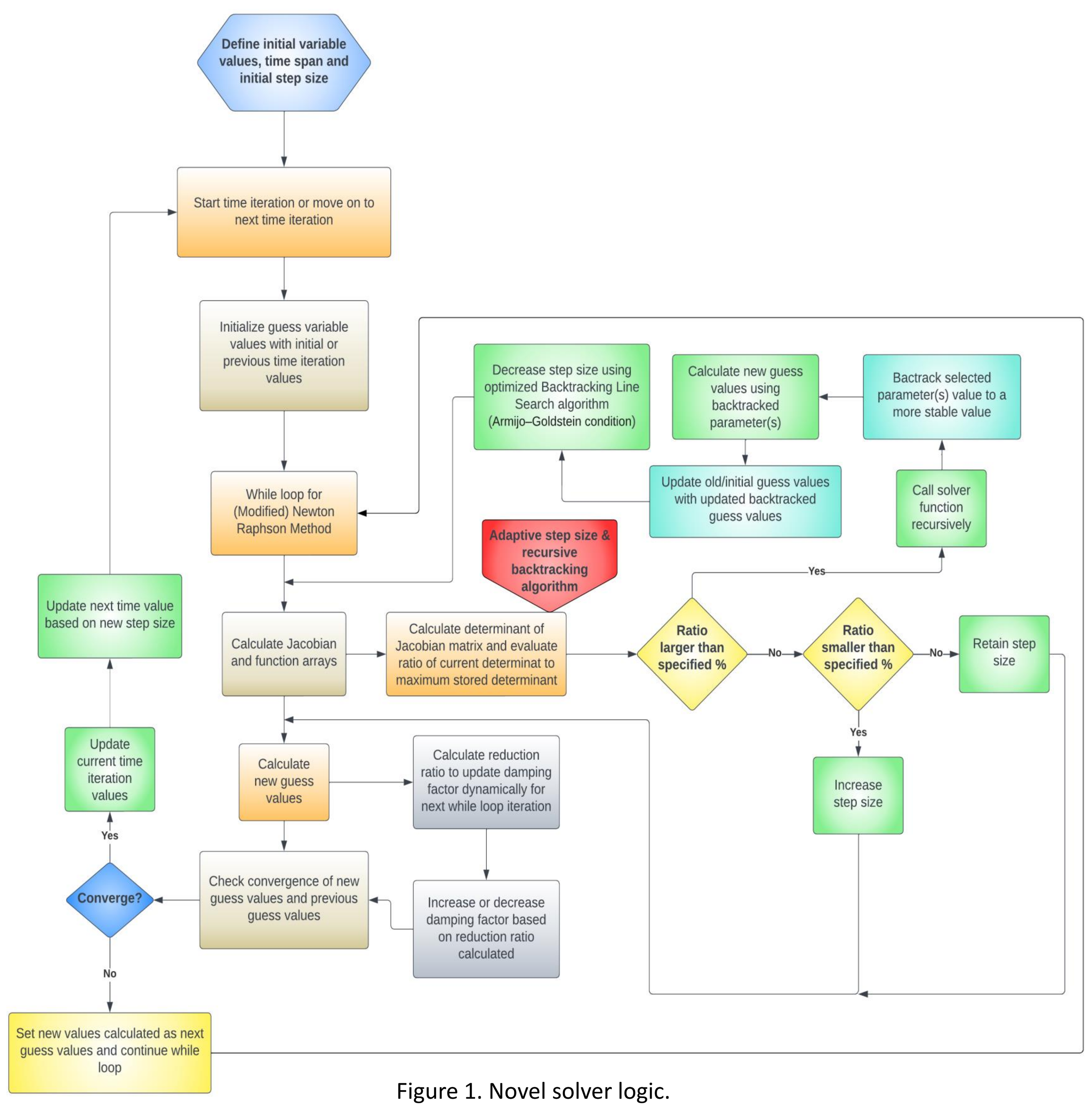

Figure 1. Novel solver logic.

1D Li-S MODEL

The 1D model is given as a 6-stage reaction, with Li electrochemistry in the anode, and a cascade reaction of polysulfide species in the cathode, given as:

$$Li \leftrightarrow Li^{+} + e^{-}$$
$$\frac{1}{2}S_{8(l)} + e^{-} \leftrightarrow \frac{1}{2}S_8^{2-}$$
$$\frac{3}{2}S_8^{2-} + e^{-} \leftrightarrow 2S_6^{2-}$$
$$S_6^{2-} + e^{-} \leftrightarrow \frac{3}{2}S_4^{2-}$$
$$\frac{1}{2}S_4^{2-} + e^{-} \leftrightarrow S_2^{2-}$$
$$\frac{1}{2}S_2^{2-} + e^{-} \leftrightarrow S^{2-}$$

EQUATIONS DISCRETISATION

The equations detailed in [1] are discretised using a Backward-Euler formulation, given by:

$$\left.\frac{df}{dt}\right|_{n+1} = \frac{f_{n+1} - f_n}{\delta t}$$

Example discretisation of the time evolution PDE of the species concentrations, C_i is given as such:

$$\frac{\partial D_i^{eff}}{\partial x} = 1.5D_i\sqrt{\epsilon_p^{m,n+1}}\left[\frac{\epsilon_p^{m+1,n+1} - \epsilon_p^{m,n+1}}{\delta x}\right]$$

$$D_i^{eff} = D_i\left(\epsilon_p^{m,n+1}\right)^{1.5}$$

$$\begin{aligned}\nabla . N_i &\\ = -&\left[\frac{D_i^{eff}\left(C_i^{m+1,n+1} - 2C_i^{m,n+1} + C_i^{m-1,n+1}\right)}{\delta x^2} + \left(\frac{C_i^{m+1,n+1} - C_i^{m,n+1}}{\delta x}\right)\left(\frac{\partial D_i^{eff}}{\partial x}\right)\right]\\ -&\frac{z_i F}{RT}\left[D_i^{eff} C_i^{m,n+1}\left(\frac{\phi_2^{m+1,n+1} - 2\phi_2^{m,n+1} + \phi_2^{m-1,n+1}}{\delta x^2}\right)\right.\\ +& D_i^{eff}\left(\frac{C_i^{m+1,n+1} - C_i^{m,n+1}}{\delta x}\right)\left(\frac{\phi_2^{m+1,n+1} - \phi_2^{m,n+1}}{\delta x}\right)\\ +& \left.C_i^{m,n+1}\left(\frac{\partial D_i^{eff}}{\partial x}\right)\left(\frac{\phi_2^{m+1,n+1} - \phi_2^{m,n+1}}{\delta x}\right)\right]\end{aligned}$$

$$\begin{aligned}\frac{\partial(\epsilon C_i)}{\partial t} &= \epsilon_p^{m,n+1}\left(\frac{C_i^{m,n+1} - C_i^{m,n}}{\delta t}\right) + C_i^{m,n+1}\left(\frac{\epsilon_p^{m,n+1} - \epsilon_p^{m,n}}{\delta t}\right)\\ &= -\nabla . N_i + r_i - R_i\end{aligned}$$

The system of equations are solved via a Newton-Raphson approach, where the Jacobian matrix is formed using the partial derivatives of the residual functions w.r.t the variables. (Residual functions obtained by re-arranging & equating discretised equations to zero).

1D Li-S COMPUTATIONAL DOMAIN

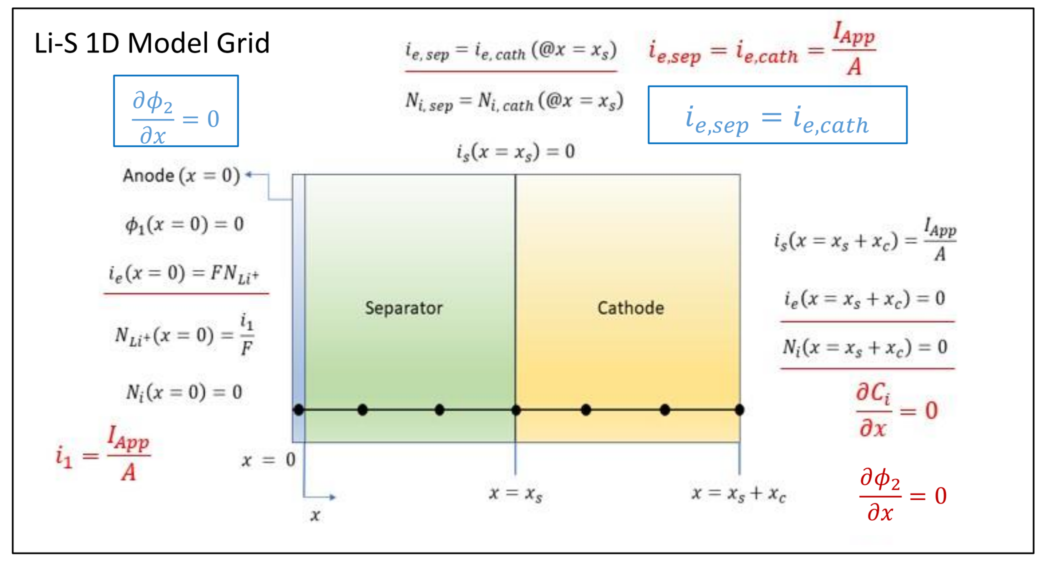

Figure 2. 1D Li-S computational domain with underlying boundary conditions.

1D Li-S MODEL WITHOUT PRECIPITATION/DISSOLUTION DYNAMICS

The precipitation/dissolution dynamics are removed to test solver validity by setting, the rate constant $k_k = 0$

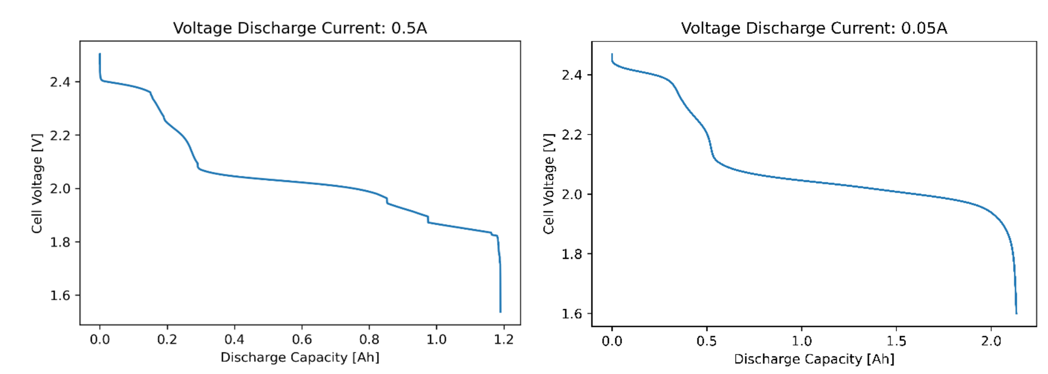

Figure 3. Voltage discharge profiles for 0.5A & 0.05A applied currents.

The cathodic species time evolution is given as:

$$C_{i,avg} = \frac{1}{L_{cath}}\int_{x=x_s}^{x=x_s+x_c} C_i\, dx = \frac{1}{L_{cath}}\sum_{\Delta x} C_i\,.\,\delta x$$

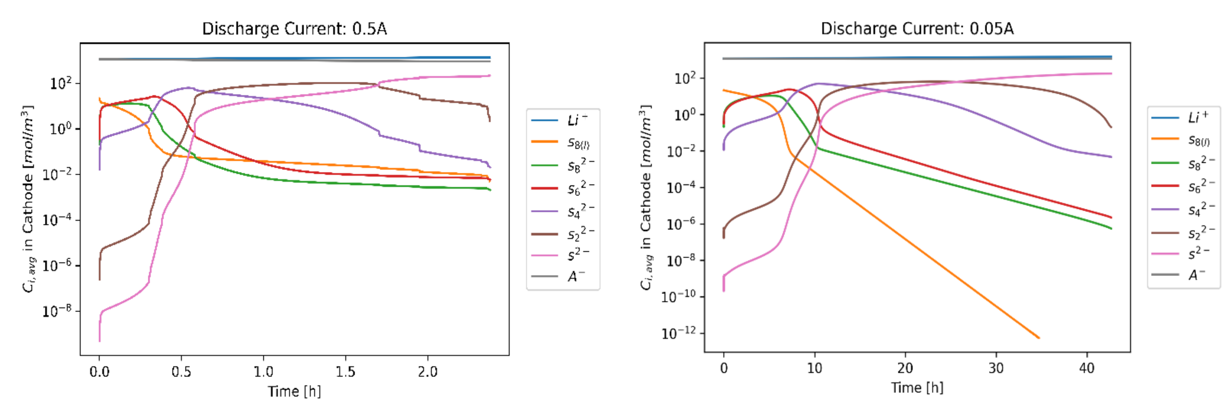

Figure 4. Average species concentrations in the cathode.

The A^{-} species mass and overall cell charge conservation equations are given by:

$$A_{total\ mass}^{-} = \frac{1}{x_s + x_c}\int_{x=0}^{x=x_s+x_c} \epsilon_p C_{A^-}\, dx = \frac{1}{x_s + x_c}\sum_{\Delta x} \epsilon_p C_{A^-}\,.\,\delta x$$

$$\sum_{i=0}^{n} \epsilon_p z_i C_i = 0$$

1D Li-S MODEL WITH PRECIPITATION/DISSOLUTION DYNAMICS

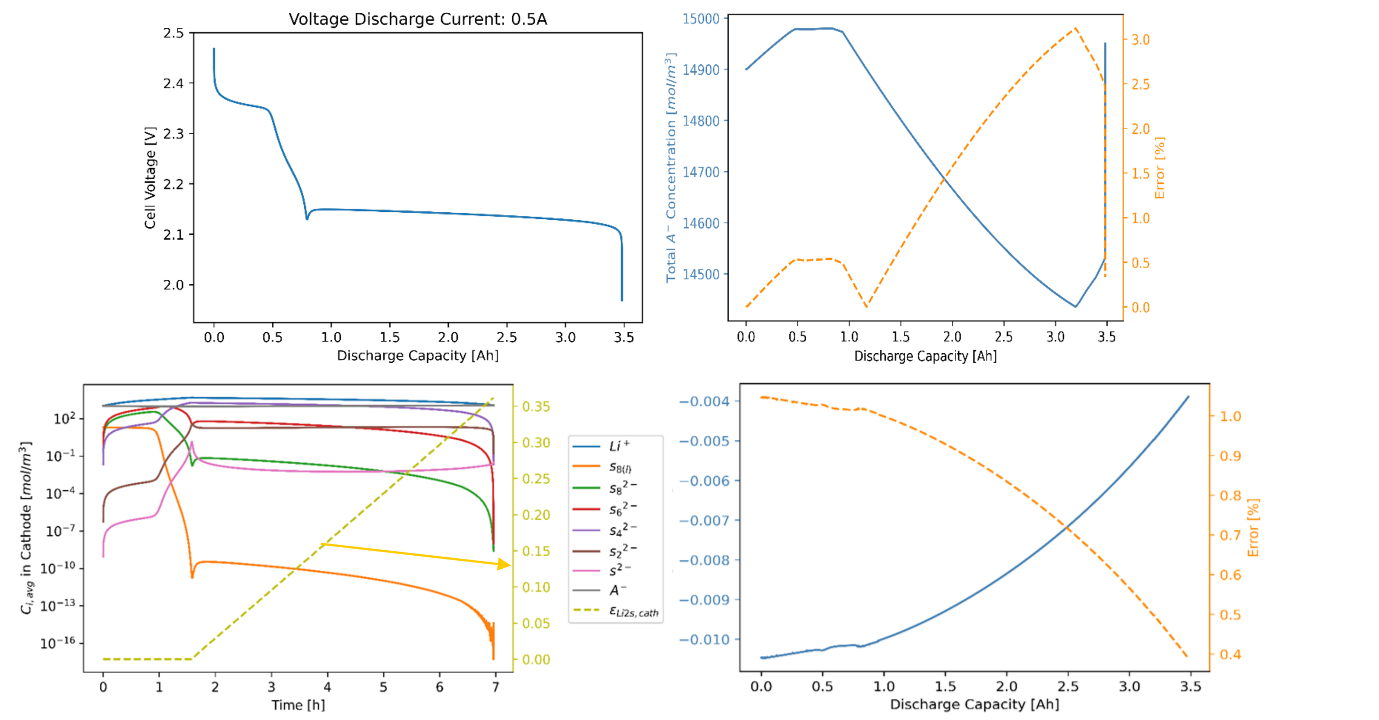

Figure 5. Voltage discharge (top left), A^{-} mass conservation (top right), species time evolution (bottom left) & cell charge conservation (bottom right) plots.

The normalized partial currents (@ cathode) are calculated as:

$$I_j^N = \frac{1}{\frac{I_{app}}{A}}\int_{x=x_s}^{x=x_s+x_c} a_v i_j\, dx = \frac{1}{\frac{I_{app}}{A}}\sum_{\Delta x} a_v i_j \delta x \quad \& \quad \sum_{j=2}^{6} I_j^N = 1$$

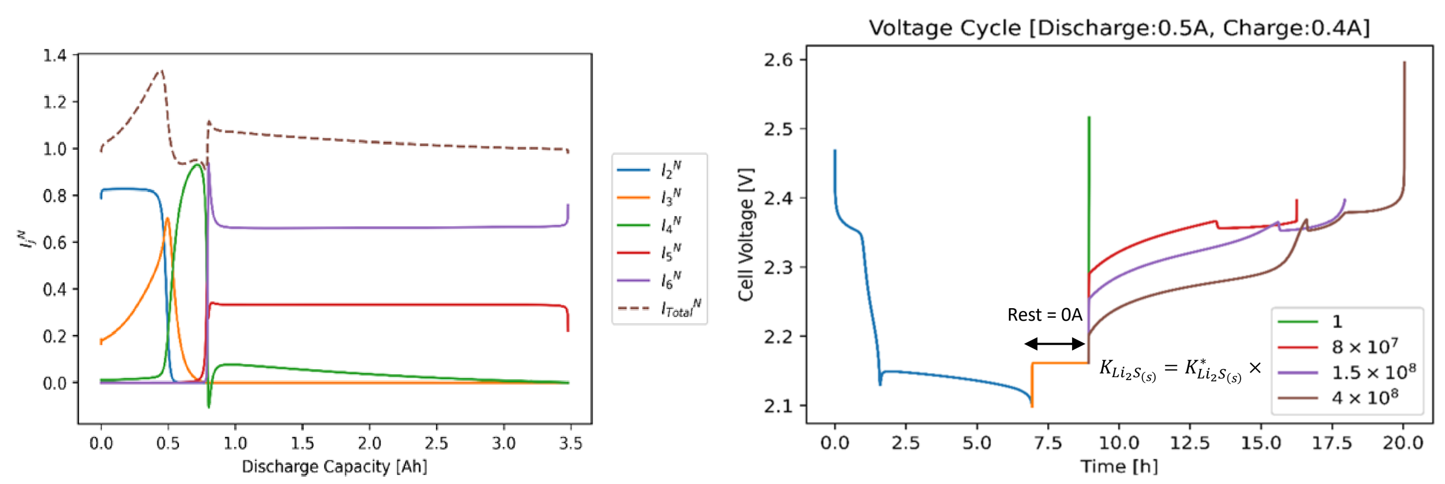

Figure 6. Normalized partial currents (left) & consecutive charge (right) tests.

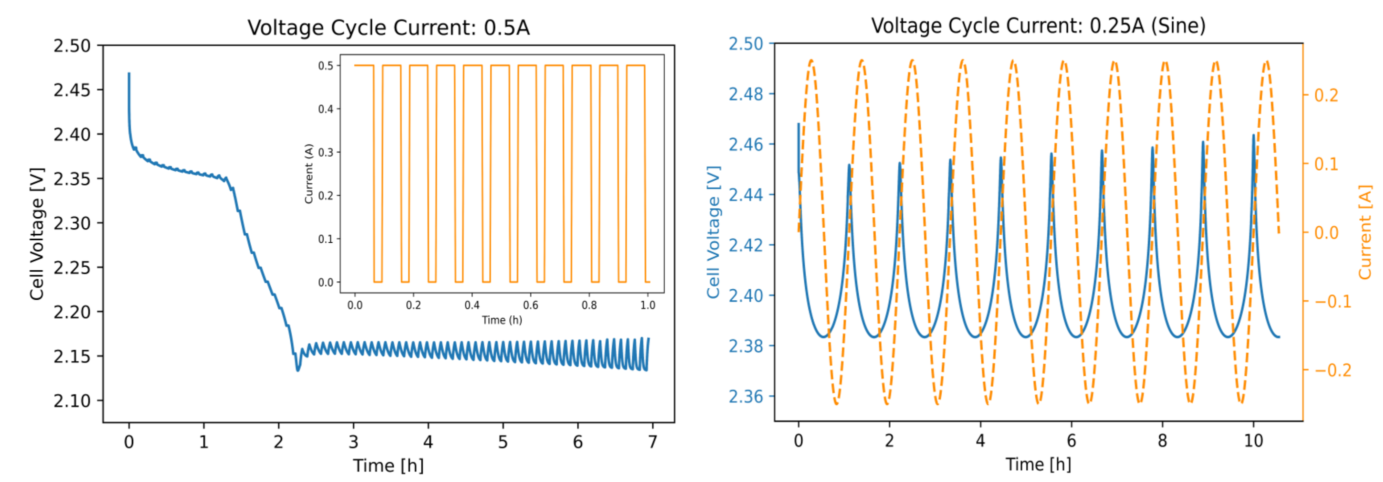

Figure 7. GITT (left) & sinusoidal current (right) tests.

CONCLUSION

- Novel solver works well & efficiently (avg simulation runtime: 10mins).
- Normalized partial currents do not sum to unity (high plateau) due to absence of higher order polysulfide precipitations for model studied.
- Numerical issues during consecutive charge similar to findings of [5].
- Developed solver capable of testing non-constant current simulations evident from GITT & sinusoidal current tests.

Imperial College London

dharshannan.sugunan20@imperial.ac.uk

1. Kumaresan K, Mikhaylik Y, White RE. A Mathematical Model for a Lithium–Sulfur Cell. *Journal of The Electrochemical Society*. 2008;155(8): A576. https://doi.org/10.1149/1.2937304.
2. Zhang T, Marinescu M, Walus S, Offer GJ. Modelling transport-limited discharge capacity of lithium-sulfur cells. *Electrochimica Acta*. 2016;219: 502–508. https://doi.org/10.1016/j.electacta.2016.10.032.
3. Ghaznavi M, Chen P. Sensitivity analysis of a mathematical model of lithium-sulfur cells part I: Applied discharge current and cathode conductivity. *Journal of Power Sources*. 2014;257: 394–401. https://doi.org/10.1016/j.jpowsour.2013.10.135.
4. Ghaznavi M, Chen P. Sensitivity analysis of a mathematical model of lithium-sulfur cells: Part II: Precipitation reaction kinetics and sulfur content. *Journal of Power Sources*. 2014;257: 402–411. https://doi.org/10.1016/j.jpowsour.2013.12.145.
5. Ghaznavi M, Chen P. Analysis of a Mathematical Model of Lithium-Sulfur Cells Part III: Electrochemical Reaction Kinetics, Transport Properties and Charging. *Electrochimica Acta*. 2014;137: 575–585. https://doi.org/10.1016/j.electacta.2014.06.033.