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Lithium Sulfur Batteries: Mechanisms, Modelling and Materials

Detecting Polysulfide Shuttle in Lithium-Sulfur Batteries with Differential Thermal Voltammetry

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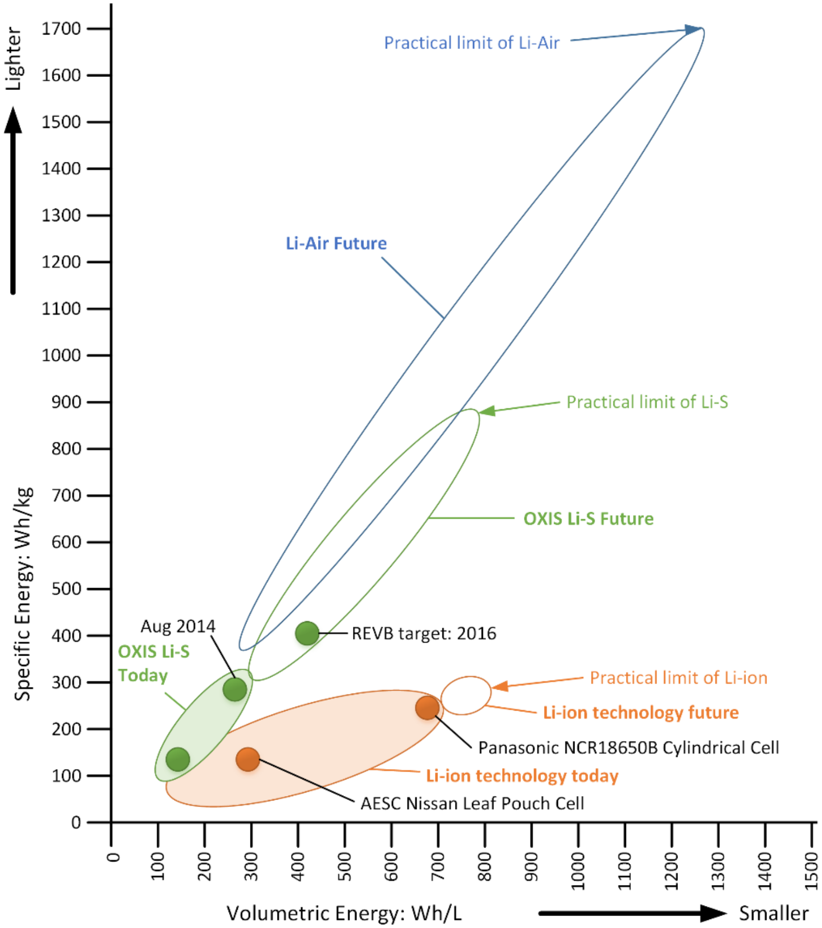
Lithium Sulfur Battery



Volumetric & Gravimetric energy density of different battery chemistries

Benefits of LiS batteries

1. High Gravimetric energy density(400 Wh/kg achieved, 600-800 Wh/kg practical limit, 2500-2600 Wh/kg theoretical limit)
2. Low-cost of sulfur material – economic advantages
3. Safety under extreme circumstances (nail penetration tested by *Hunt et al, Journal of Energy Storage, 2, 25 (2015)*)

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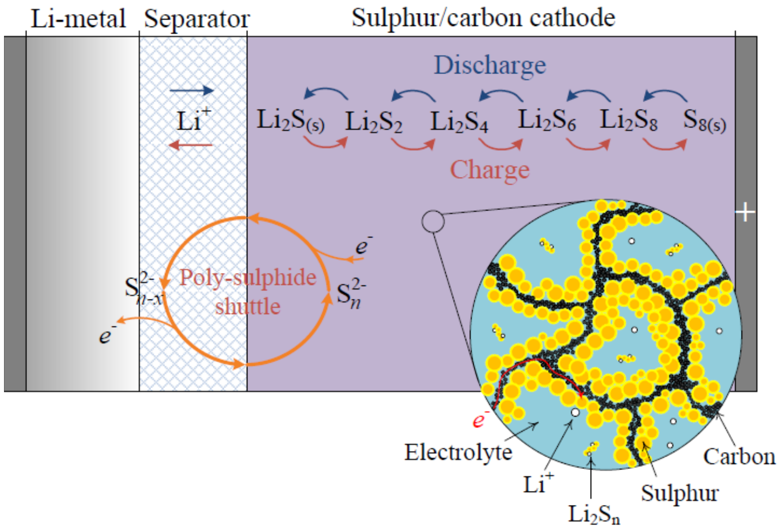
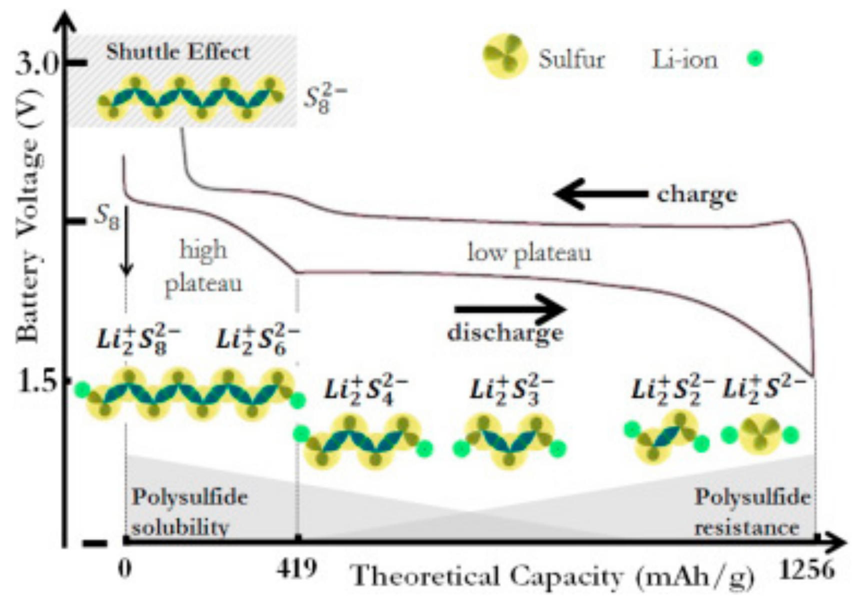


- Reactions occur in 'liquid'
- During discharge, the reduction of S would form various polysulphides and then react and combine with Li to ultimately produce Li_2S



- During charge, the oxidation of polysulfide would form solid sulfur ($S_{8,solid}$)
- $S_{8,solid}$ may dissolve in the electrolyte, or react with polysulfide to form a polysulfide species with longer chain length.
- Shuttle Effect

shorter chain polysulfide

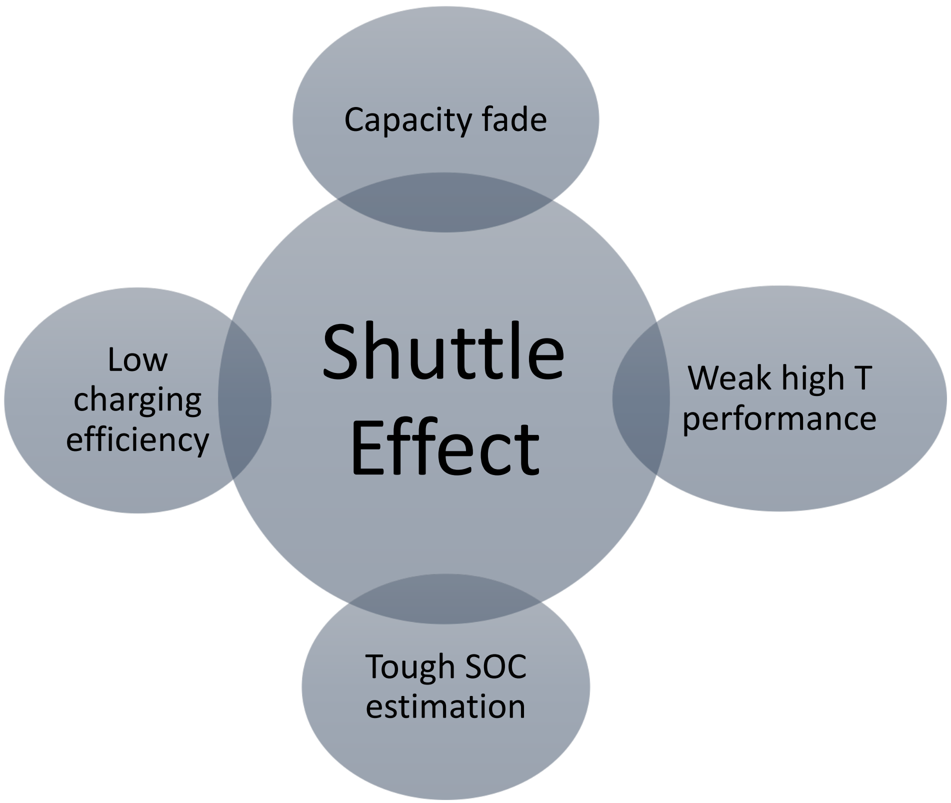
Be reduced ↑ ↓ Be oxidised

longer chain polysulfide

K. Propp et al. *Journal of Power Sources*, 2016, 328, Pages 289-299

M. Wild et al. *Energy Environ.Sci.*, 2015, 8, Pages 3477-3494

Challenge: Shuttle



Conclusion:

1. Shuttle is related to most drawbacks
2. Material Science research is still under R&D
3. Mechanism solutions could bring immediate benefits
4. In literature, Cell self-heating mainly comes from shuttle (Y.V.Mikhaylik, ECS, 2004)
5. Temperature measurements & thermal study become essential for solving shuttle

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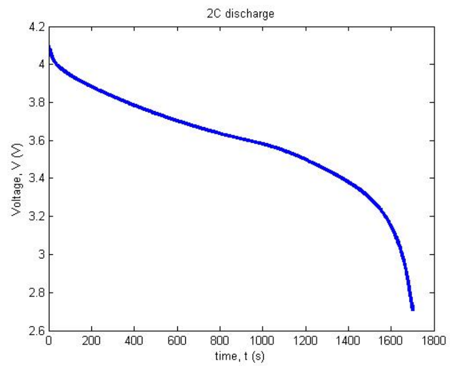
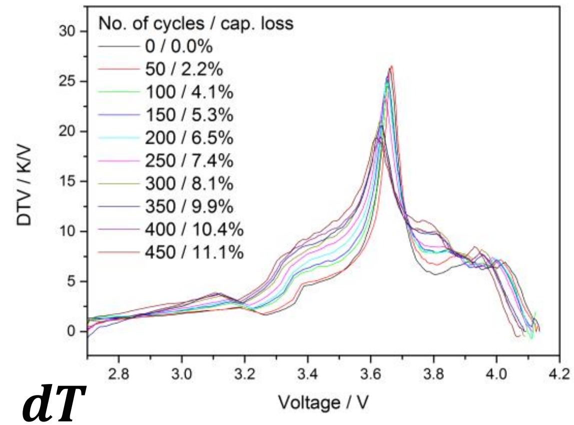
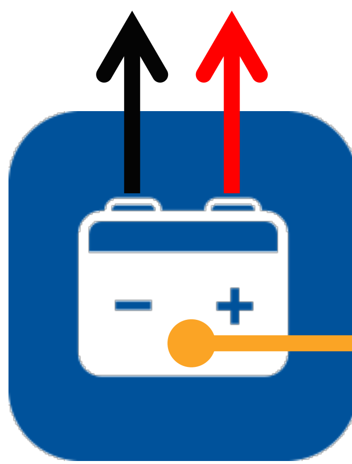
Differential Thermal Voltammetry (DTV)

- Novel in-situ battery diagnosis method for tracking degradation (Lithium-ion Batteries e.g. LFP or NMC/NCA)
- Cheap and easy
- Needs surface temperature and voltage readings
- dT/dV plotted against cell voltage

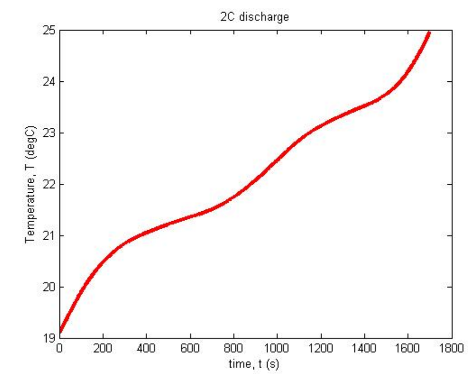




$$\frac{dV}{dt} \rightarrow \frac{dT}{dV}$$



$$\frac{dT}{dt}$$



B. Wu et al. Journal of Power Sources, 2015, Volume 273, Pages 495-501

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Experimental Details

1. Cells were placed individually in the centre of one air convection thermal incubator
2. DTV characterisation tests on 10 Ah OXIS pouch cells (150x100x7.25 mm)
3. Variable ambient temperature & variable charging current DTV tests

Experiments	Ambient Temperature/°C	Charging Current/A	Discharging Current/A	Voltage Range
#1 Δ T				
	20	1	2	1.5V-2.45V
	30	1	2	1.5V-2.45V
	40	1	2	1.5V-2.45V
	45	1	2	1.5V-2.45V
#2 Δ I				
	30	1	2	1.5V-2.45V
	30	2	2	1.5V-2.45V
	30	3	2	1.5V-2.45V
	40	1	2	1.5V-2.45V
	40	2	2	1.5V-2.45V
	40	3	2	1.5V-2.45V

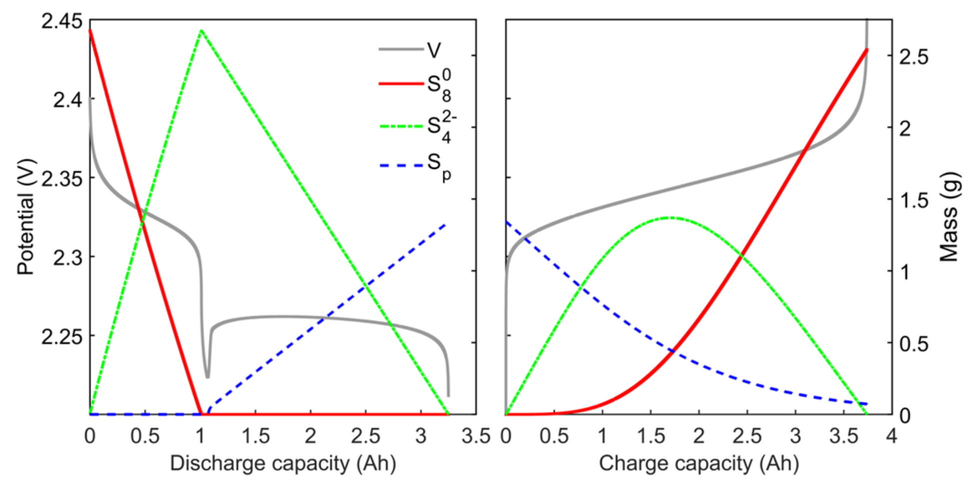
Table 1: Experimental Set-up

X. Hua, M. Marinescu, Y. Merla, R. Purkayastha, T. Zhang, G.J.Offer, 2018, *in preparation*

Model Formulation

- $\frac{dV}{dt}$ can be achieved by using Li-S 0-D model.
  - M. Marinescu, *PCCP*, 18 (2016) 584–593 (2016)

- $$\frac{dT}{dt} = \frac{1}{mc_h}[k_s(T)q_H[S_H]V_H - \alpha(T - T_0)]$$
  - m : Cell mass
  - c_h : Cell heat capacity
  - $k_s(T)$: Shuttle constant
  - q_H: High plateau sulfur specific capacity
  - S_H : The amount of high plateau sulfur
  - V_H : Voltage at high plateau
  - α : Cell heat-transfer coefficient
  - Yuriy V. Mikhaylik *Journal of The Electrochemical Society*, **151** (11) A1969-A1976 (2004)



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Experimental Results

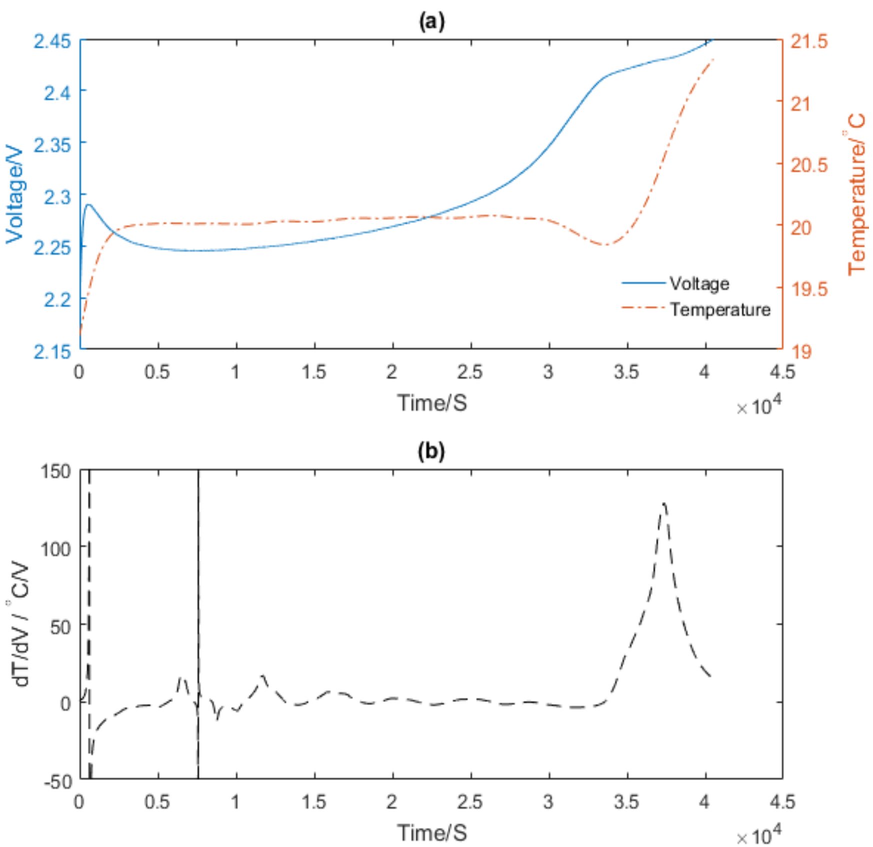

Figure 1. DTV profiles during charge

1. 0.1C (1A) charge at 20 ℃
2. Noticeable temperature drop at high voltage plateau – could due to the dissolution of polysulfides into the electrolyte
3. After the drop, temperature continue to increase significantly, which is most likely caused by shuttle
4. Two infinites at beginning of charge are the consequences of changing sign of dV/dt
5. Finite DTV peak occurs at end of charge/higher charge plateau, also is where shuttle occurs

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Experimental Results

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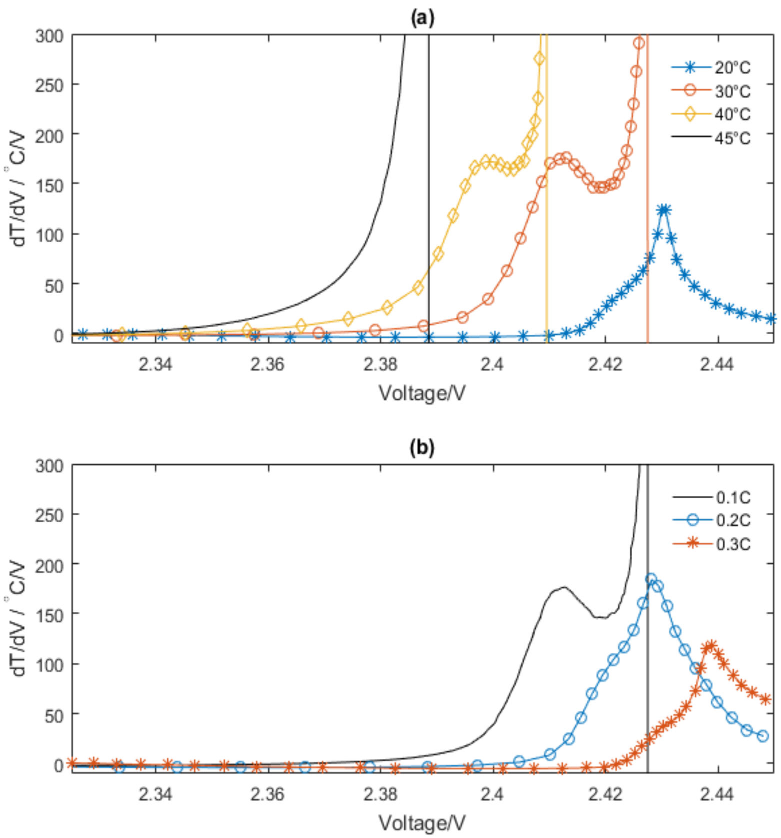

Figure 2. Rate and temperature dependence of DTV curves*

1. 0.1C (1A) charge at 20 ℃ to 45 ℃
2. 0.1C (1A) to 0.3C (3A) at 30 ℃
3. Higher ambient T/smaller charge current, larger value of DTV peaks and shift to lower voltage value
4. Higher ambient T leads to higher solubility and mobility of dissolved polysulfides, increasing shuttle
5. Higher charge rate leads to dissolution bottleneck of Li2S, limits amount of dissolved polysulfides that can participate in shuttle, decreasing shuttle

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*Line symbols correspond to 1 in 300 measurements collected, to improve visibility.

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Modelling Results

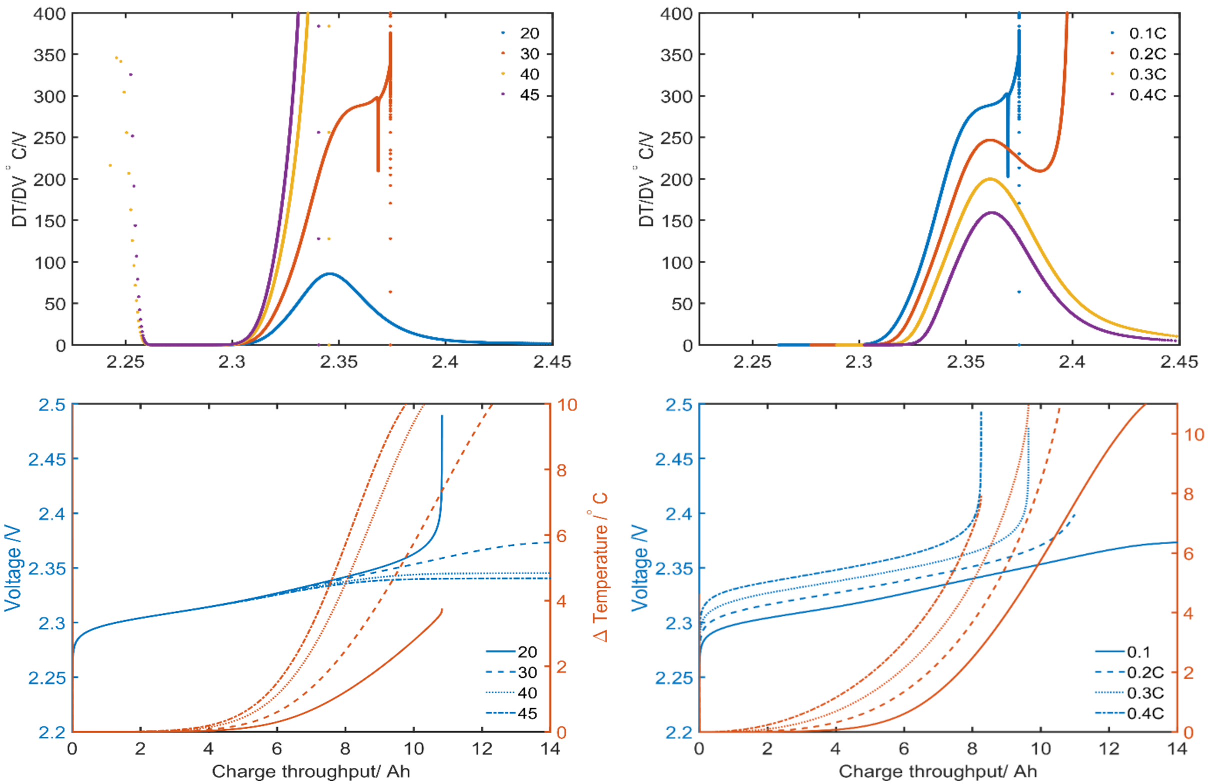

Figure 3. Model predictions for DTV during variable ambient T and charge rate & Corresponding cell voltage and temperature

1. Thermally coupled 0D model predict similar trends on the DTV peak changes: greater impact on shuttle, exhibit larger value of DTV peaks e.g. from finites to infinites

2. Validated the experimental data that DTV technique is able to detect Polysulfide Shuttle, particularly at high charge plateau/end of charge

X. Hua, M. Marinescu, Y. Merla, R. Purkayastha, T. Zhang, G.J.Offer, 2018, *in preparation*

Conclusion

1. DTV technique is able to detect Polysulfide Shuttle in Lithium-Sulfur batteries.
2. Thermally-coupled Li-S 0D model is developed, which allows quantitative interpretations of the experimental DTV curves.
3. DTV technique is a potential promising tool for real-time detection of shuttle in applications to prevent overheating and accelerated degradation
4. The model and DTV technique help to quantify answers to questions such as: ***'What is worse for Li-S cells: decreasing the charging current by certain Ampere or increasing the temperature by certain Kelvin? '*** or in other words, model and DTV technique are essential for choosing conditions for the smart charging algorithms in future Li-S applications.

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Thanks!

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