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Advanced modelling for Li-ion battery design, diagnostics and R&D

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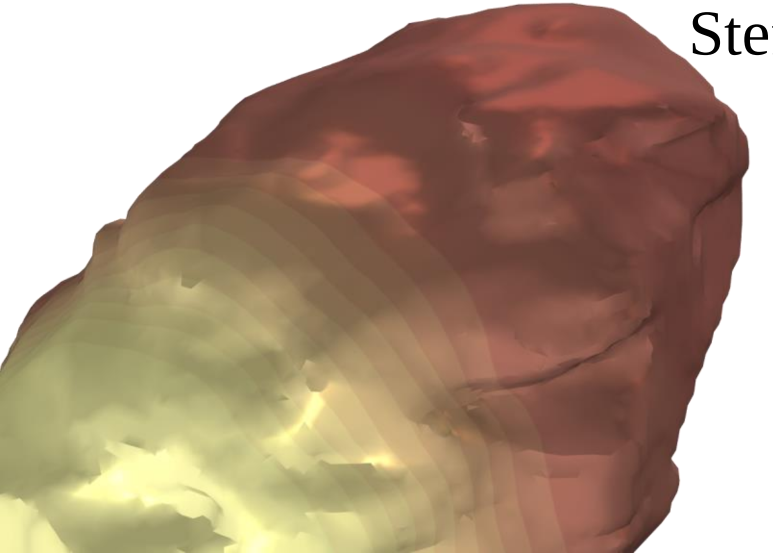

Li-ion batteries in dynamic operations

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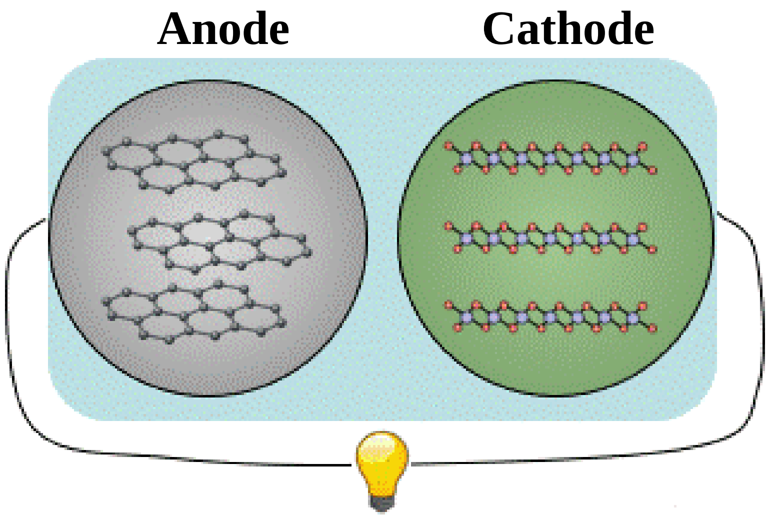
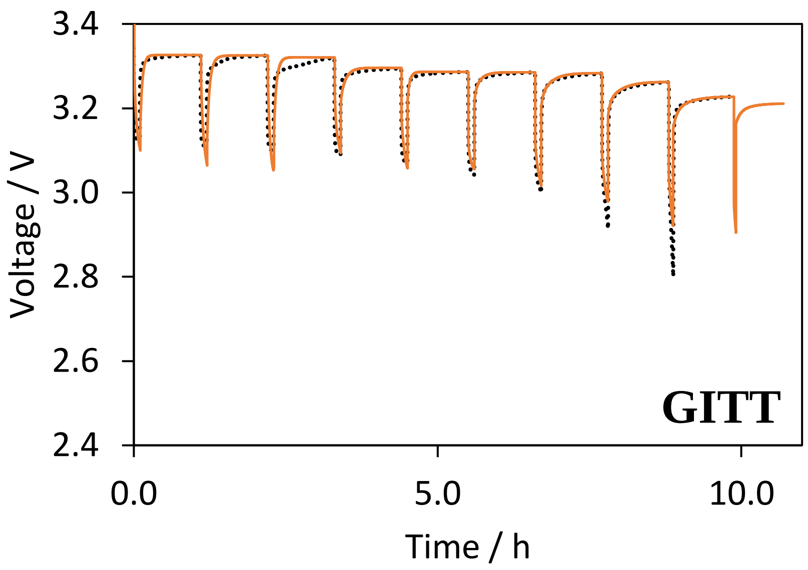
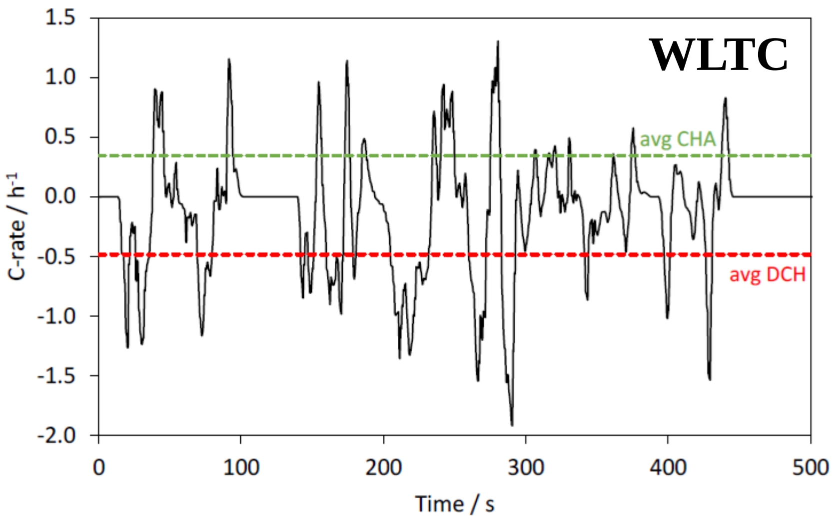
Li-ion batteries are energy storage devices → no steady-state operation

We need to characterise dynamic processes: reactions, charge transport, diffusion, degradations, etc.







What hinders fast charging

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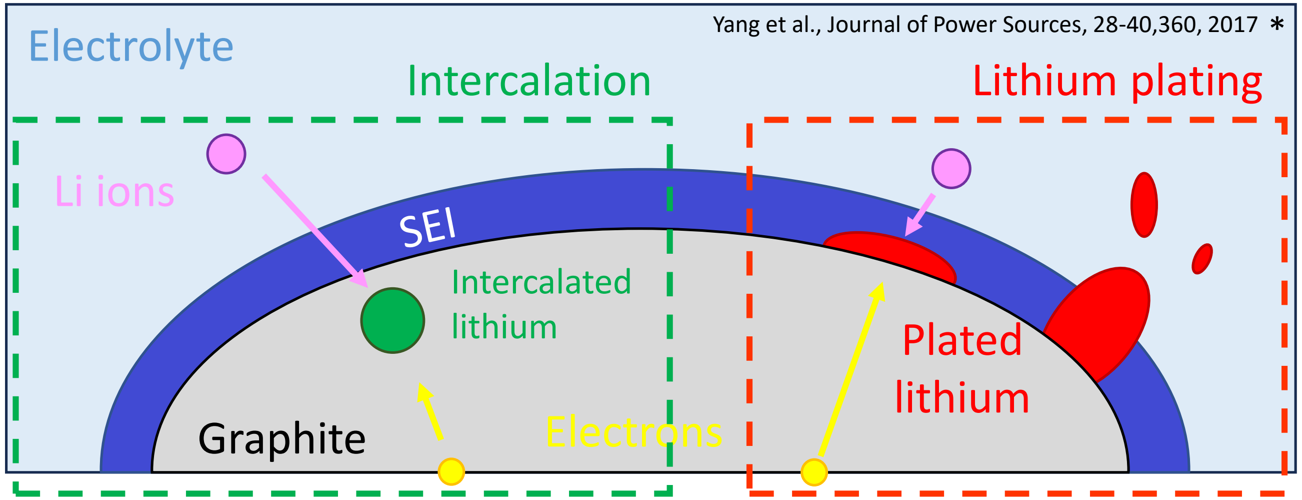
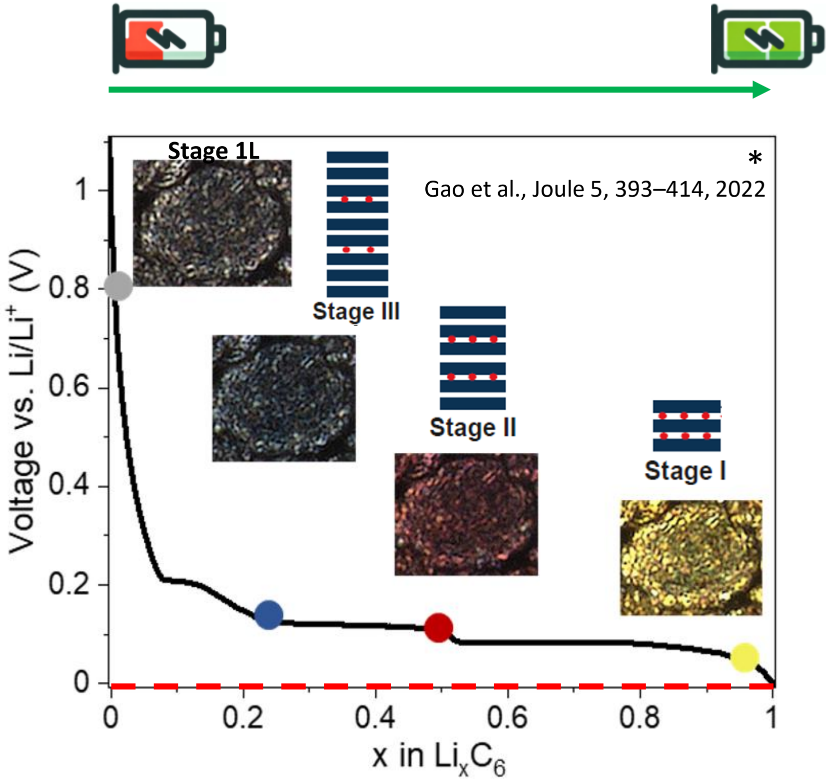
Desired reaction: Li intercalation in graphite

$$xLi^{+}_{(ey)} + xe^{-}_{(gr)} + C_{6(gr)} \rightarrow Li_{x}C_{6(gr)}$$

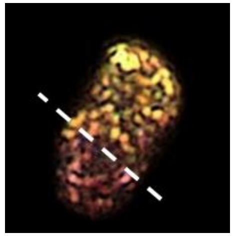


Undesired reaction: Li plating

$$Li^{+}_{(ey)} + e^{-}_{(gr)} \rightarrow Li_{(Li)} \quad \text{for } E < 0 \text{ V vs Li}$$



Phase separation in Li-rich and Li-poor phases



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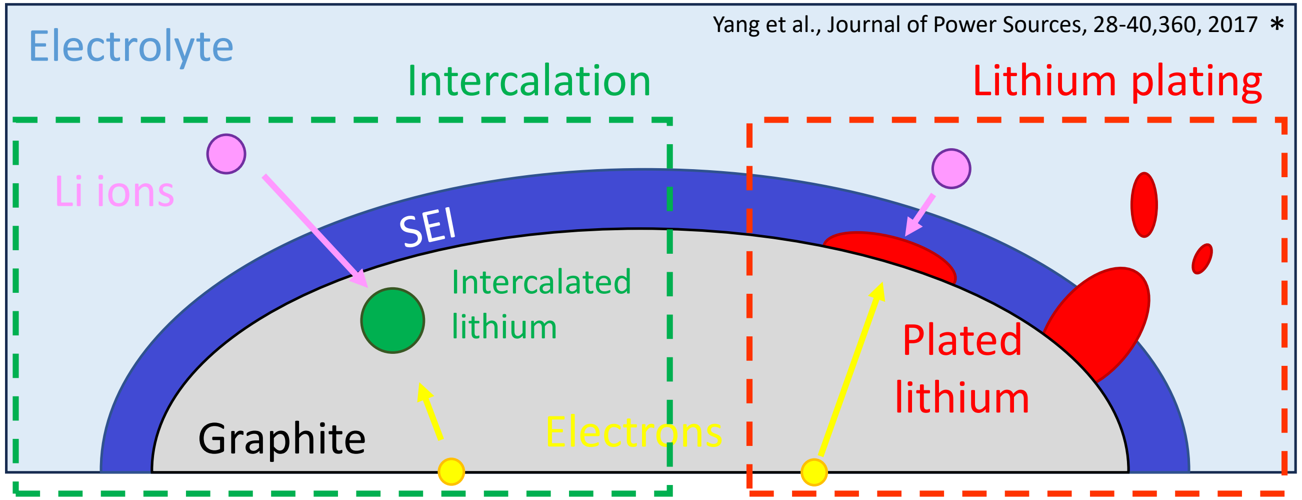

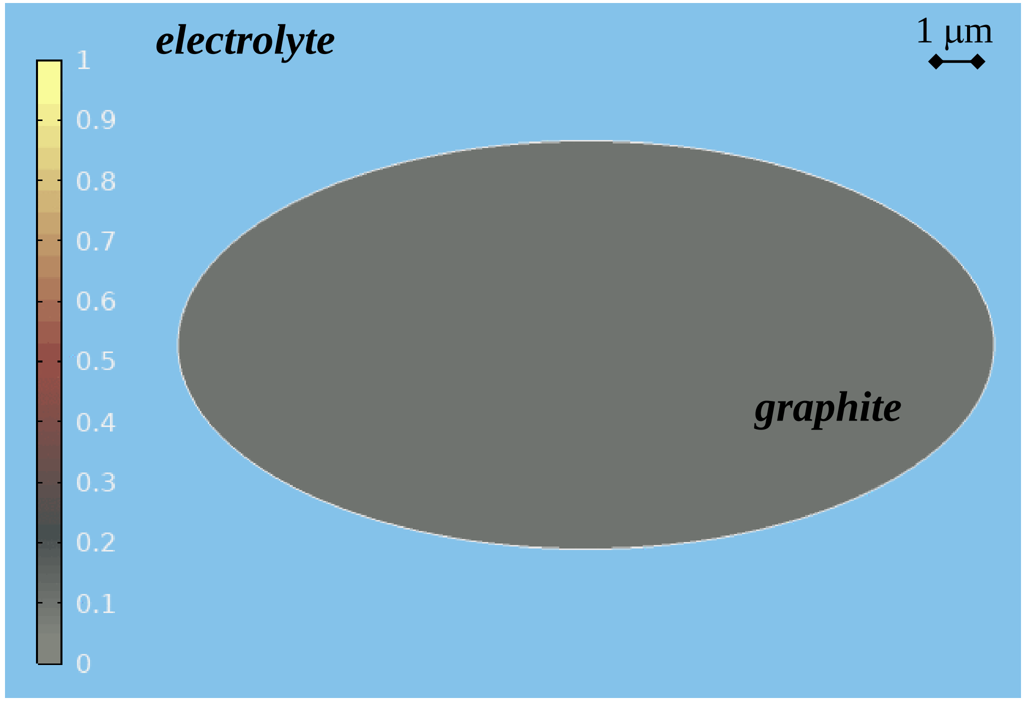

Undesired reaction: Li plating

$$Li^{+}_{(ey)} + e^{-}_{(gr)} \rightarrow Li_{(Li)} \quad \text{for } E < 0 \text{ V vs Li}$$

Goals of the study

1. Model the interplay between graphite phase-separation and Li plating

2. Quantify kinetic and transport parameters

3. Develop model-guided fast-charging protocols

Electrochemical modelling: from 1D to 3D

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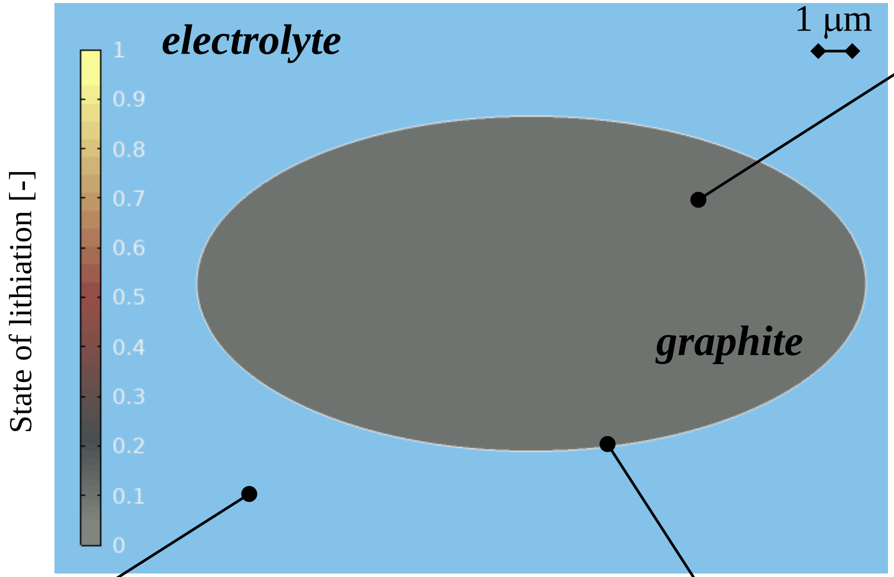


Electron and Li conservation

$$e^- : \nabla \cdot J_e = 0$$

$$Li : F c_s^{\max} \frac{\partial sol}{\partial t} + \nabla \cdot J_s = 0$$

$$J_e = -\sigma_e \nabla \tilde{\mu}_e^*$$

$$J_s = -F \frac{D_s}{RT} (1 - sol) c_s \nabla \mu_{Li-C}$$

$$\mu_{Li-C} = \mu_{Li-C}^{eq} (sol) - RTa^2 \nabla^2 sol$$

General Form PDE
+
Boundary ODEs
+
Phase-field approach

Ion conservation

$$Li^+ : F \frac{\partial c}{\partial t} + \nabla \cdot J_+ = 0$$

$$PF_6^- : -F \frac{\partial c}{\partial t} + \nabla \cdot J_- = 0$$

$$J_+ = -t_+ \sigma \nabla \tilde{\mu}_+^*$$

$$J_- = \frac{F\tilde{D}}{t_+} \nabla c - (1 - t_+) \sigma \tilde{\mu}_+^*$$

Kinetics of intercalation and plating

$$xLi_{(ey)}^+ + xe_{(gr)}^- + C_{6(gr)} \rightleftharpoons Li_x C_{6(gr)}$$

$$J_{int} = i_{0,int} \left[\exp\left(\alpha_{int} \frac{F}{RT} \eta_{int} \right) - \exp\left(-(1 - \alpha_{int}) \frac{F}{RT} \eta_{int} \right) \right]$$

$$i_{0,int} = k_{int} \left(\frac{c}{c_{ref}} \right)^{\alpha_c} \left(\frac{c_s}{c_s^{\max}} \right)^{\alpha_a} \left(\frac{c_s^{\max} - c_s}{c_s^{\max}} \right)^{\alpha_c}$$

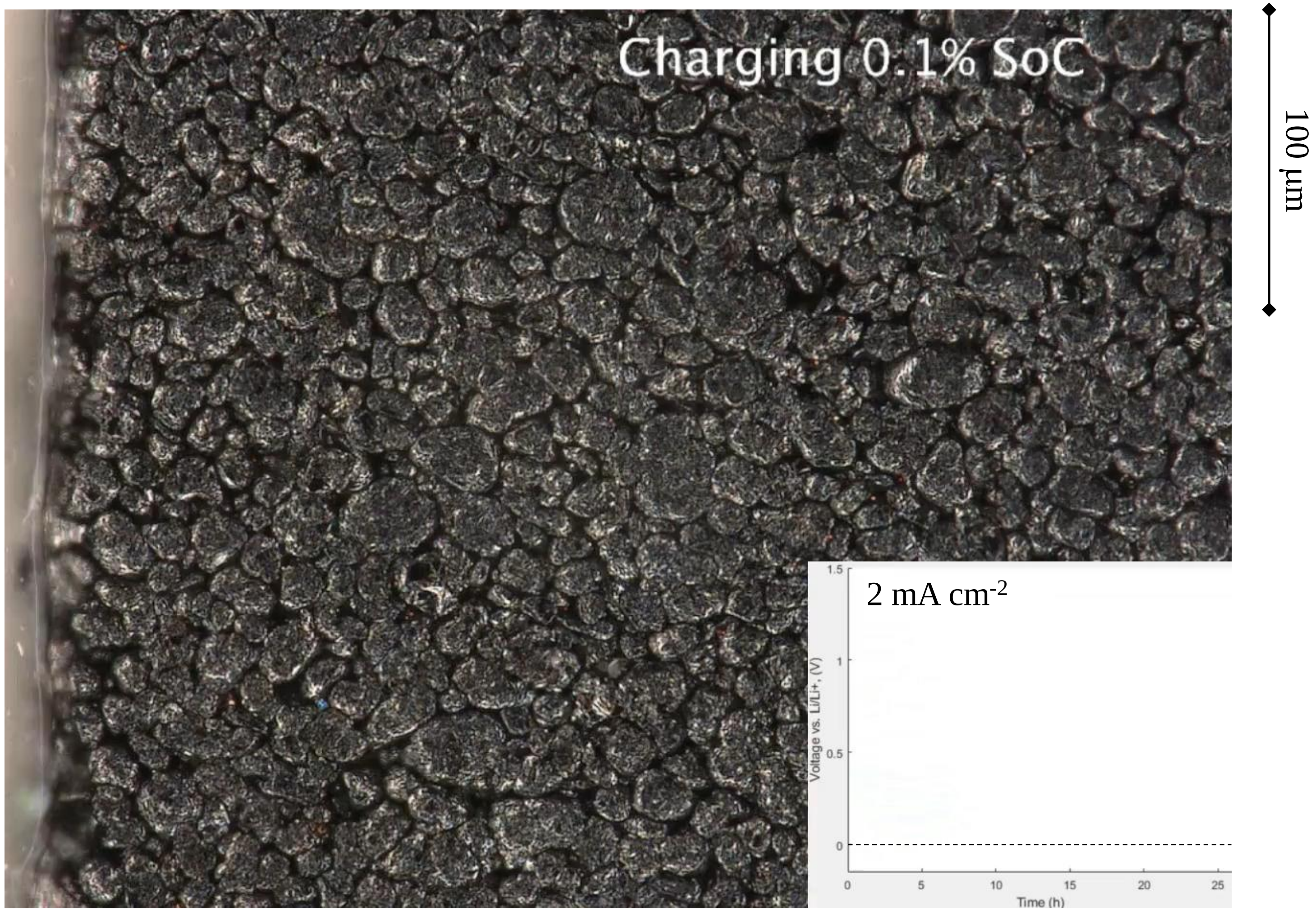
$$\eta_{int} = \tilde{\mu}_e^* - \tilde{\mu}_+^* - V_{eq} \qquad V_{eq} = E^\circ - \frac{\mu_{Li-C}}{F}$$

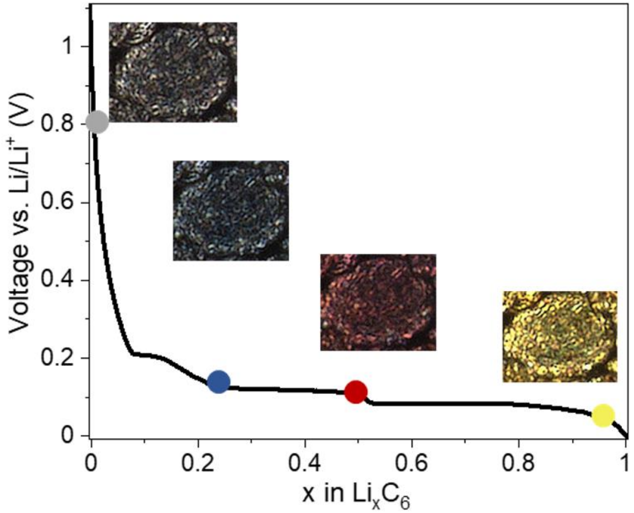
$$Li_{(ey)}^+ + e_{(gr)}^- \rightleftharpoons Li_{(Li)}$$

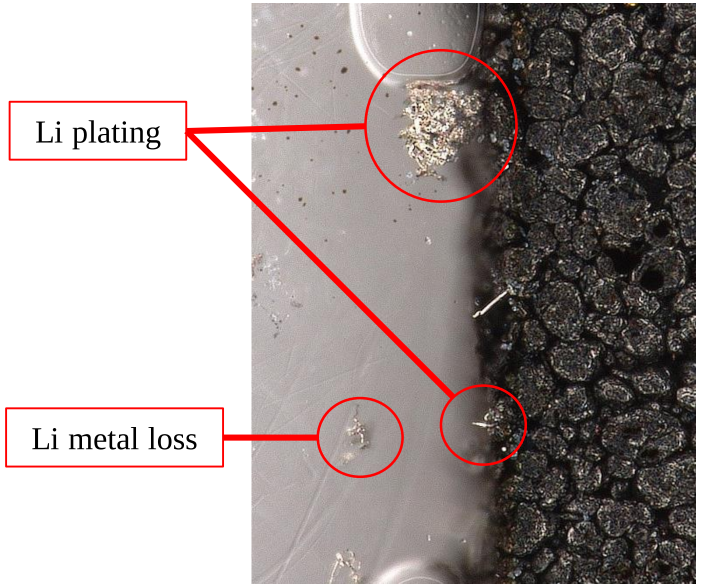
$$J_{plt} = i_{0,plt} \left[\exp\left(\alpha_{plt} \frac{F}{RT} \eta_{plt} \right) - \exp\left(-(1 - \alpha_{plt}) \frac{F}{RT} \eta_{plt} \right) \right]$$

$$\eta_{plt} = \tilde{\mu}_e^* - \tilde{\mu}_+^* - V_{nucl} \qquad V_{nucl} = -e^{-\delta_{plt}/\delta_{ref}}$$

Optical visualisation of intercalation and plating*







*X. Lu et al., Nat. Comm. 14 (2023) 5127

Revealing the internal Li distribution

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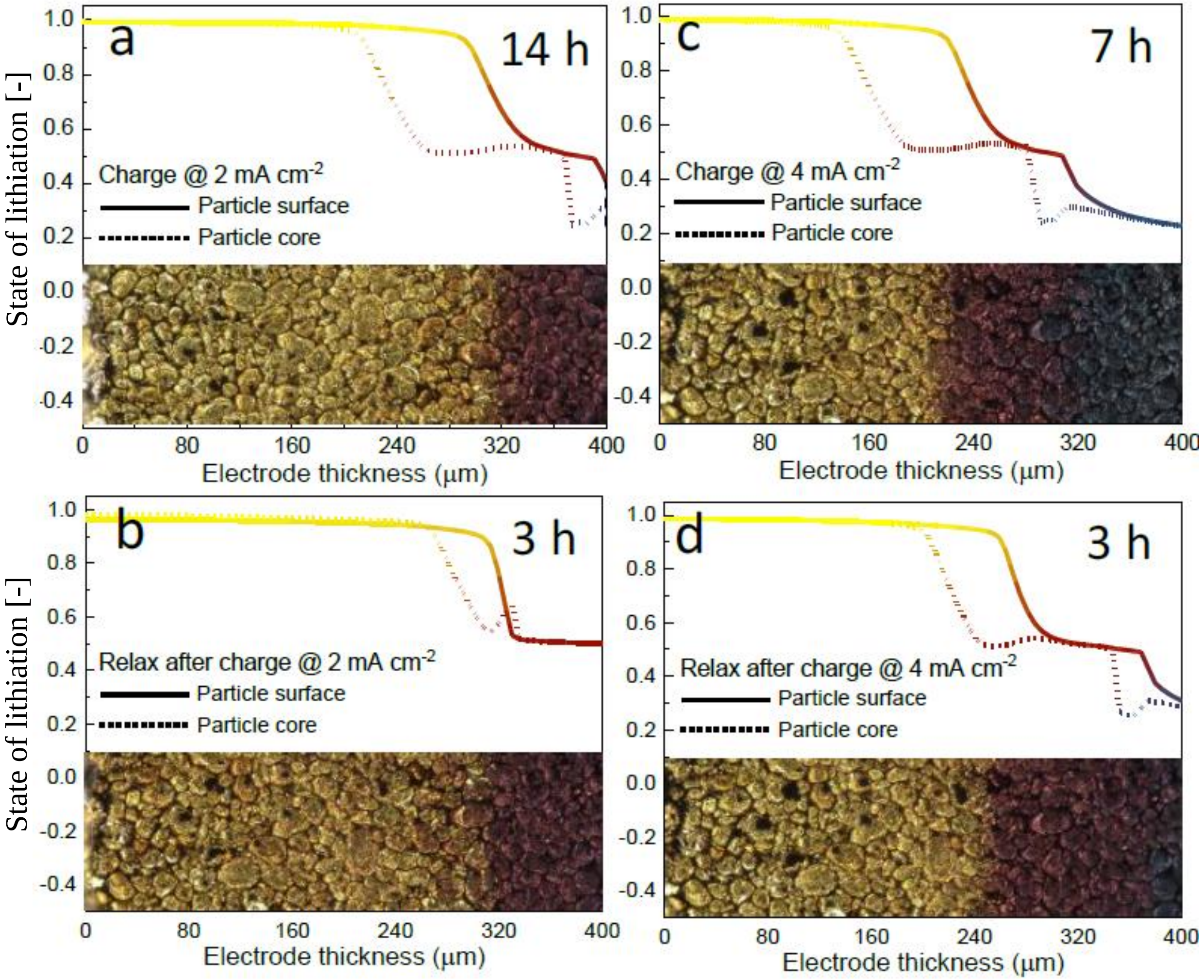

- Model allows us to “look inside the particles” (radial distribution & diffusion limitations)
- Model captures full evolution at all times:
  - electrolyte transport
  - phase separation
  - lithium intercalation
  - reversible plating
- Strong validation of model and parameters

Kinetics of Li intercalation and Li plating/stripping

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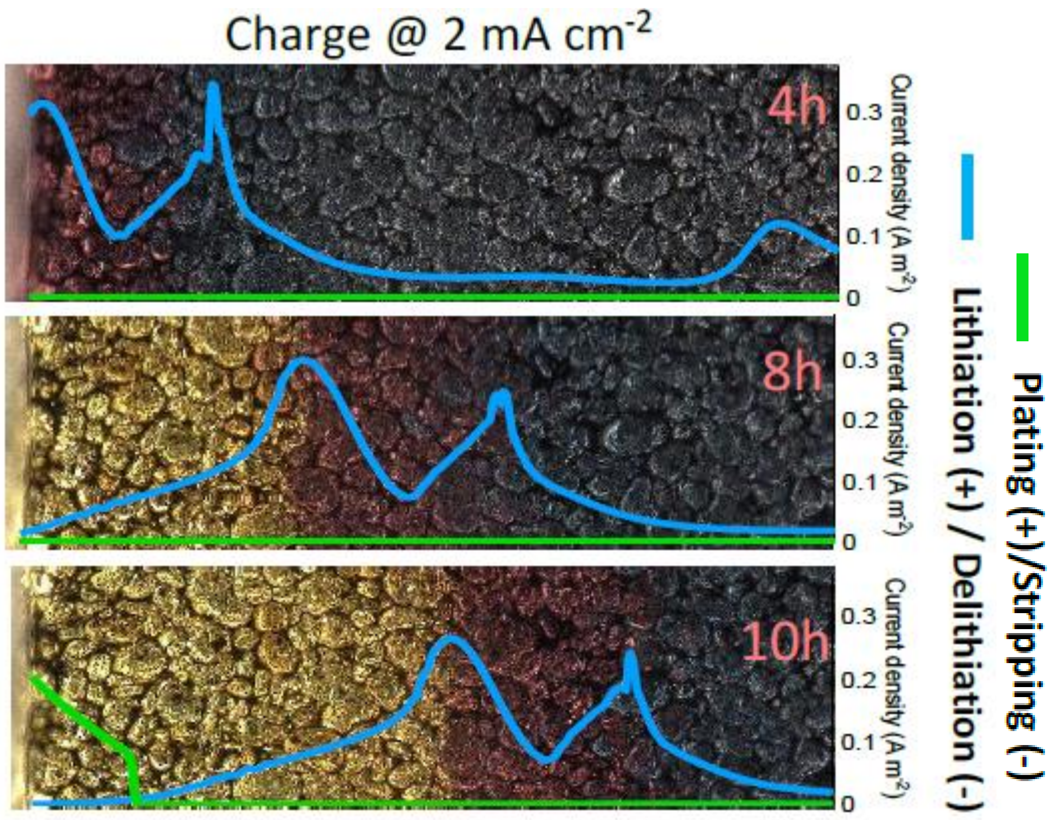

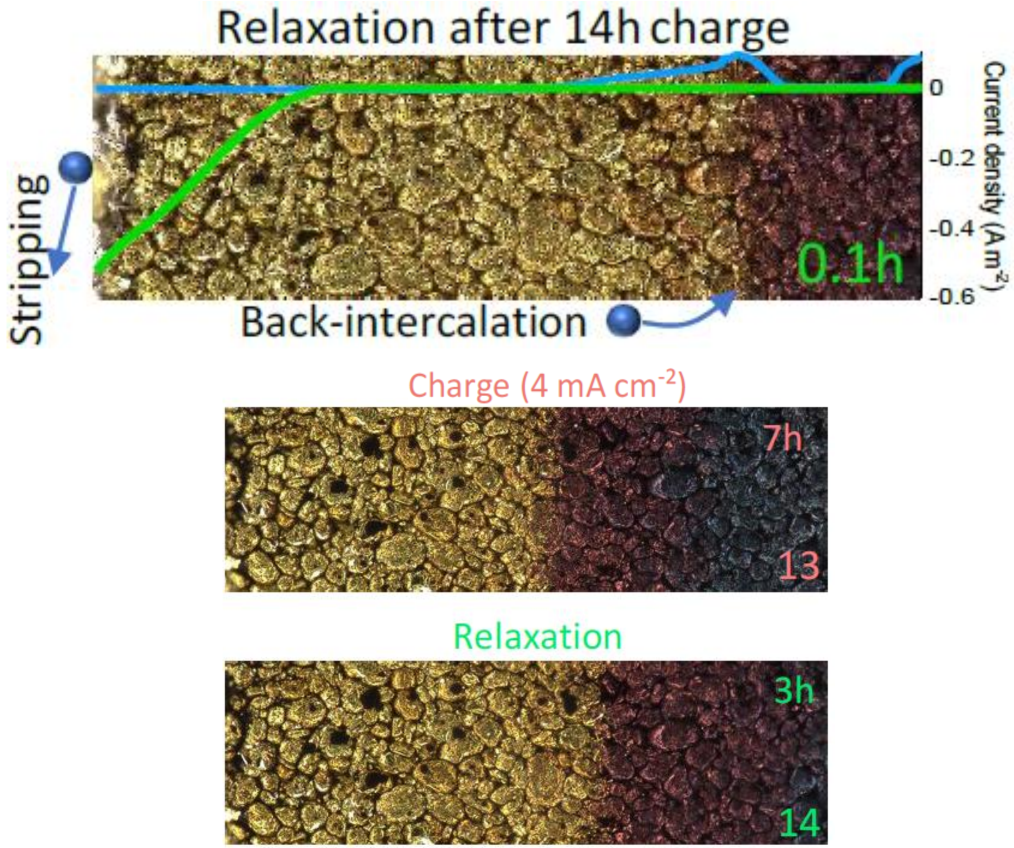

- Li intercalation occurs at phase boundaries
- Plating takes place only on saturated graphite
- Li plating is (partly) reversible
- Back-intercalation at the phase boundary

Lessons learned for model-guided charging protocols

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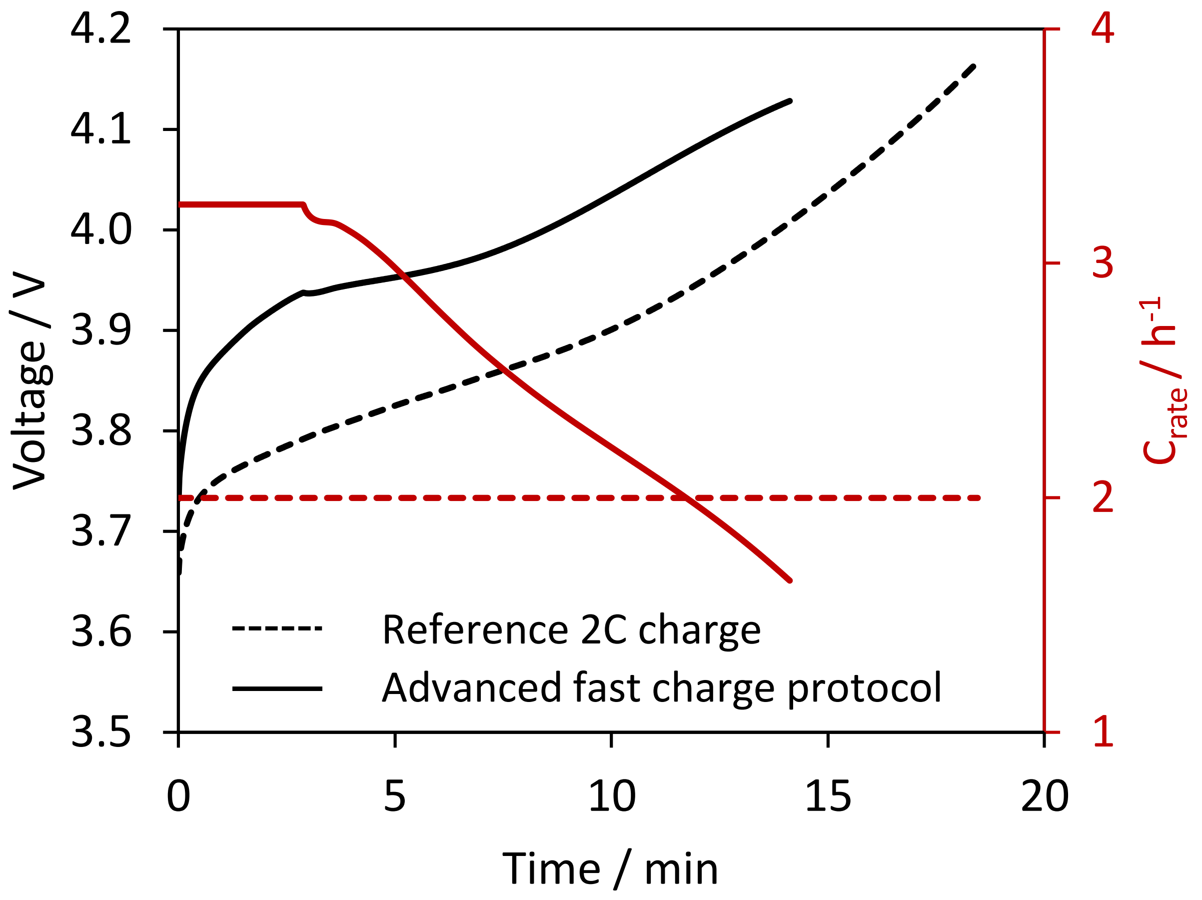

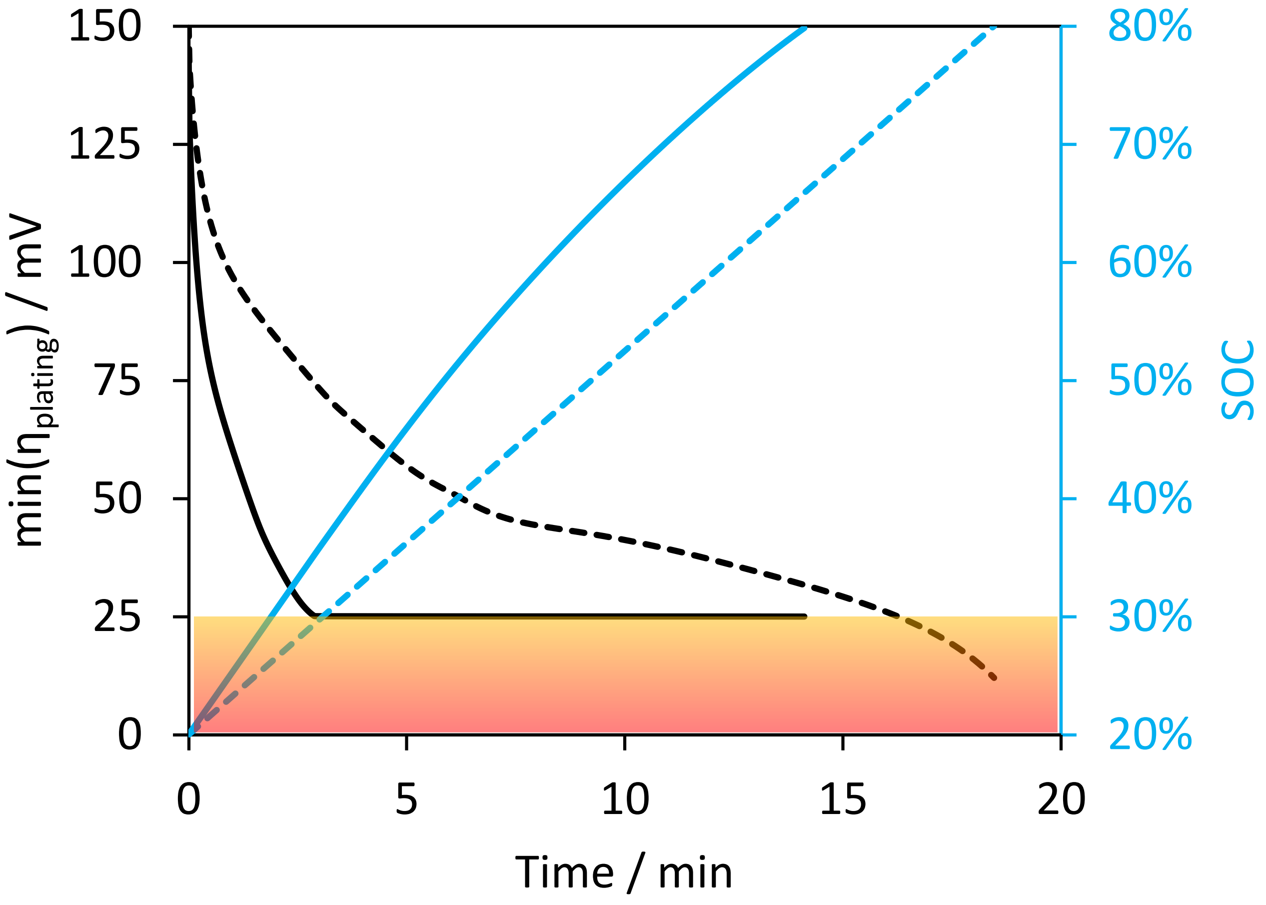

Take-home messages

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- Graphite phase separation and Li plating kinetics implemented in the model
- Coupling with operando optical experiments for validation
- Model-guided protocols enable fast-charging in 15 min
- Non phase-separating anode materials (e.g., disordered carbon)

ACS APPLIED ENERGY MATERIALS

Chemical Origins of a Fast-Charge Performance in Disordered Carbon Anodes

Sunyhik Ahn,[†] Marco Lagnoni,[†] Yi Yuan, Anton Ogarev, Elena Vavrinyuk, George Voynov, Eleanor Barrett, Alexander Pelli, Alexander Atrashchenko, Alexei Platonov, Sergey Gurevich, Maksim Gorokhov, Dmitry Rupasov, Alex W. Robertson, Robert A. House, Lee R. Johnson, Antonio Bertei, and Denis V. Chernyshov*

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Thank you!