Imperial College London

CATAPULT High Value Manufacturing

Advances in online lithium plating quantification following fast charging

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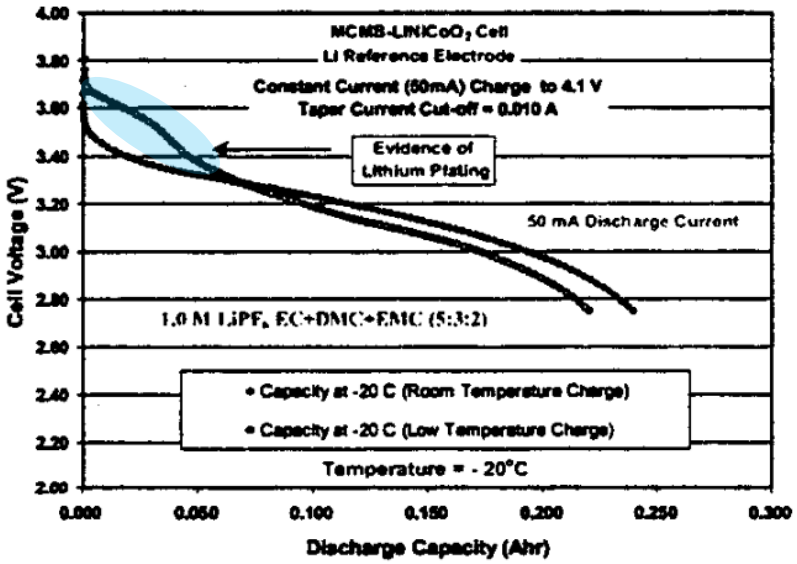
In-situ Lithium Plating Detection Options

$$Li_xC_6 \underset{\text{reduction}}{\overset{\text{oxidation}}{\rightleftharpoons}} xLi^+ + xe^- + 6C \qquad [1]$$

$$Li^0 \underset{\text{reduction}}{\overset{\text{oxidation}}{\rightleftharpoons}} (1-x)Li^+ + (1-x)e^- \qquad [2]$$



M C Smart, B V Ratnakumar, L Whitcanack, K Chin, M Rodriguez, and S Surampudi. Performance Characteristics of Lithium Ion Cells at Low Temperatures. pages 16–20, 2002.

I want my BMS to detect lithium plating

..but my BMS can't disassemble cells

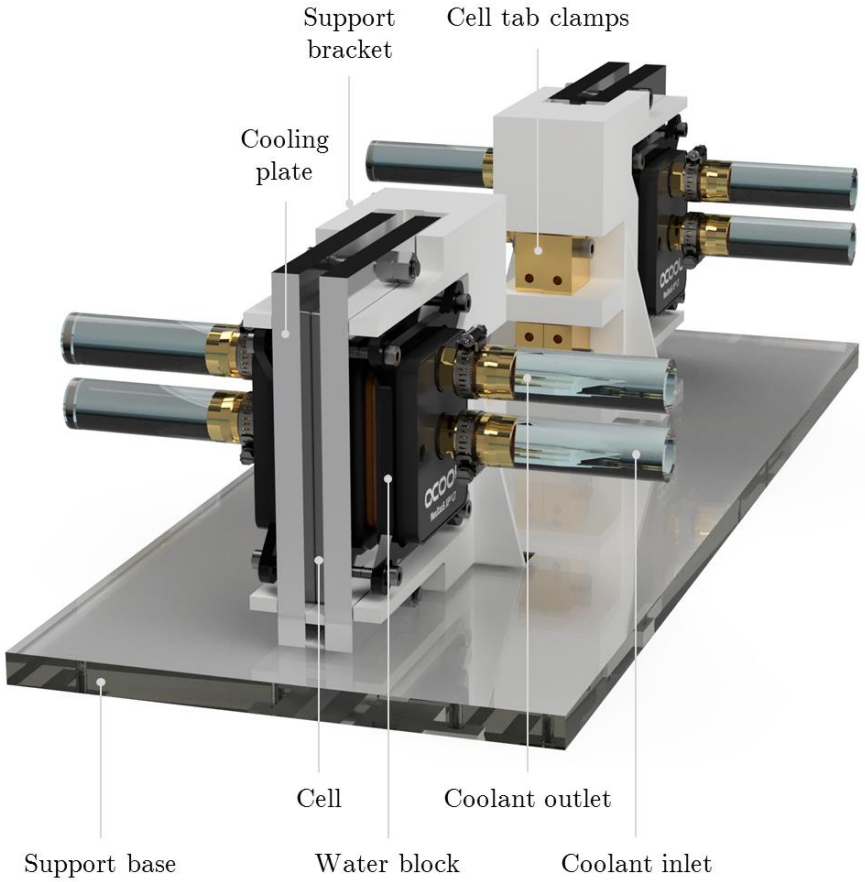
Work	Max. rate (Low T_{amb})	T_{amb}, (°C)
Smart et al.[22]	$\frac{1}{8}$ C	-40, -20, 23
Smart et al.[23]	$\frac{1}{3}$ C	-40, -20, 0, 23
Fan & Tan[10]	$\frac{1}{1.25}$ C	-30, -20, RT[a]
Smart & Ratnakumar[21]	$\frac{1}{5.7}$ C	-40, -30, -20, 25
Zinth et al.[31]	$\frac{1}{5}$ C	-20
Petzl & Danzer[16]	1 C	-26, -24, -22, -20
Danzer, Bauer, Schindler & Petzl[6]	1 C	-20, 25
Waldmann et al.[27]	$\frac{1}{2}$ C	0, 5, 25, 45
Waldmann & W-Mehrens[28]	$\frac{1}{2}$ C	0
Kowal et al.[11]	3 C	−20, -10, 0
Yang et al.[30]	5 C	0

[a] RT refers to Room Temperature, where authors did not specify a value

Two Cooling Scenarios

Natural convection

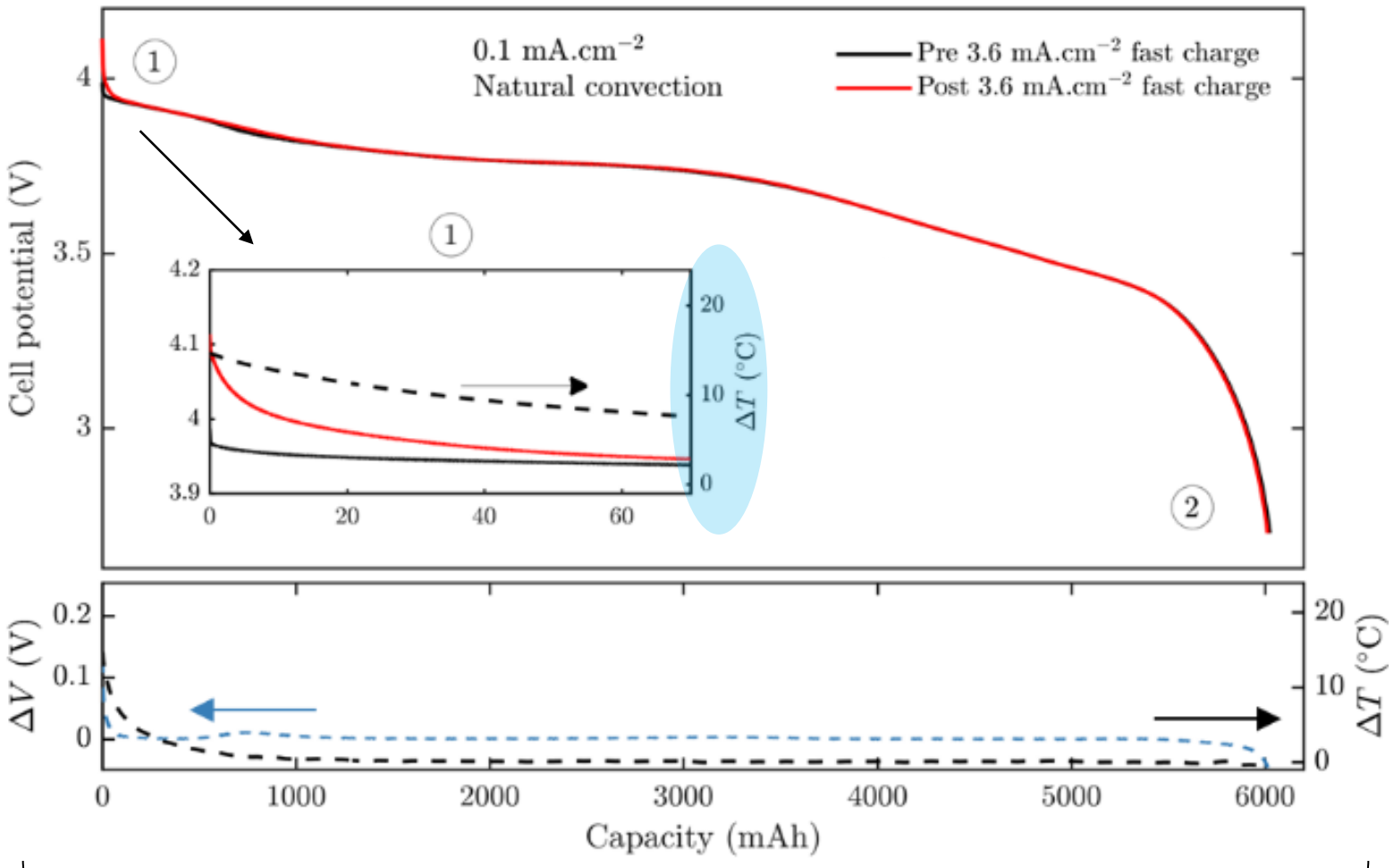
Conduction & forced convection



Voltage Plateau with Fast Charging

False Positives & Obfuscation

2C



Natural convection

Voltage Plateau with Fast Charging
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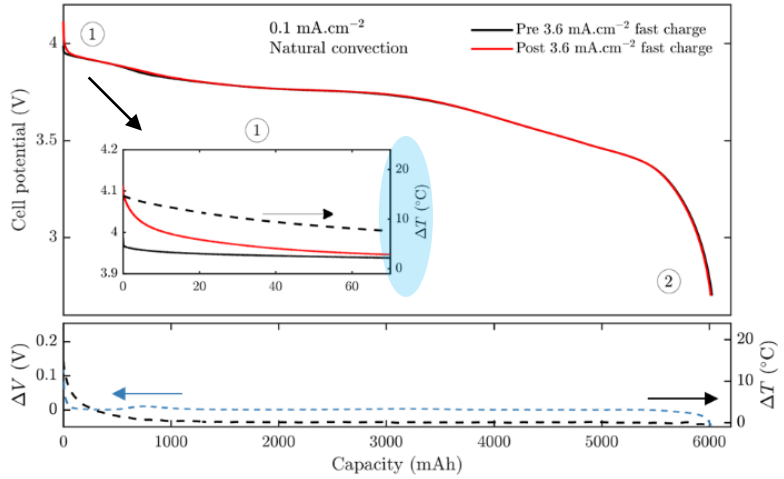
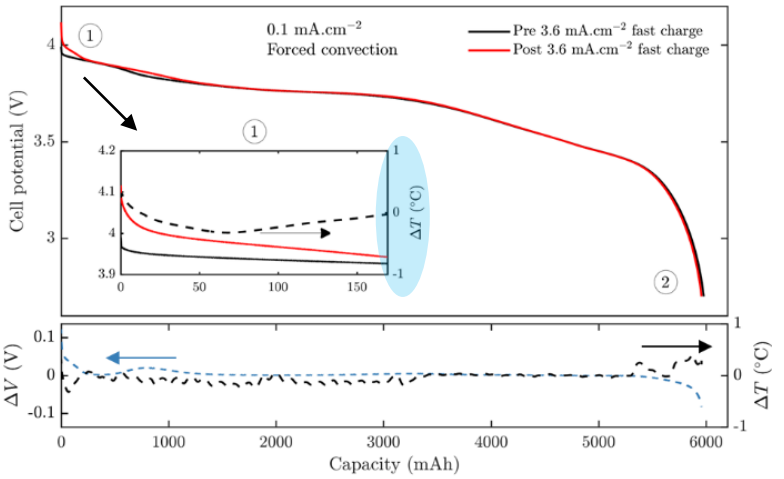
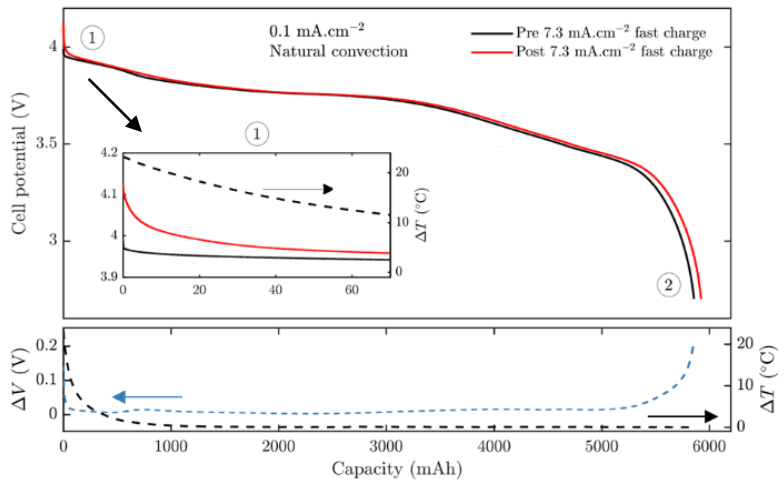
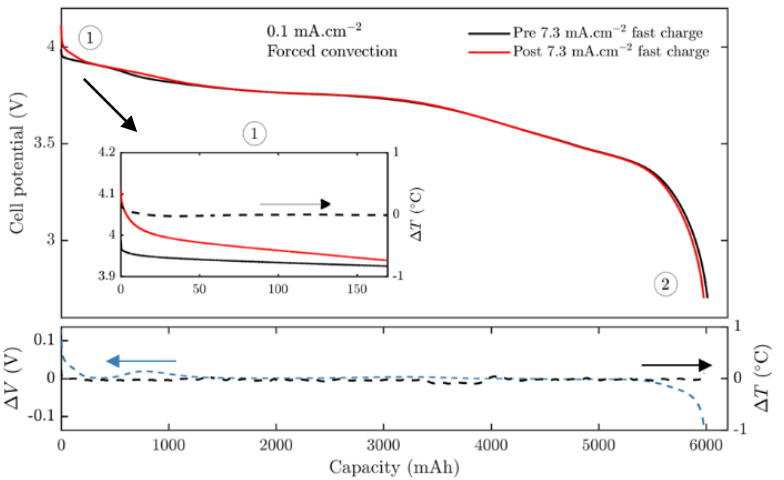




4C

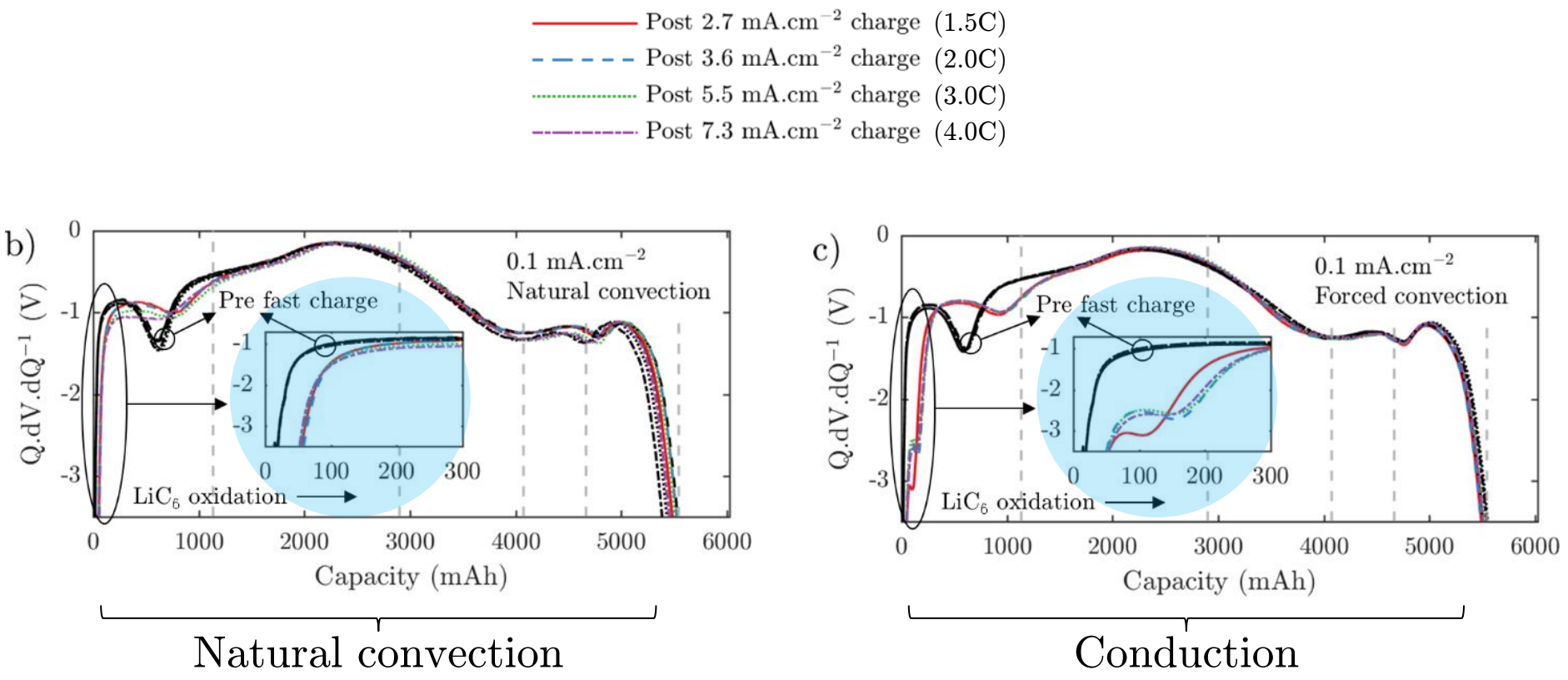




Natural convection

Conduction

Differential Voltage Analysis for Robust Identification

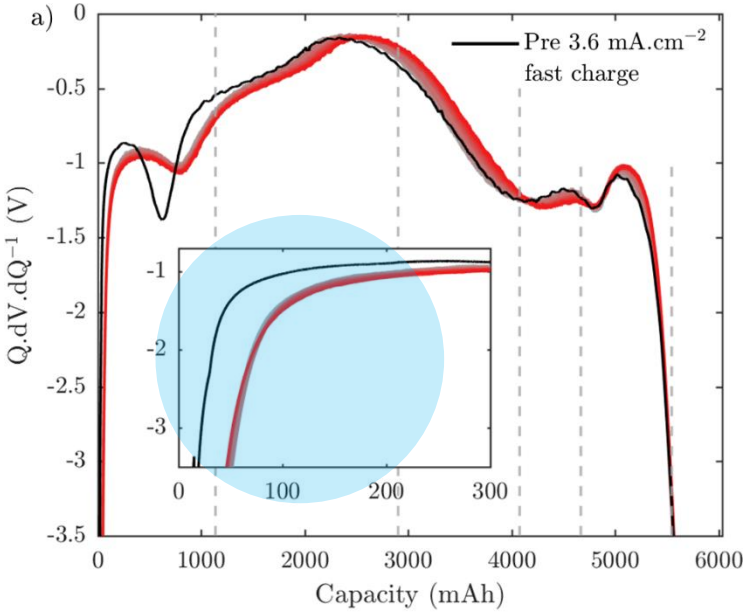


What's New?

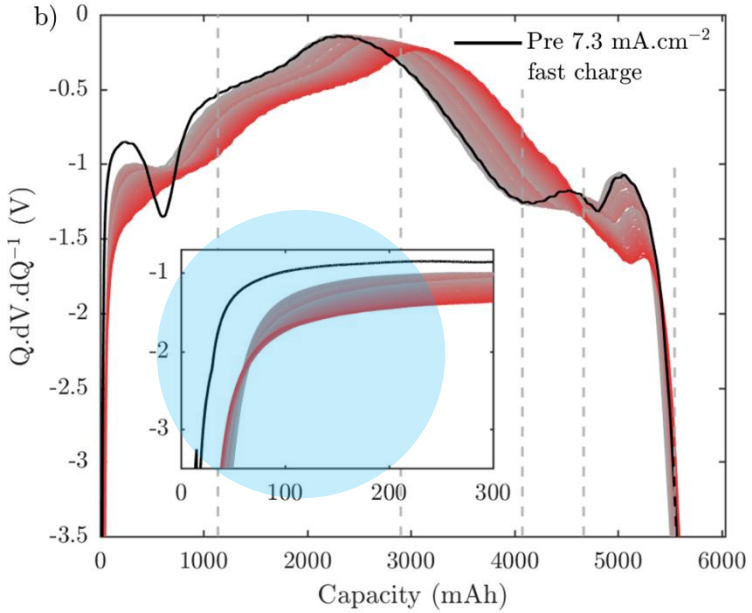
Fast charging & high heat gen.: dV/dQ *necessary* for robust identification

Beware the False Negative

- Natural convection
- Cell charging at 2C & 4C, discharging at C/20
- 63 complete cycles per cell



2C



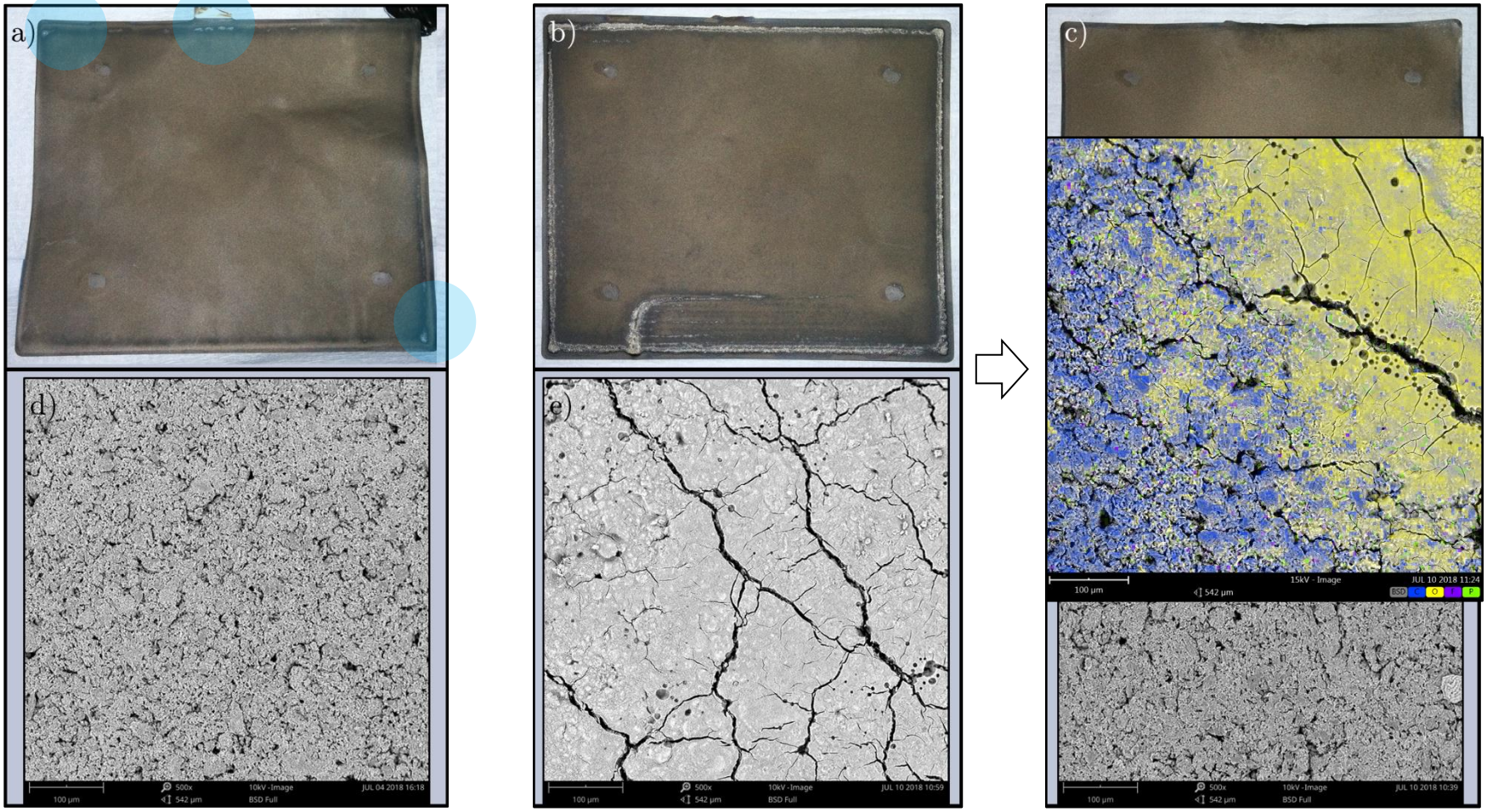
4C

Electrode Imaging & SEM

2C (3.6 mA.cm^{-2})

4C (7.3 mA.cm^{-2})

Fresh cell



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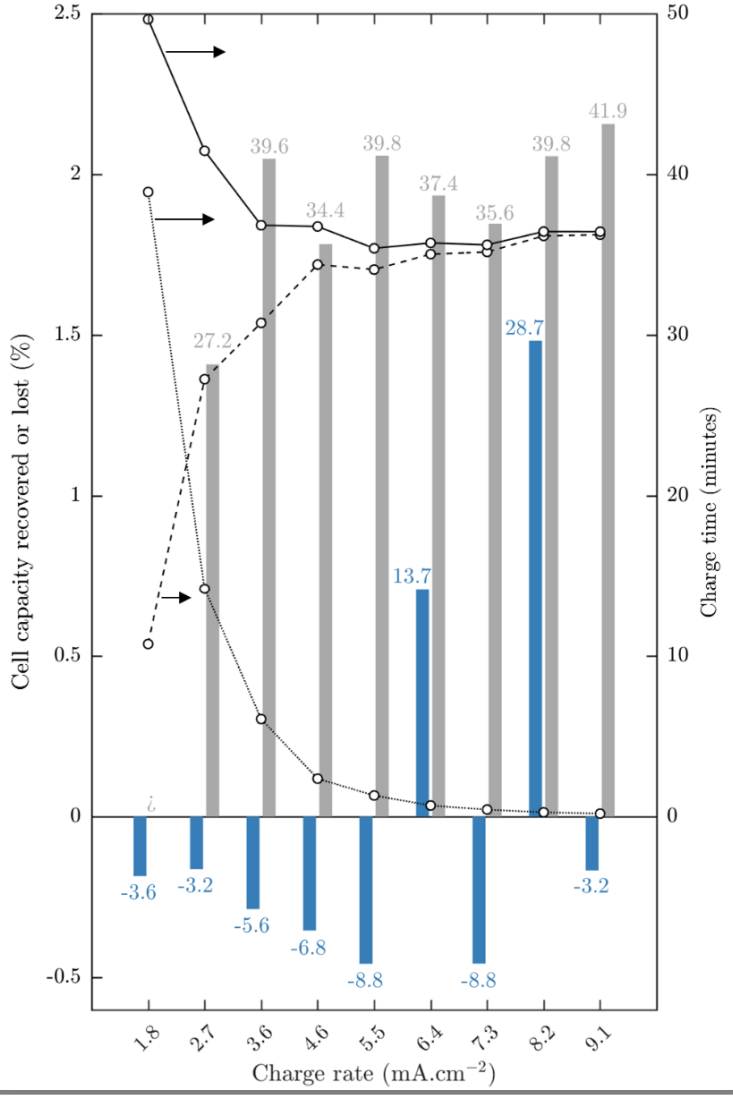
Fast charging & high heat gen.: dV/dQ *necessary* for robust identification

No stripping signature? Plating might still be occurring

Drivers of Results & Quantification Errors



ΔQ, irreversible LLI
ΔQ, recovery via Li^0 stripping
CC phase only
CV phase only
Total

$$\left|\sum\left(Li_{stripped} + Li_{lost}\right)\right| = \left|Li_{plated}\right|$$

- CC vs. CV phase duration
- t_{charge} ↓ $t_{chemical}$ ↑
- Stripping quantification ≠ plating quantification
- High-precision coulometry required

What's New?

Fast charging & high heat gen.: dV/dQ *necessary* for robust identification

No stripping signature? Plating might still be occurring..

$$\left|\sum\left(Li_{stripped} + Li_{lost}\right)\right| \neq \left|Li_{plated}\right|$$

$$= \left|Li_{plated}\right| - \left|Li_{chemical}\right|(t_{charge})$$

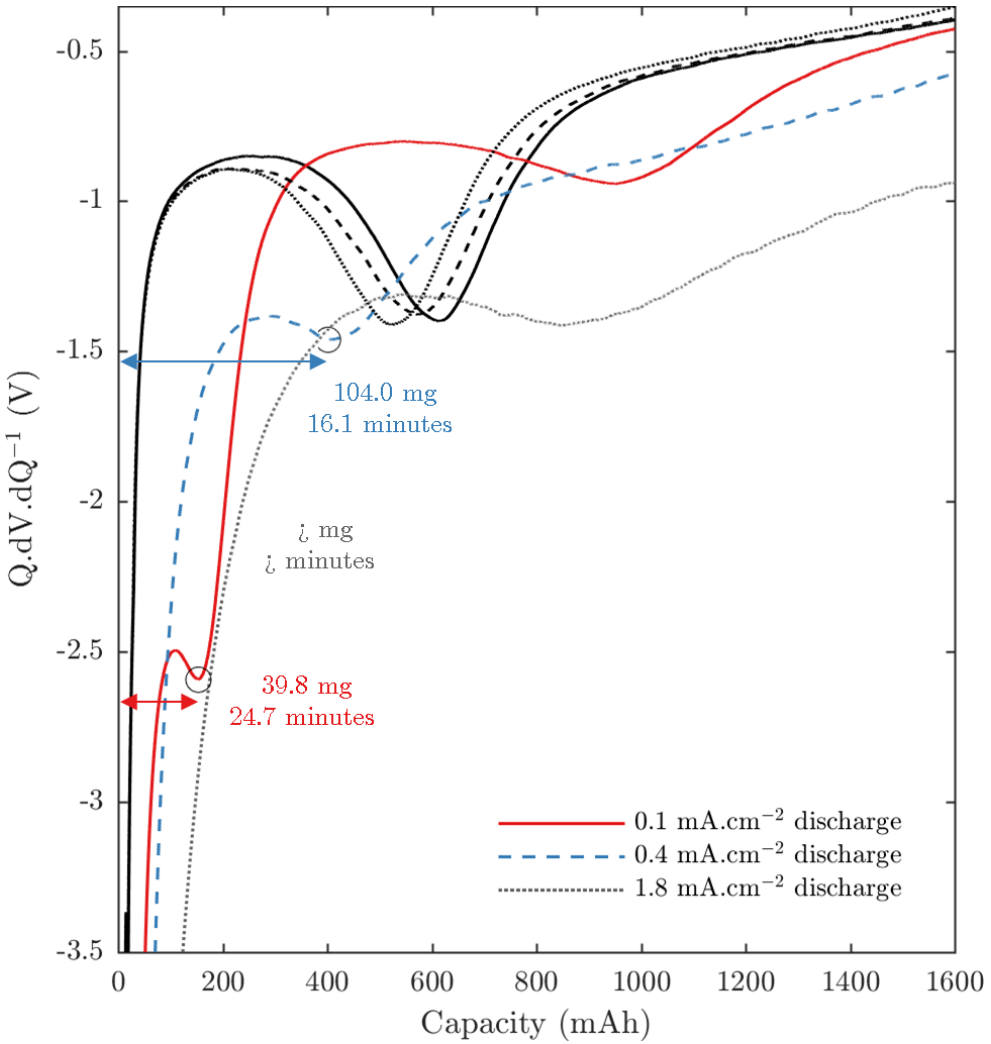
Accelerating Quantification

- 3 different cells
- 3 different discharge rates
- Conduction BC

- Cell charging at 5.5 mA.cm^{-2} (3C)

- Discharge at C/20, C/5, 1C

- dV/dQ inflections suppressed



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$$\left|\sum\left(Li_{stripped} + Li_{lost}\right)\right| \neq \left|Li_{plated}\right|$$

$$= \left|Li_{plated}\right| - \left|Li_{chemical}\right|(t_{charge})$$

$$\left|\sum\left(Li_{stripped}(I_{discharge}) + Li_{lost}\right)\right| = \left|Li_{plated}\right| - \left|Li_{chemical}\right|(t_{charge})$$

Acknowledgements

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