Work Package 1 Batteries

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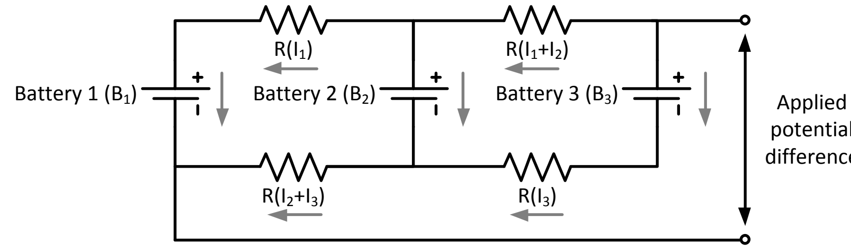
Aims

- To develop the knowledge & tools that industry needs:
  - To make better systems around electrochemical energy storage devices (i.e. batteries & supercapacitors)
- By
  - Creating degradation aware models
  - Designing new experiments
  - Pushing the boundaries of our knowledge

All cells are not always equal

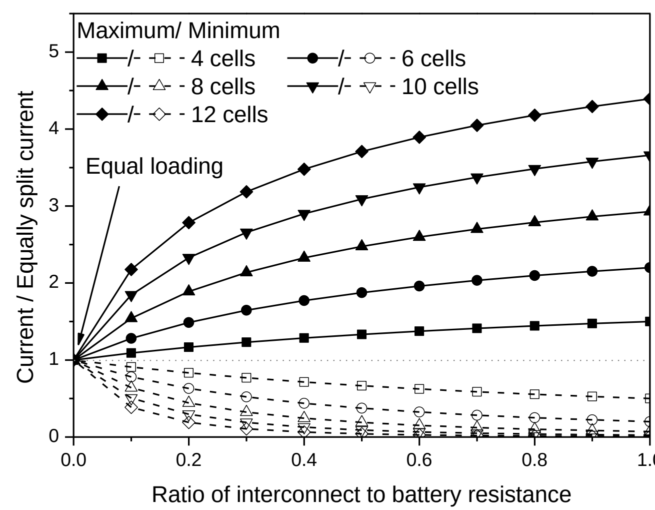
- Parallel cells
  - Rarely in the same electrical environment
  - Even if in the same temperature environment
  - If T is not managed, things can go badly wrong
  - Even if T is managed cells can still be unequally stressed
- Series cells
  - Same problem as uneven current distribution in large form factor cells



$$V_{\mathrm{app}} = OCV_1 + \eta_1 + R_{\mathrm{IC}}(2I_1 + I_2)$$

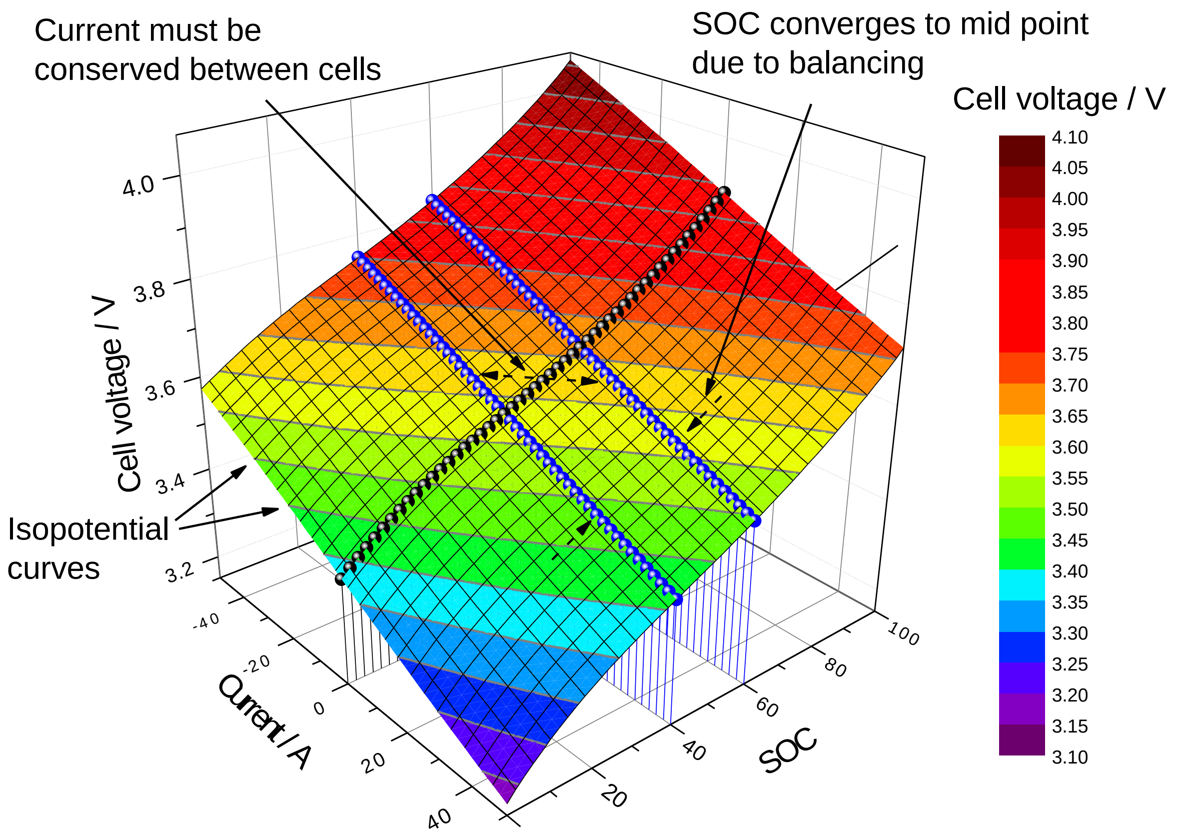
$$V_{\mathrm{app}} = OCV_2 + \eta_2 + R_{\mathrm{IC}}(I_1 + 2I_2 + I_3)$$

$$V_{\mathrm{app}} = OCV_3 + \eta_3 + R_{\mathrm{IC}}(I_2 + 2I_3)$$



Wu B, Yufit V, Marinescu M, et al., 2013, Coupled thermal–electrochemical modelling of uneven heat generation in lithium-ion battery packs, **Journal of Power Sources, 43, 2013, 544–554**

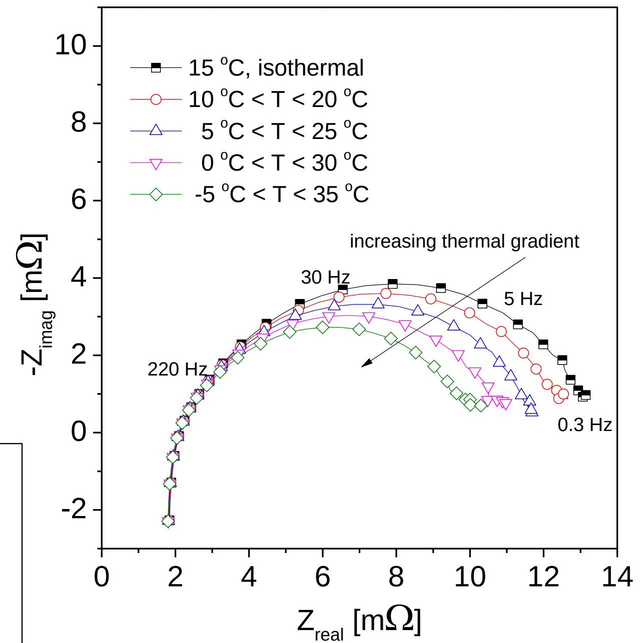
Dynamic rebalancing



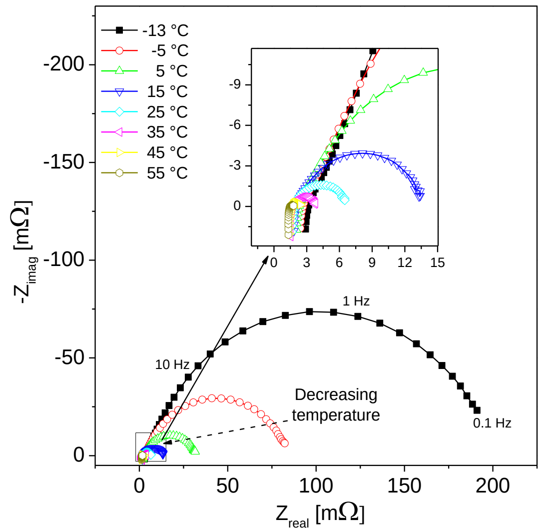
Wu B, Yufit V, Marinescu M, et al., 2013, Coupled thermal–electrochemical modelling of uneven heat generation in lithium-ion battery packs, **Journal of Power Sources, 43, 2013, 544–554**

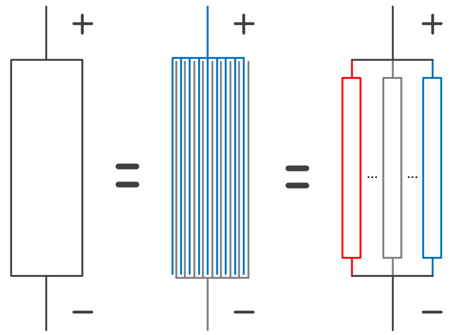
The effect of thermal gradients

- Under thermal gradients, a cell behaves like one with a higher average temperature



Effect is due to non-linear temperature dependence on charge transfer resistance

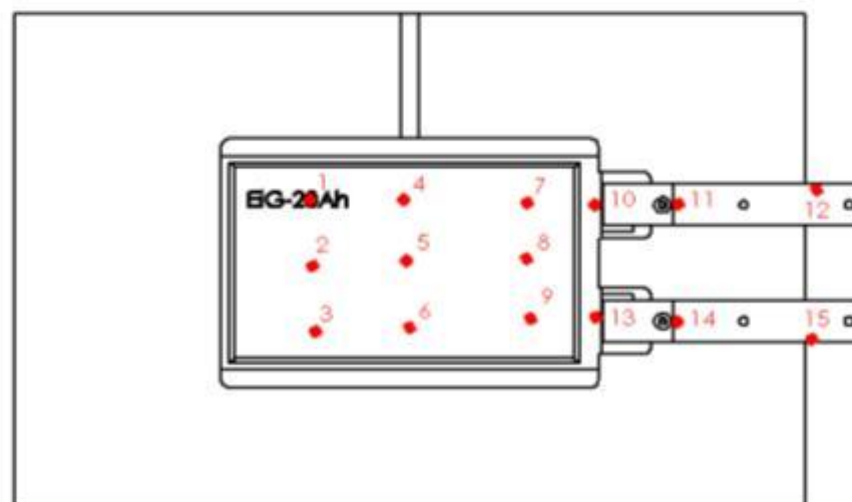




Troxler Y, Wu B, Marinescu M, Yufit V, Patel Y, Marquis AJ, Brandon NP, Offer GJ, The effect of thermal gradients on the performance of lithium-ion batteries, **Journal of Power Sources, 247, 2014, 1018-1025**

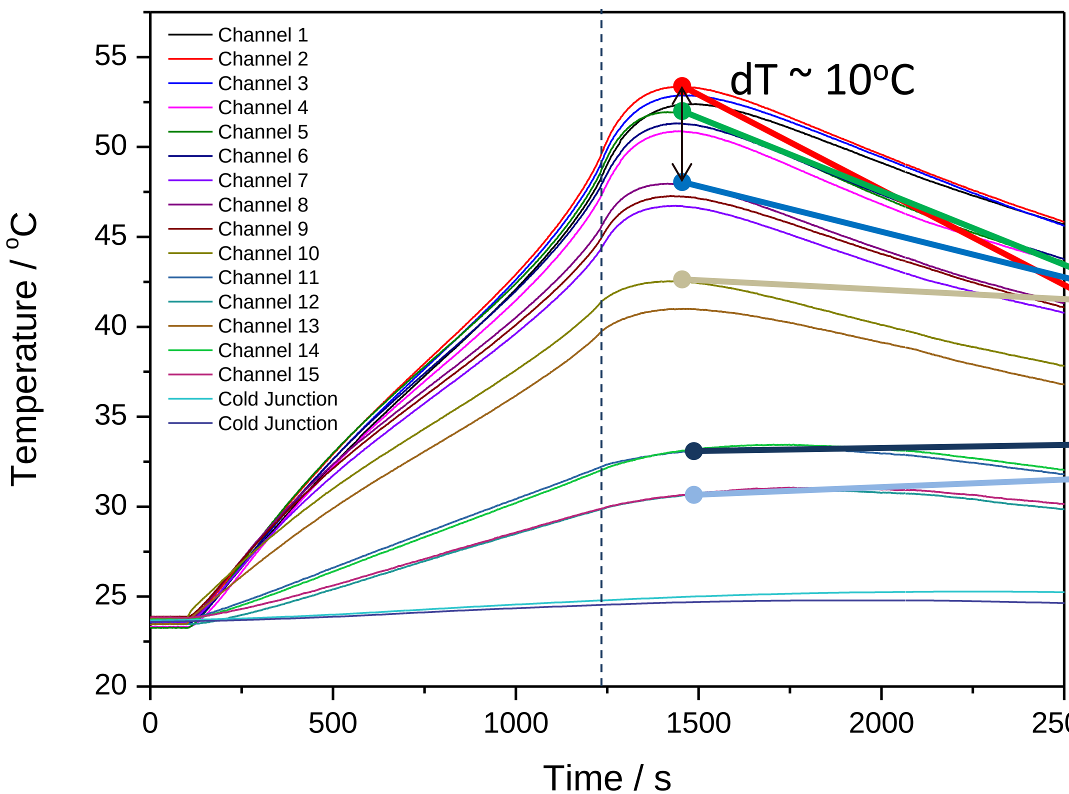
3C discharge of 20Ah EIG NCM battery

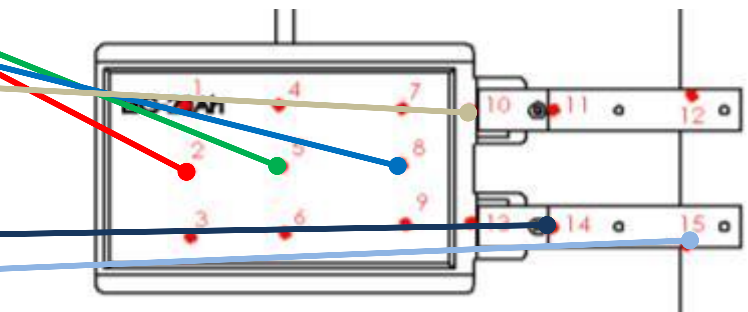
There is a need to manage thermal boundary conditions properly during experiments

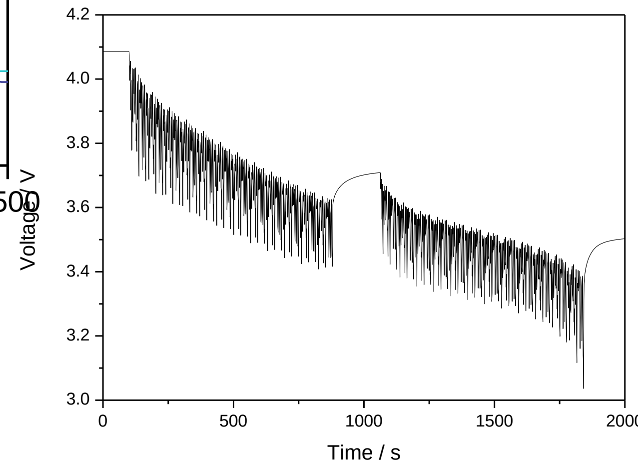


3C discharge of 20Ah EIG NCM battery

- Strong effect thermal boundaries
- Opposite behaviour to normally reported
- Caused by bus bars
- Similar to cell tab cooling
- Region high current is the coolest
- Significant extra heating 3-4oC

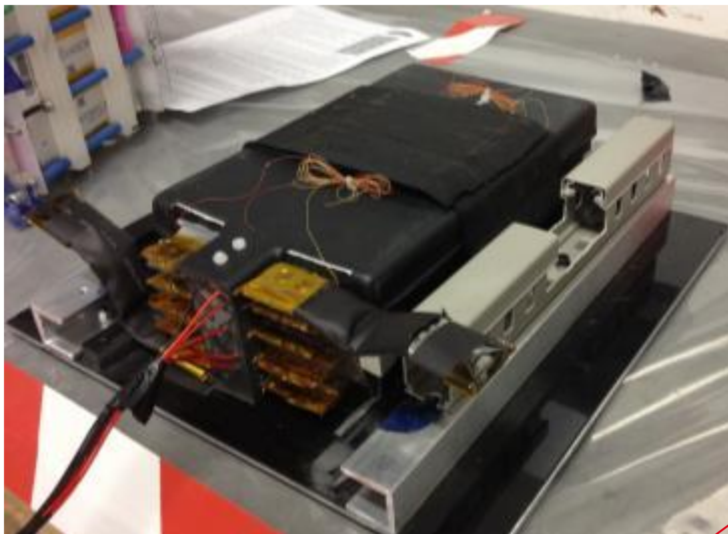




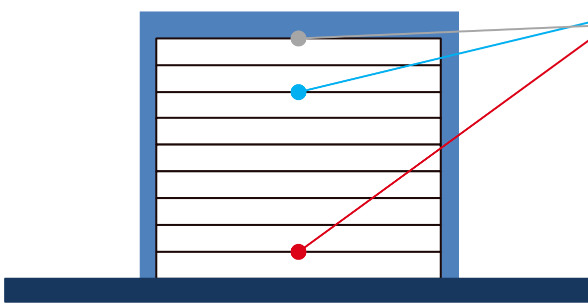


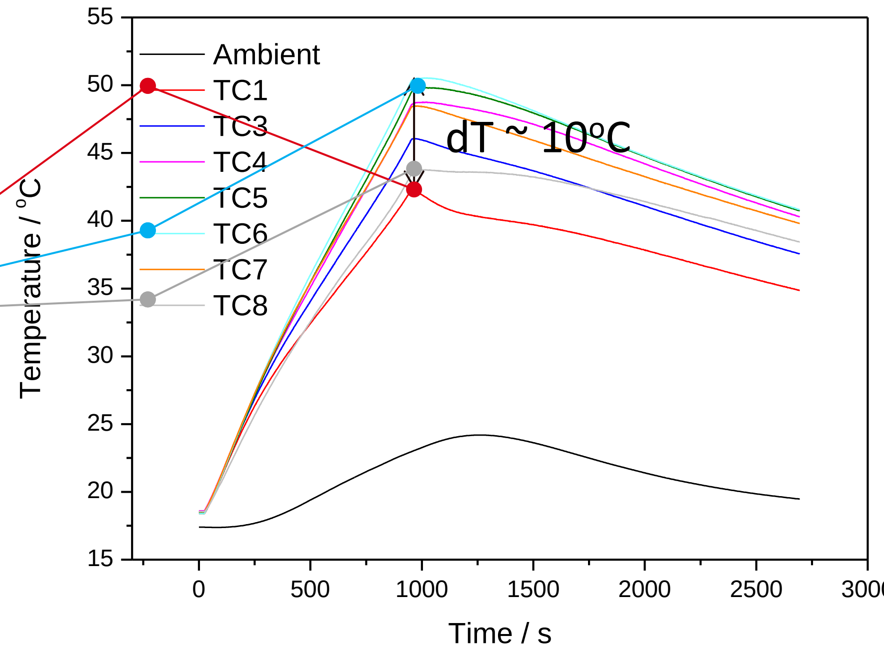
- Constant current, or real life load cycle = similar thermal behaviour

3C discharge of 9 cell x 20Ah EIG NCM battery



Prototype for testing
- Thermally conducting base plate *
- Insulated other boundaries
- Air exposed cell tabs *
- No thermal mgmt. system *





* All different in actual battery pack

Effect of cooling strategy

- In-between cells
  - <1mm total thickness
- Slip between cells in a stack
- Design of cooling channels important.

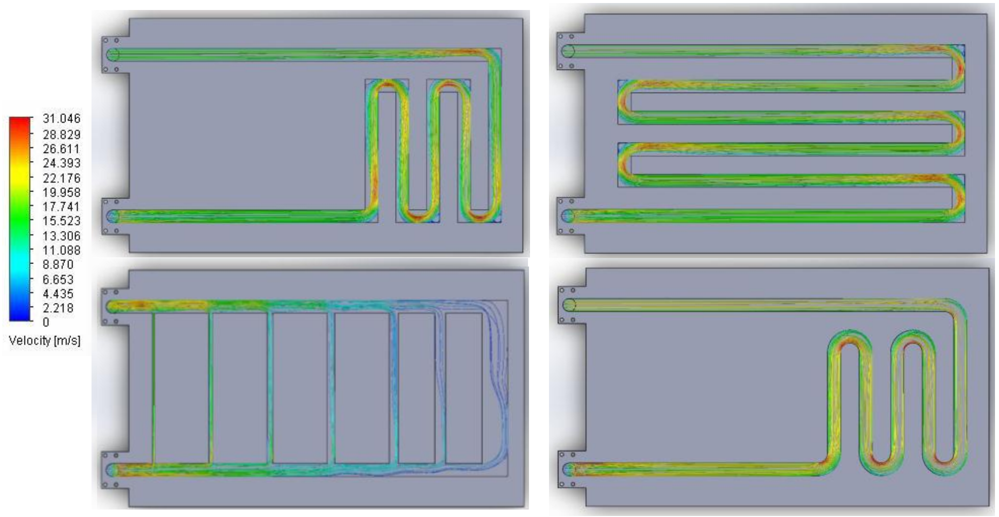
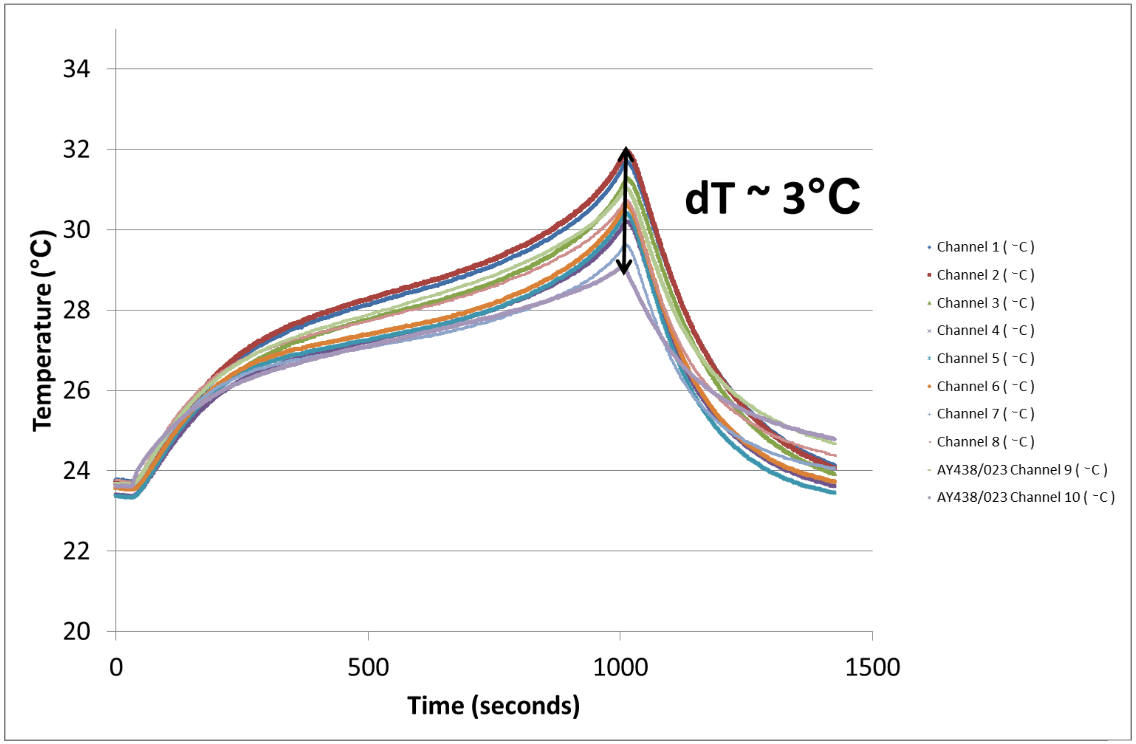
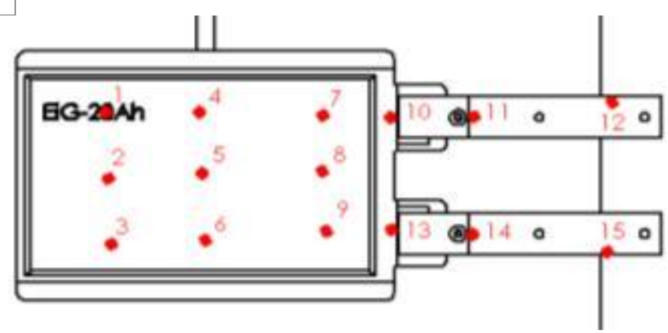


Plate cooling

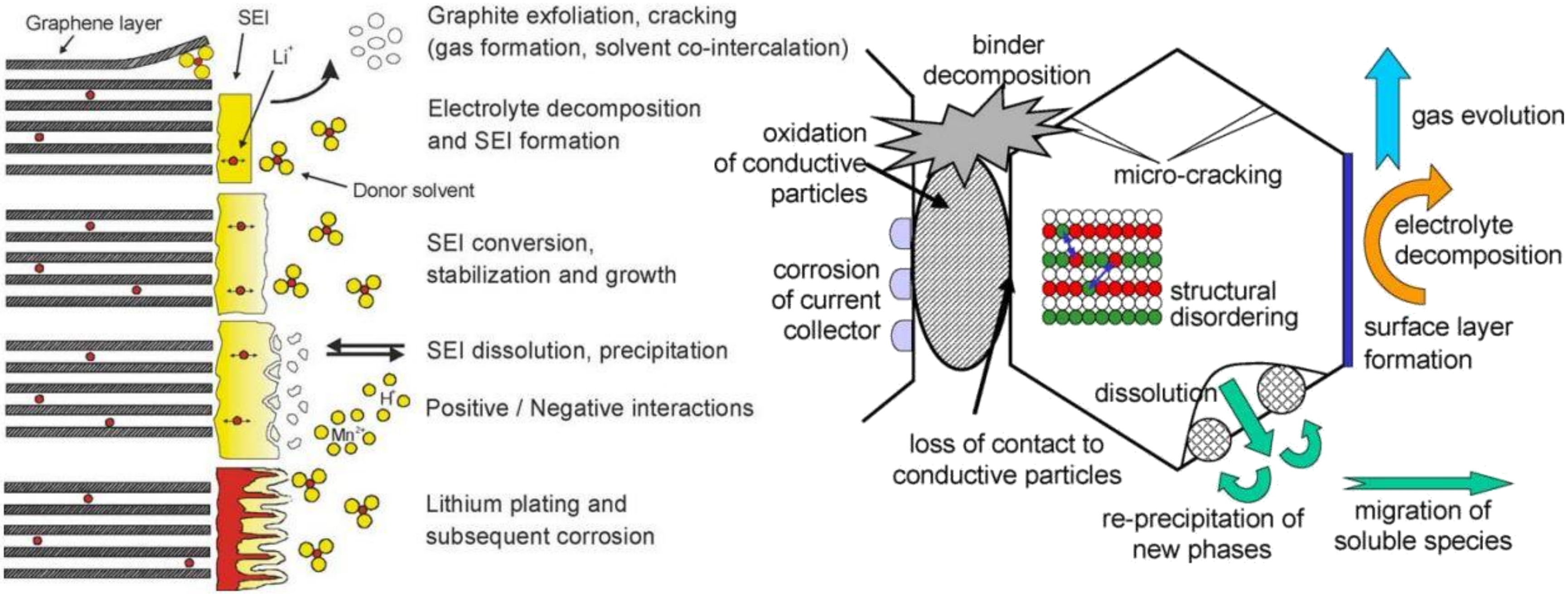


- Temperature difference is much smaller.
- Design of cooling channels could be optimised further.
- Will lead to temperature gradients in ‘z’ direction.



Degradation in lithium-ion batteries

- Lithium-ion batteries degrade
- Various irreversible losses over the lifetime of a cell lead to capacity fade and power fade
- Monitoring of degradation in batteries is of critical importance



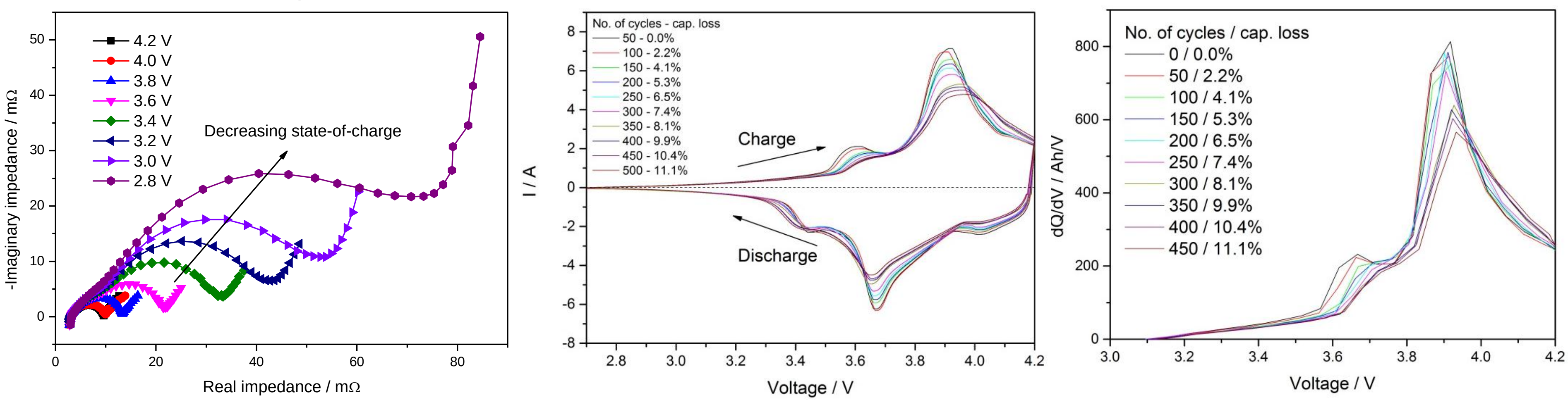
Schematics of various degradation mechanisms at the anode-electrolyte interface and the cathode region

Aging mechanisms in lithium-ion batteries.
Vetter et. al Journal of Power Sources doi:10.1016/j.jpowsour.2005.01.006.

Existing degradation diagnostics

- Electrochemical Impedance Spectroscopy (EIS)
- Slow-Rate Cyclic Voltammetry (SRCV)
- Incremental Capacity method (IC)

EIS SRCV IC

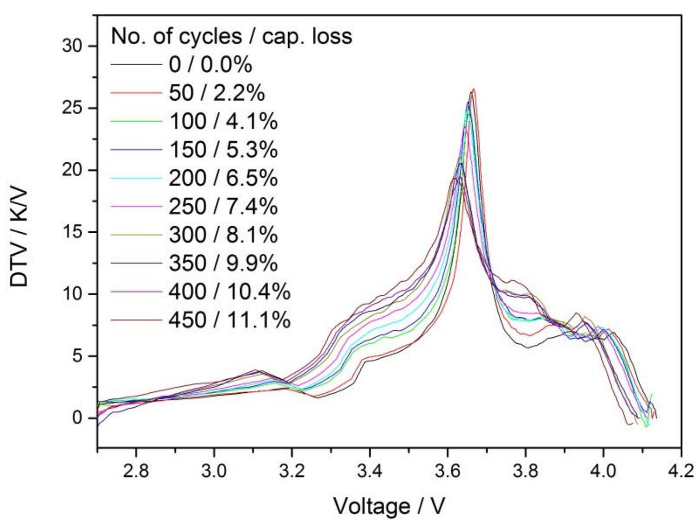


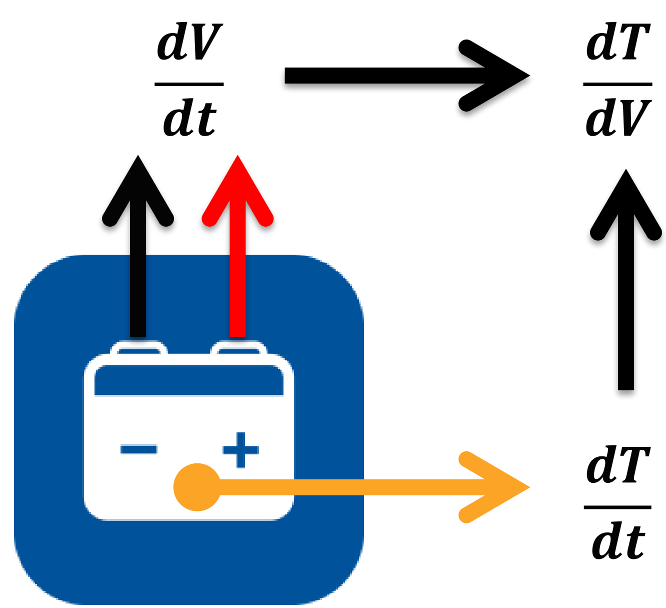
Experimental results of a 4.8 Ah Kokam lithium-polymer cell at different voltages/states of capacity fade. EIS (left), SRCV (middle), IC curve (right).

Wu B, Yufit V, Merla Y, Martinez-Botas RF, Brandon NP, Offer GJ, Differential thermal voltammetry for tracking of degradation in lithium-ion batteries, **Journal of Power Sources 2015, 273, Pages 495-501**

Differential Thermal Voltammetry

- New in-situ battery diagnosis method for tracking degradation
- Uses the temperature profile under constant current discharge to infer the same data as SRCV/IC but in a much reduced time
- $DTV = \frac{dT}{dt} / \frac{dV}{dt} = \frac{dT}{dV}$
- Plotted against cell voltage, it may be possible to give an indication of the entropy changes in carefully controlled conditions
- Peaks represent phase transformation





Wu B, Yufit V, Merla Y, Martinez-Botas RF, Brandon NP, Offer GJ, Differential thermal voltammetry for tracking of degradation in lithium-ion batteries, **Journal of Power Sources 2015, 273, Pages 495-501**

Advantages / Disadvantages

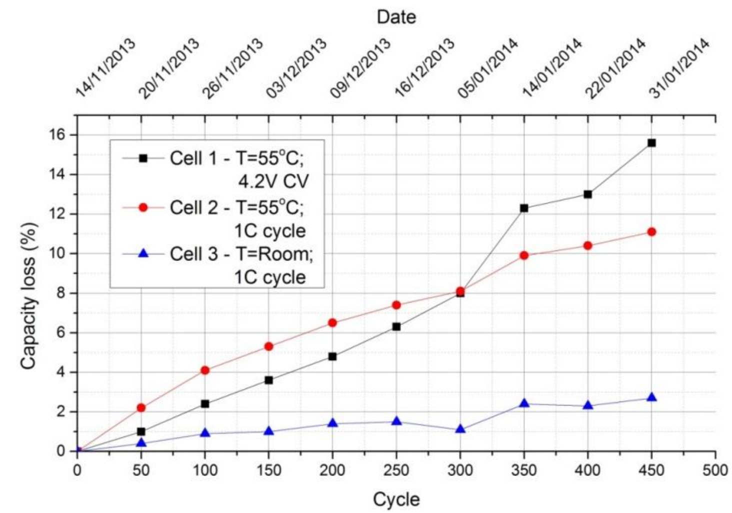
- Made for application in real world systems
  - Extract the same amount of information as a SRCV/IC
  - Takes only a few minutes
  - Simple computation : dT/dV
  - Only requires voltage and temperature measurements (useful in parallel packs)
  - Does not require iso-thermal condition

Requirements	Differential Thermal Voltammetry	Electrochemical Impedance Spectroscopy	Slow-rate Cyclic Voltammetry (SRCV)	Incremental Capacity (dQ/dV)
Measurements	Temp., Voltage	Impedance	Current, Voltage	Current, Voltage
Time	Minutes	Minutes	Hours	Hours
Computation	Simple	Complex	Simple	Simple
Temperature	Natural	Constant	Constant	Constant

Wu B, Yufit V, Merla Y, Martinez-Botas RF, Brandon NP, Offer GJ, Differential thermal voltammetry for tracking of degradation in lithium-ion batteries, **Journal of Power Sources 2015, 273, Pages 495-501**

Accelerated Degradation Experiment

- 4.8Ah Lithium polymer batteries made by Dow Kokam
- Carbon anode and Nickel-Manganese-Cobalt cathode
- 3 cells stored/operated at various conditions
- EIS, SRCV, IC and DTV carried out at every 50 cycles at room temperature to track degradation



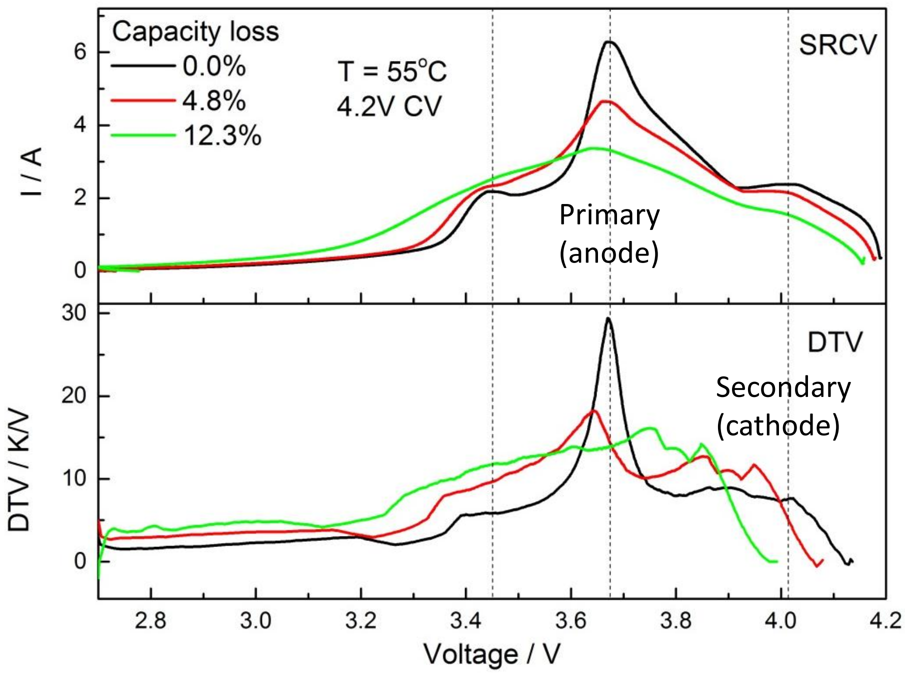
Cell	Temperature	Loading
1	55°C	4.2V Hold
2	55°C	1C cycling
3	Room	1C cycling

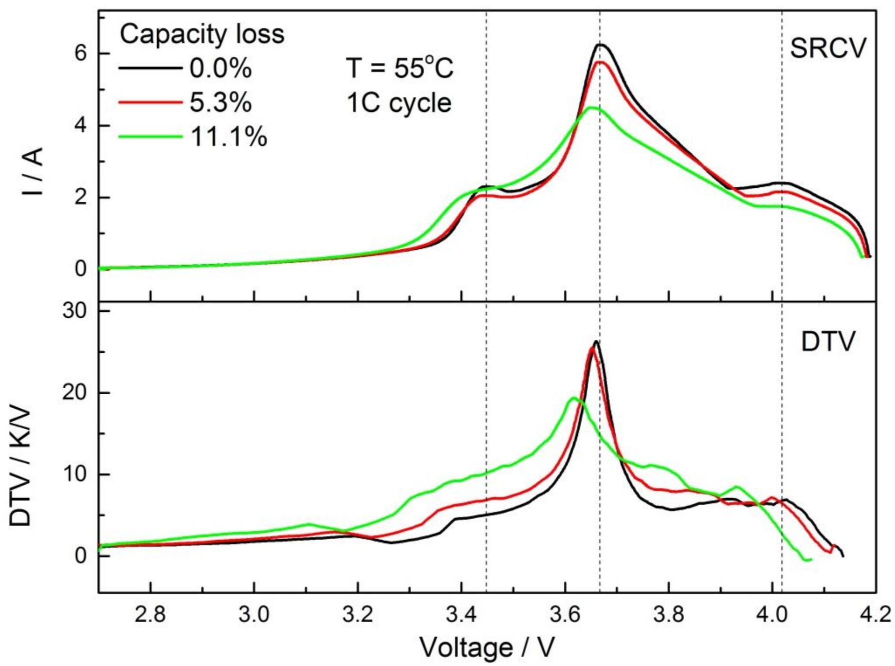
4.8Ah lithium polymer Kokam cell

Wu B, Yufit V, Merla Y, Martinez-Botas RF, Brandon NP, Offer GJ, Differential thermal voltammetry for tracking of degradation in lithium-ion batteries, **Journal of Power Sources 2015, 273, Pages 495-501**

SRCV vs. DTV

- Similar peak potentials and changes through capacity loss between the two methods
- 3 hours for SRCV and 30 minutes for DTV
- Cell held at 4.2V: significant change in both peaks, anode and cathode
- Cycled cell: small change in the anode peak but negligible for the cathode



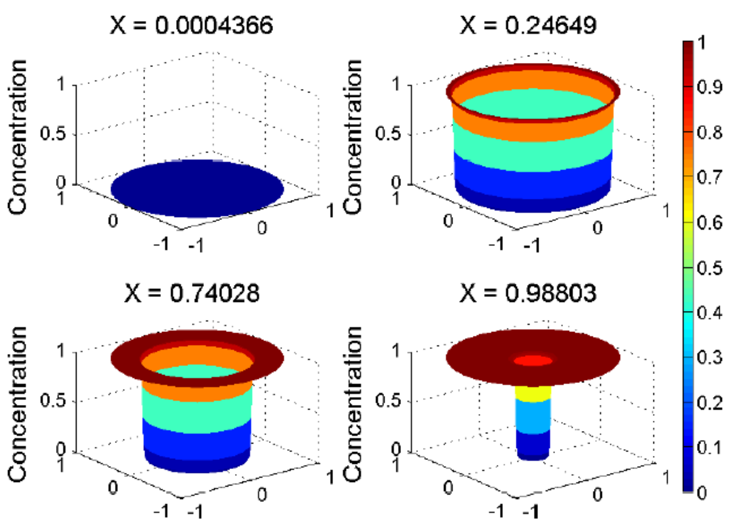


Comparison of experimental SRCV and DTV results for a 4.8Ah lithium polymer Kokam cell at various stages of capacity fade

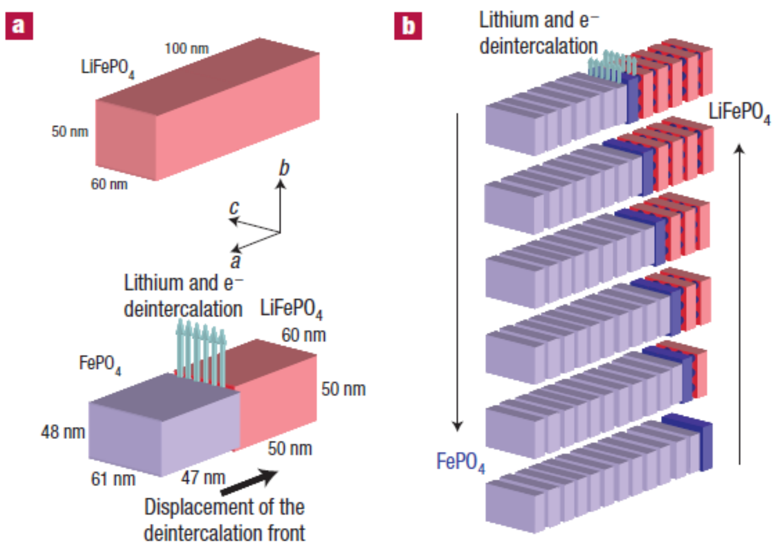
Wu B, Yufit V, Merla Y, Martinez-Botas RF, Brandon NP, Offer GJ, Differential thermal voltammetry for tracking of degradation in lithium-ion batteries, **Journal of Power Sources 2015, 273, Pages 495-501**

Current Research Problem

- Modelling Lithium Iron Phosphate (LFP) cathodes
- Phase change material with flat voltage profile & large hysteresis effect
- Competing models, shrinking core vs. domino cascade, both work but the latter is more 'physically' correct



Zeng, Y. I., Bazant, Martin Z.



Delmas, C., Maccario, M., Croguennec, L., Le Cras, F., Weill, F

Thank You for your time!

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