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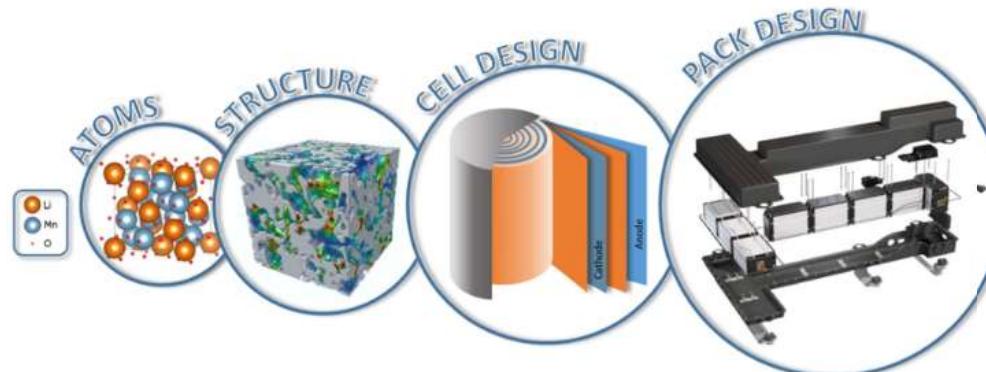


Atomistic modelling and experimental validation of voltage and entropy profiles in Li-ion cells

07-11-2018 Michael Mercer, Harry Hoster

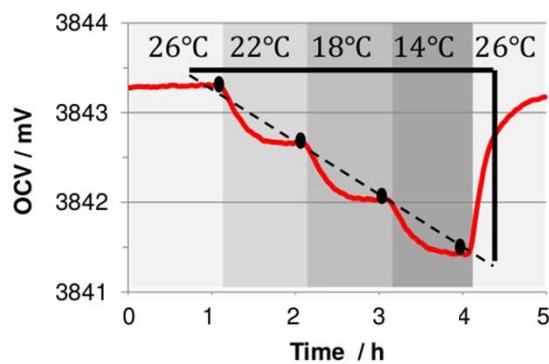


Introduction to MultiScale Modelling project

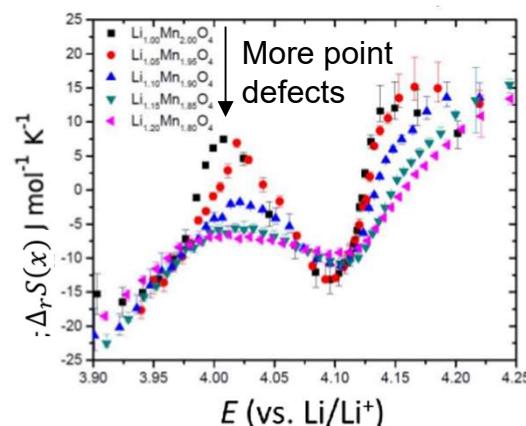


To advance current models and develop design tools which can accurately predict the performance and lifetime of existing and future batteries requires a fully integrated and tightly coordinated programme, drawing together the key modelling capabilities into a multi-scale approach, across length and time scales.

- First step: quantify voltage and entropy information dependent on electrode material structure.



$$\left(\frac{\partial E_{\text{OCP}}(x)}{\partial T} \right)_{p,x} = \frac{1}{nF} \Delta_r S(x)$$

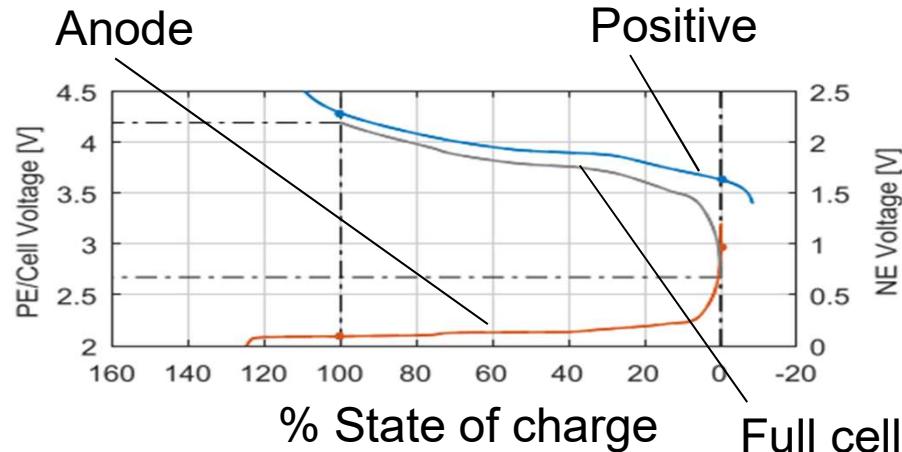


- Use lattice gas methods (Monte Carlo and mean field):
 - Rational understanding of voltage and entropy information

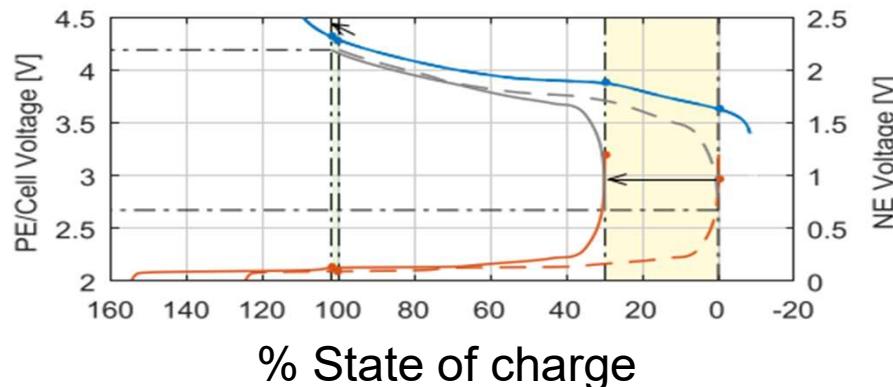
Battery aging: voltage vs. peak amplitude shifts

Pristine cell

Voltage

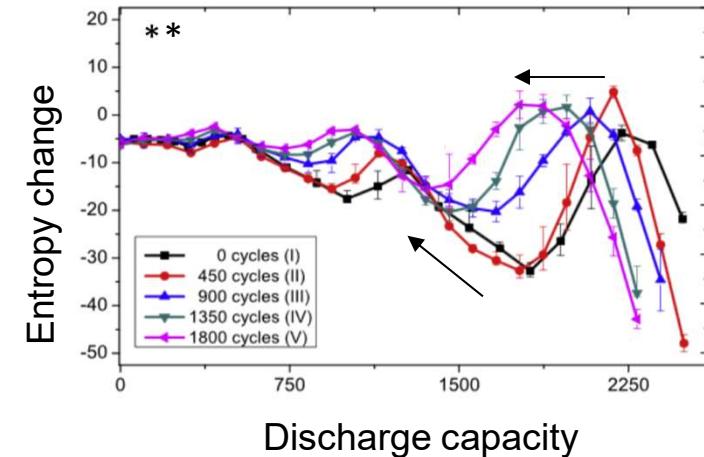


30% Loss of Li inventory



*C.R. Birkl *et al.*, J. Power Sources **241** (2017) 373-386

Amplitude



Horizontal shift:
Loss of lithium and/or active material.

Vertical shift:
Structural changes in electrode materials (defects)

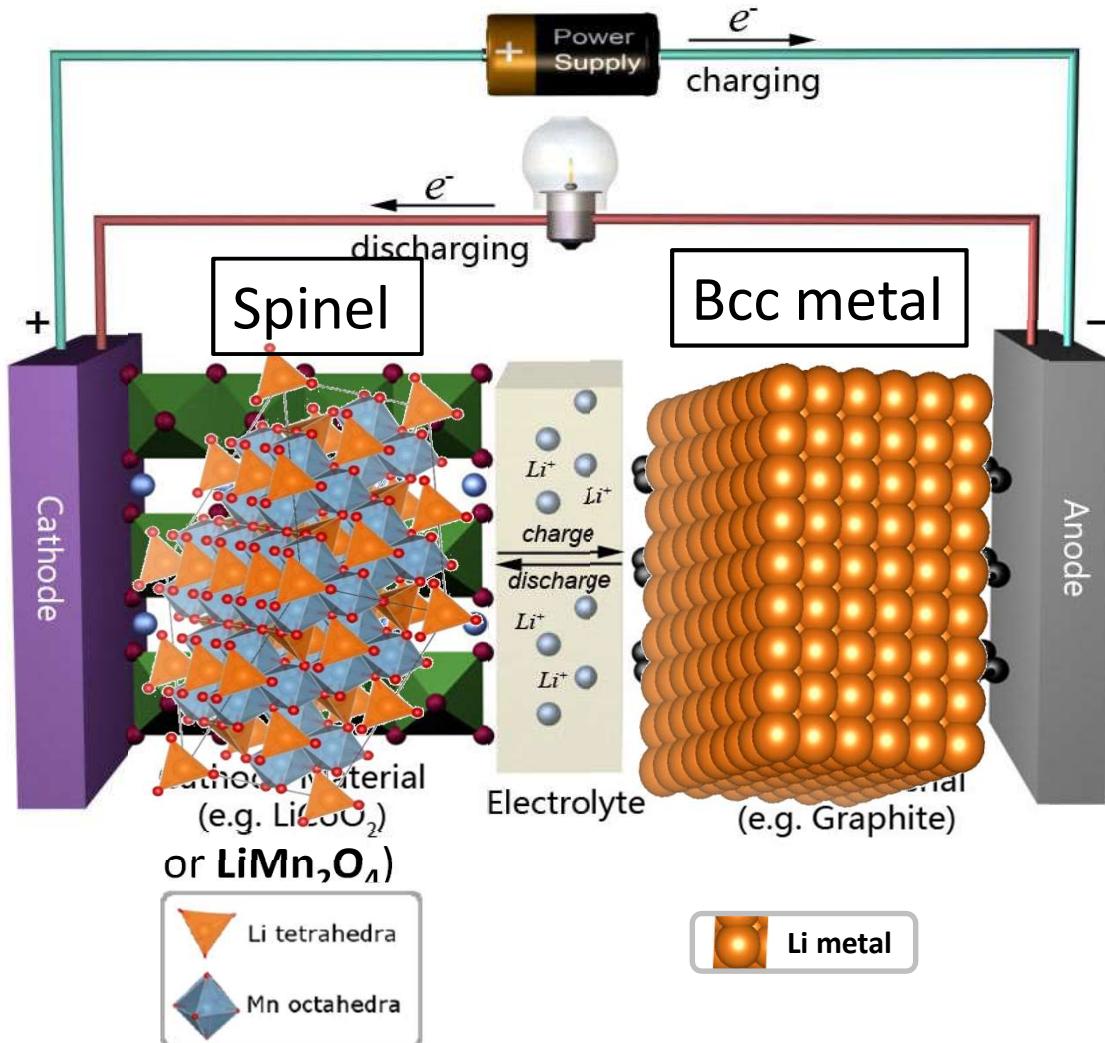
P. Osswald et al., Electrochim. Acta **177 (2015) 270-276

Li-ion cells with systematically varied cathode compositions

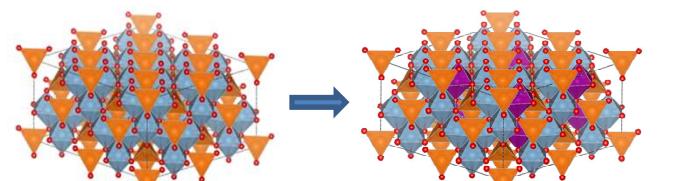


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$$E_{\text{cell}} = -\frac{\Delta G}{nF}$$
$$= -\frac{\mu_{\text{cathode}}}{nF}$$



Lithium manganese oxide (LMO) spinel

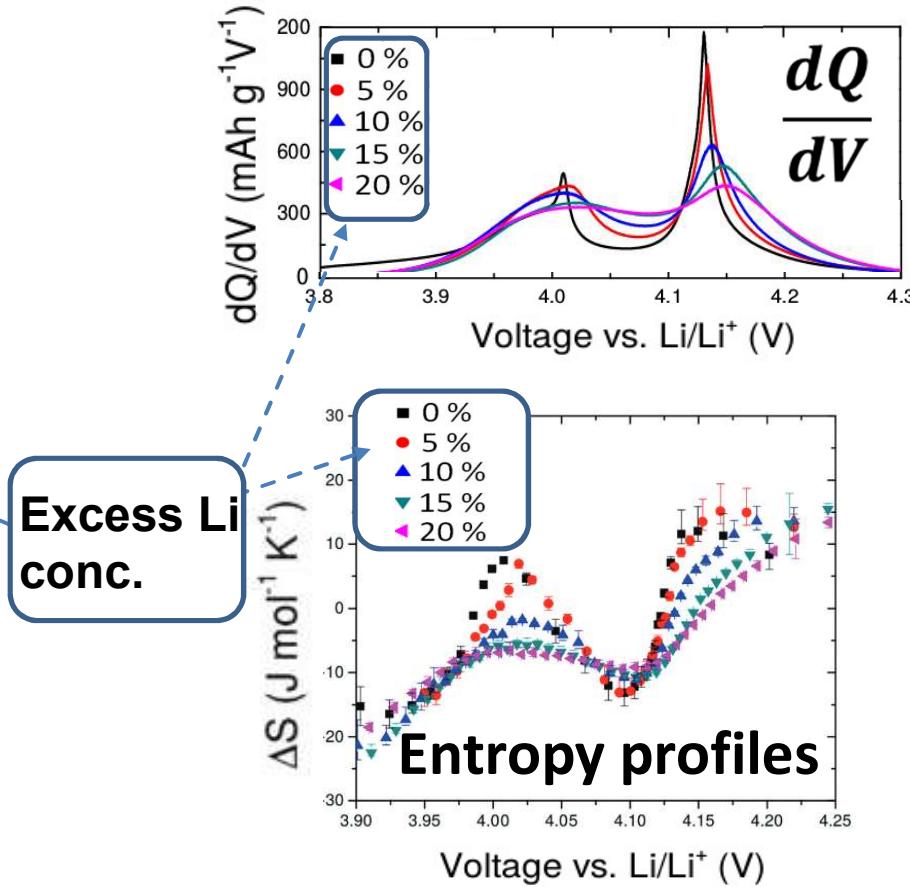
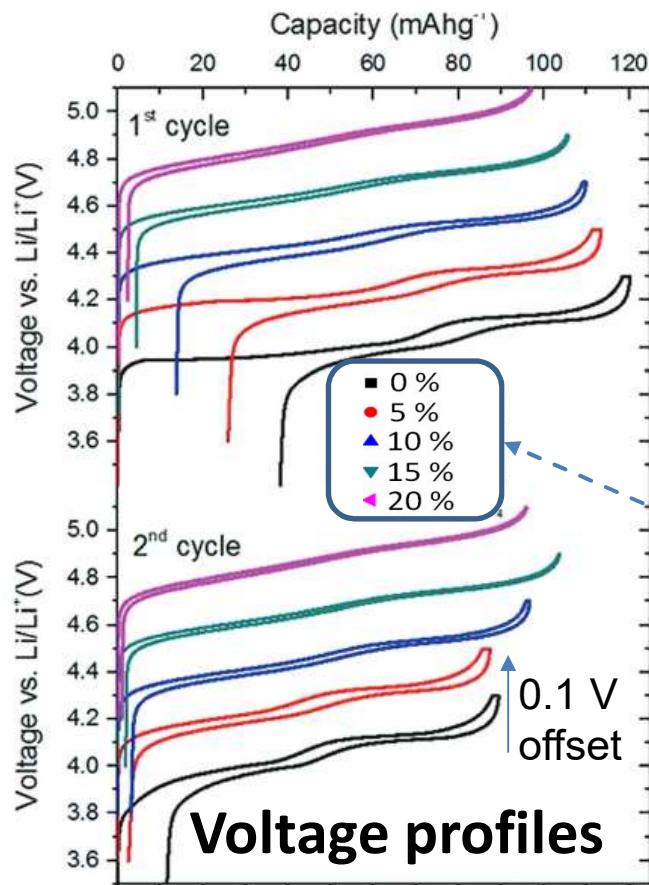
Point defects (excess Li)
added to cells and models
in fraction y



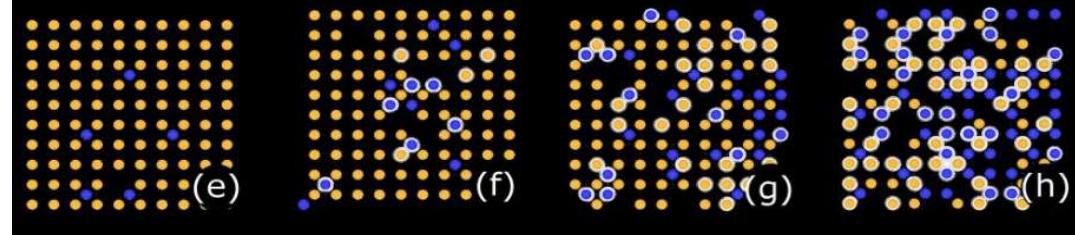
Varied y over 5 compositions:
 $0 \leq y \leq 0.2$

Image: borrowed and modified from Ran Liu's group homepage, Penn State

Experimental results: Variable defect fraction



Simulated
Li/vacancy
occupations



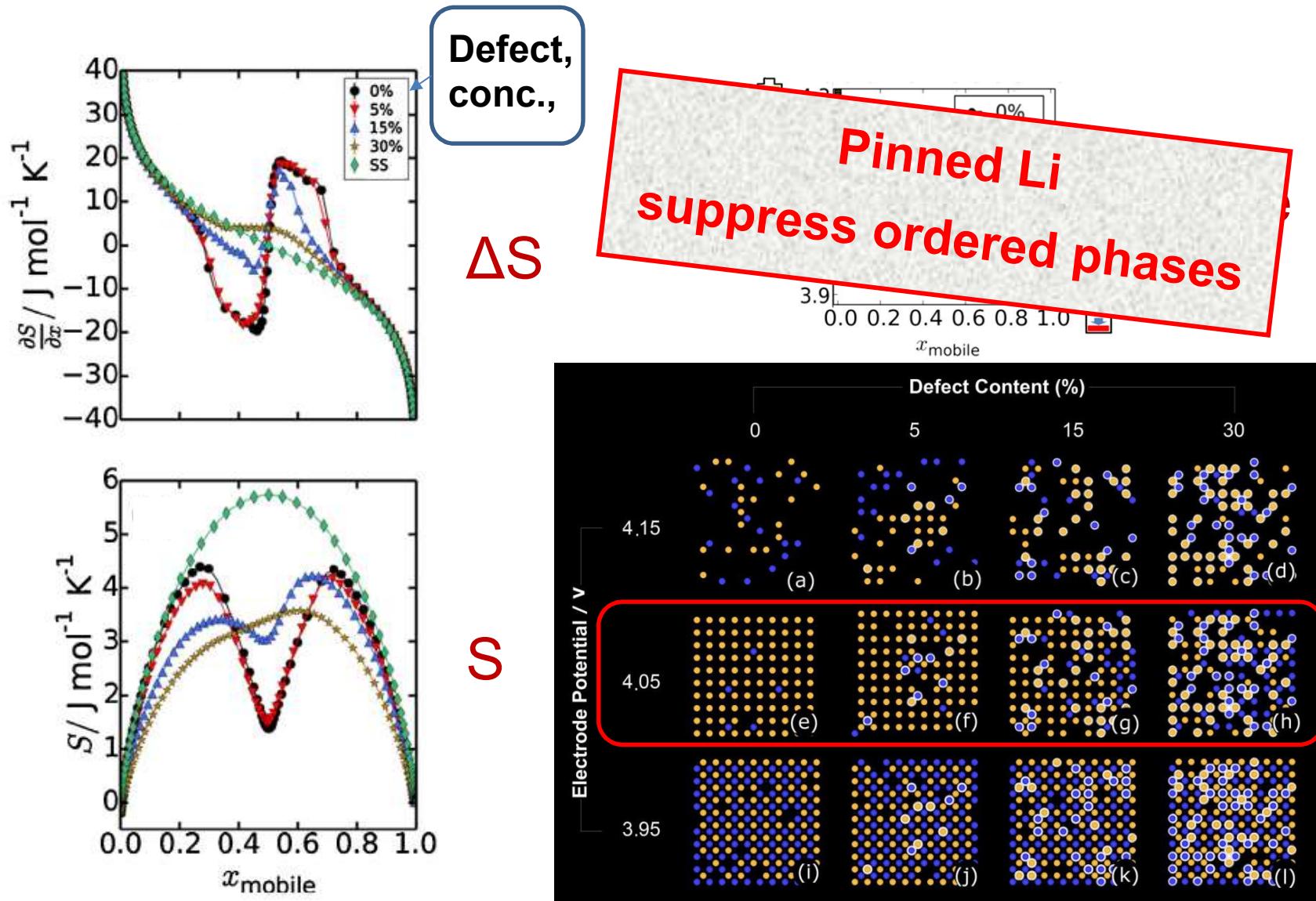
S. Schlueter, R. Genieser, D. Richards, H.E. Hoster,
M.P. Mercer*, PCCP 20 (2018) 21417

Monte Carlo simulations: effect on entropy profiles



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Mean field:

Li occupation-dependent parameters

- Mean field approach: rapid atomistic model.

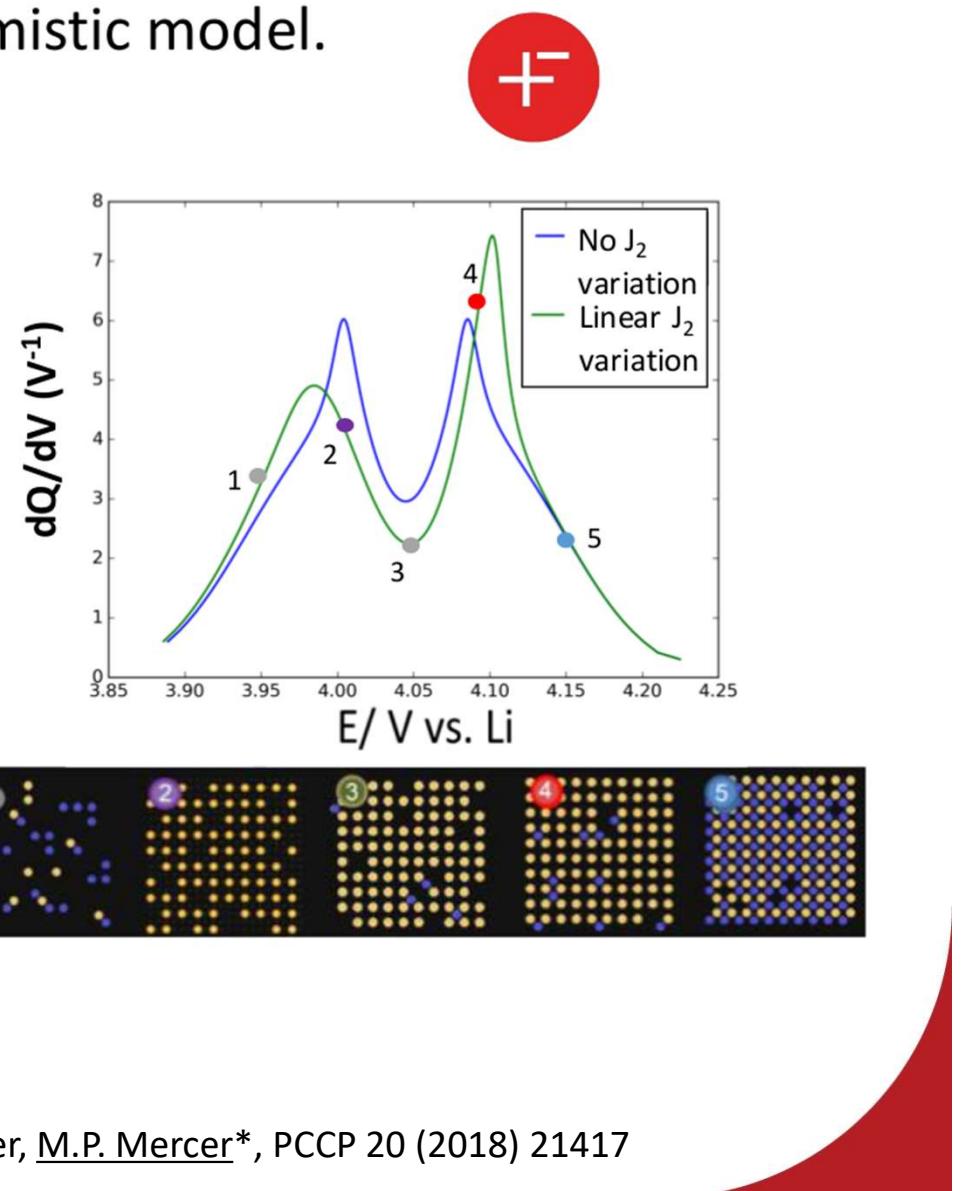
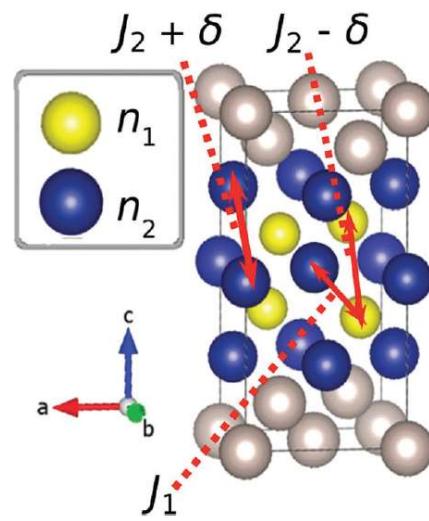
- Hamiltonian: $H = \varepsilon_1 N_1 + \varepsilon_2 N_2$

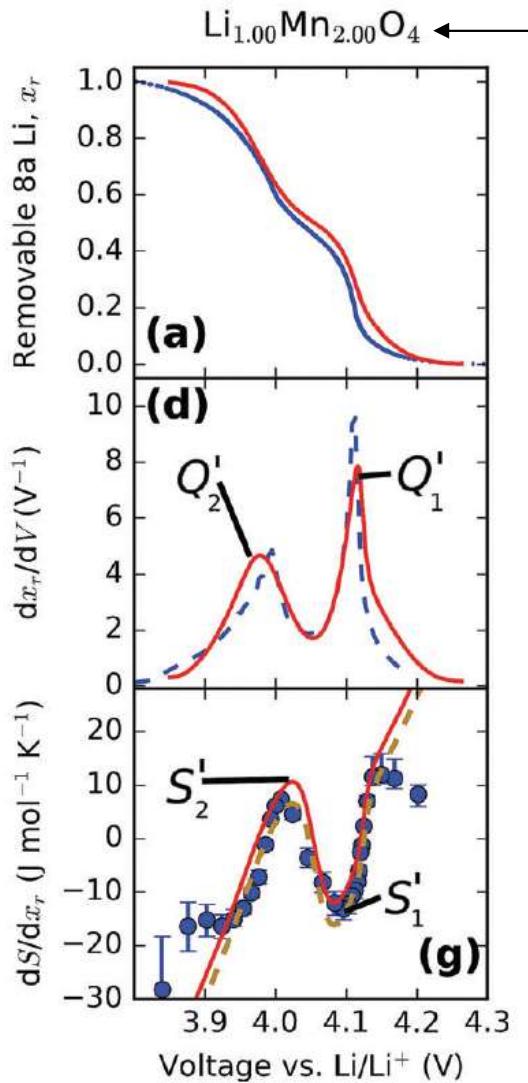
- $H = E_0(N_1 + N_2)$

$$+ 4J_1 N_1 N_2 / N$$

$$+ 6(J_2 + \delta)N_1^2 / N$$

$$+ 6(J_2 - \delta)N_2^2 / N$$





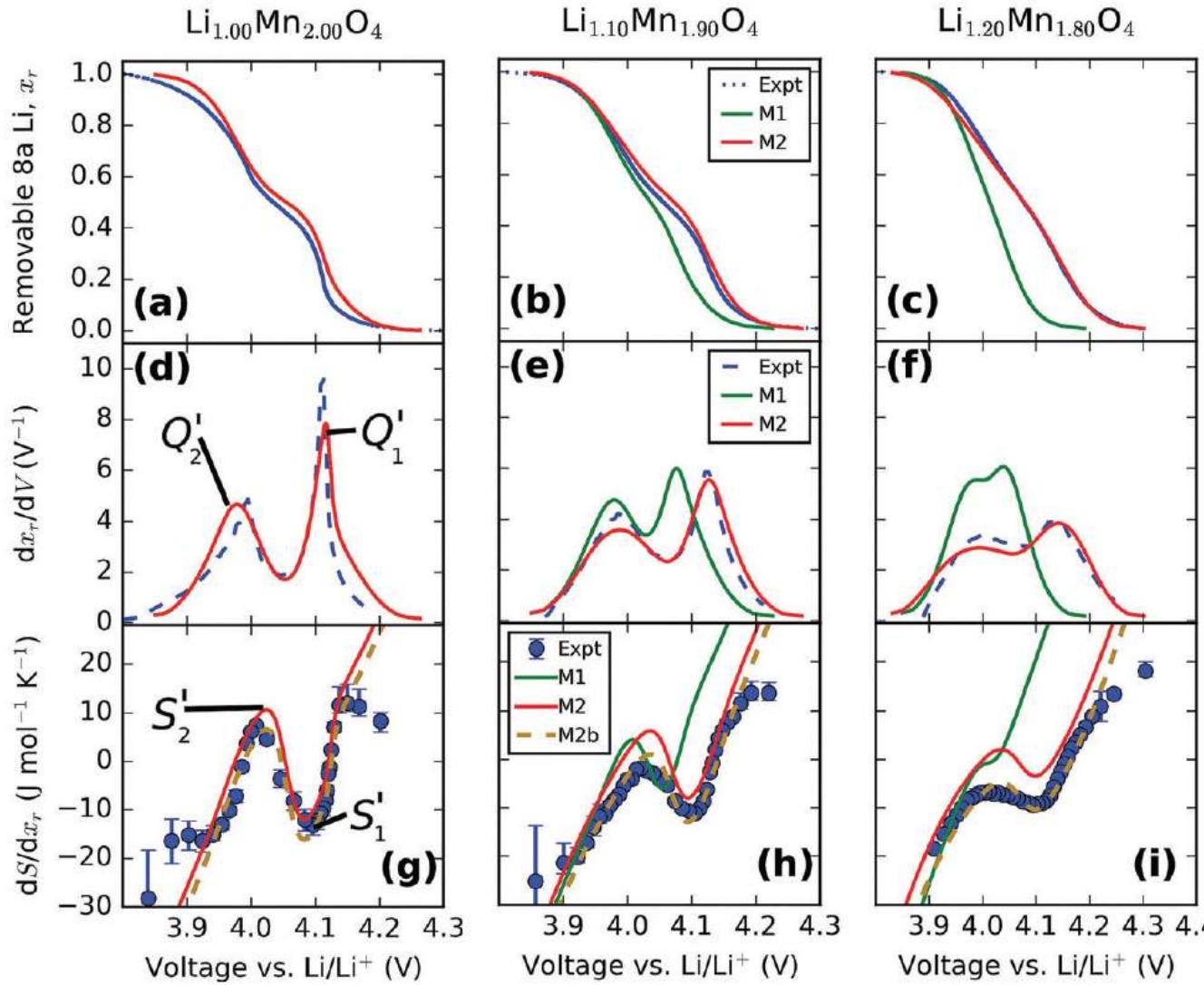
Cathode composition

Voltage profile

Incremental
capacity analysis
(dQ/dV)

Entropy (ΔS)
profile

Experiment/model comparison



M1: Best fit parameters assumed to be valid for all compositions
Pinned Li only

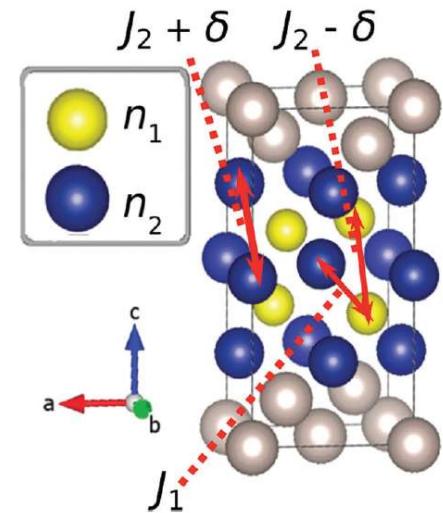
M2: Optimal parameters fitted over all compositions
Pinned Li + best parameters

M2b: including vibrational entropy
Pinned Li + best parameters

Mean field simulations: Trends in the fitting parameters

S. Schlueter, R. Genieser, D. Richards, H.E. Hoster, M.P. Mercer*, PCCP 20 (2018) 21417

| Composition | E_0 / eV | J_1 / meV | J_2 / meV | δ / meV |
|--|------------|-------------|-------------|----------------|
| LiMn_2O_4 | -4.11 | 32.8 | -0.6 | 1.4 |
| $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ | -4.13 | 35.2 | -0.6 | 1.8 |
| $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ | -4.17 | 35.6 | 1.8 | 3.0 |
| $\text{Li}_{1.15}\text{Mn}_{1.85}\text{O}_4$ | -4.22 | 37.2 | 6.2 | 4.4 |
| $\text{Li}_{1.2}\text{Mn}_{1.8}\text{O}_4$ | -4.32 | 43.1 | 12.7 | 5.1 |



Point term E_0 : Decreases. Lattice becomes more attractive to Li

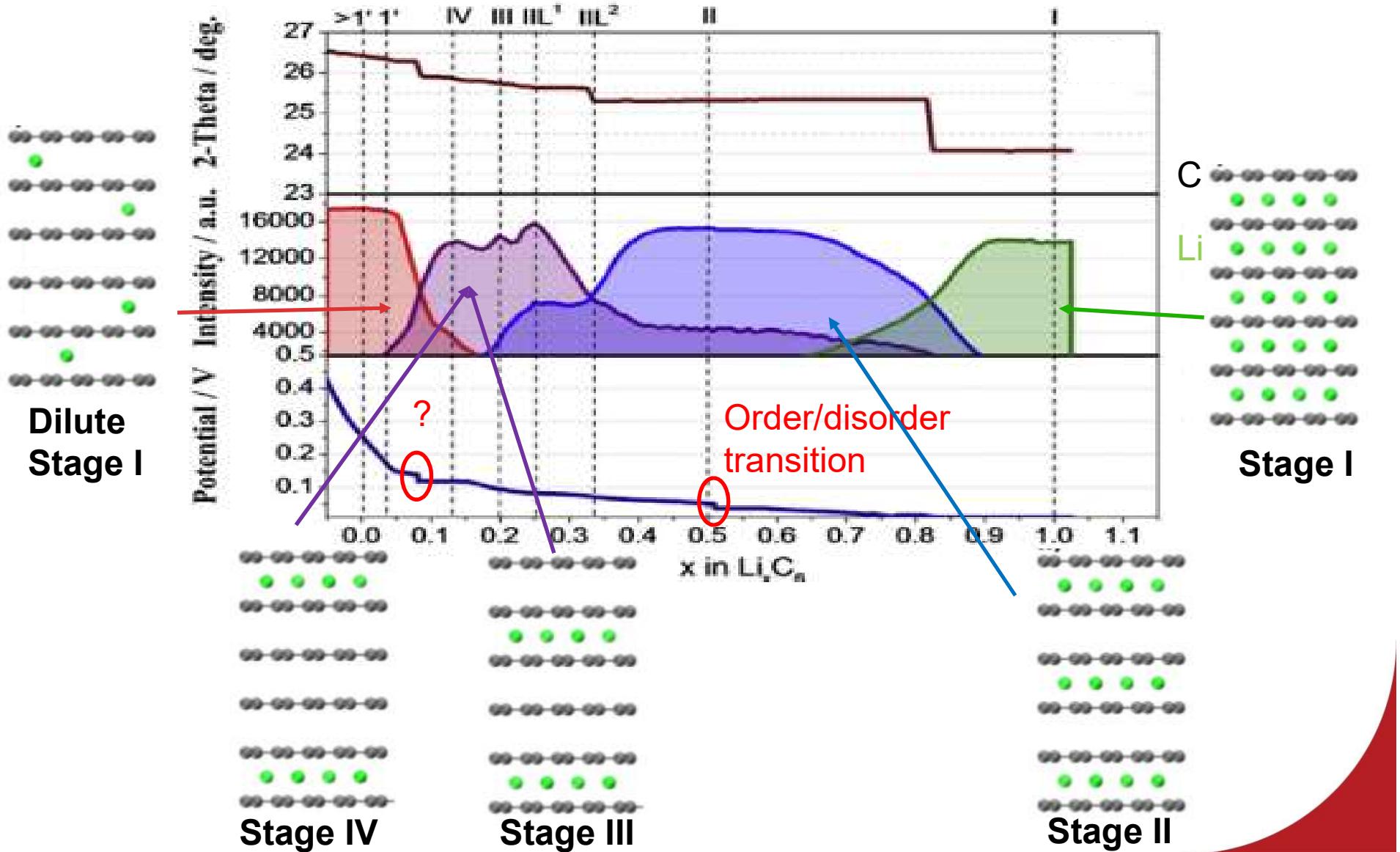
Li-Li terms J_1 , J_2 , δ : all increase (more repulsion)

Explanation:

- Unit cell shrinks with more Li excess
- Mn oxidation state changes

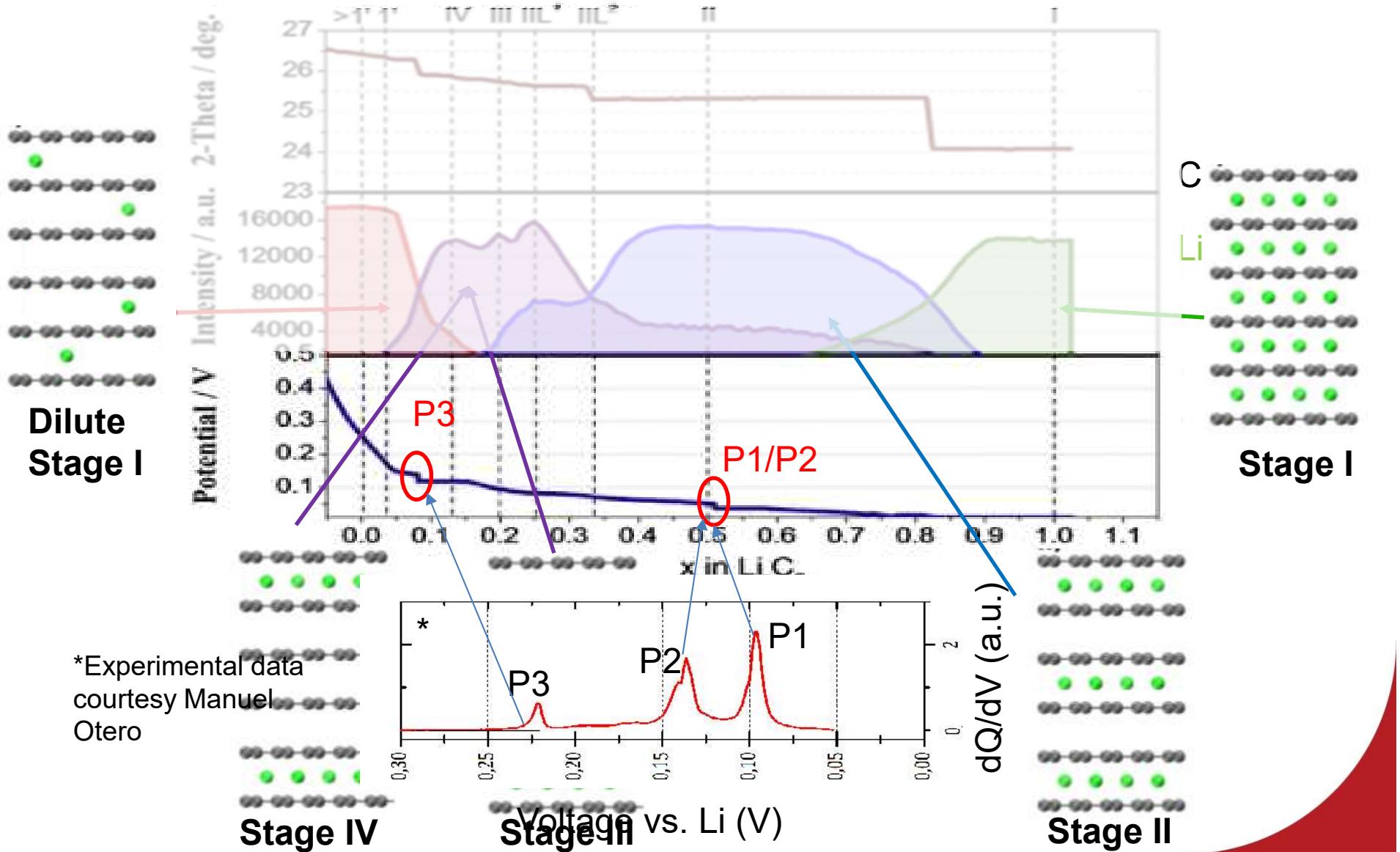
Li intercalation in graphite: staging phenomena

In-situ XRD, 30°C, from N. Cañas et al., Carbon 116 (2017) 255-263



Li intercalation in graphite: staging phenomena

In-situ XRD, 30°C, from N. Cañas et al., Carbon 116 (2017) 255-263



Li intercalation in graphite: staging phenomena

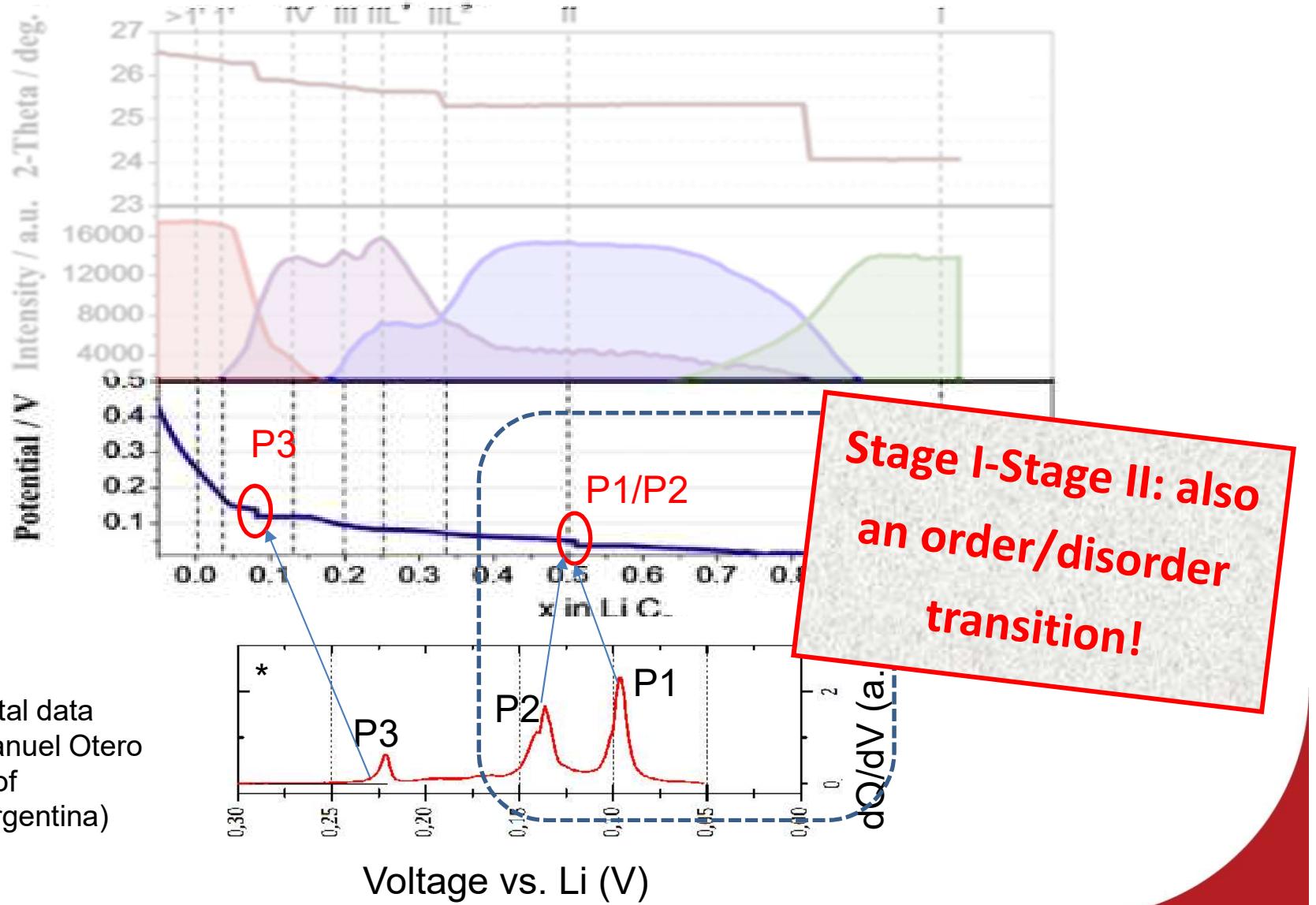


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In-situ XRD, 30°C, from N. Cañas et al., Carbon 116 (2017) 255-263



*Experimental data
courtesy Manuel Otero
(University of
Cordoba, Argentina)

Li intercalation in graphite: staging phenomena

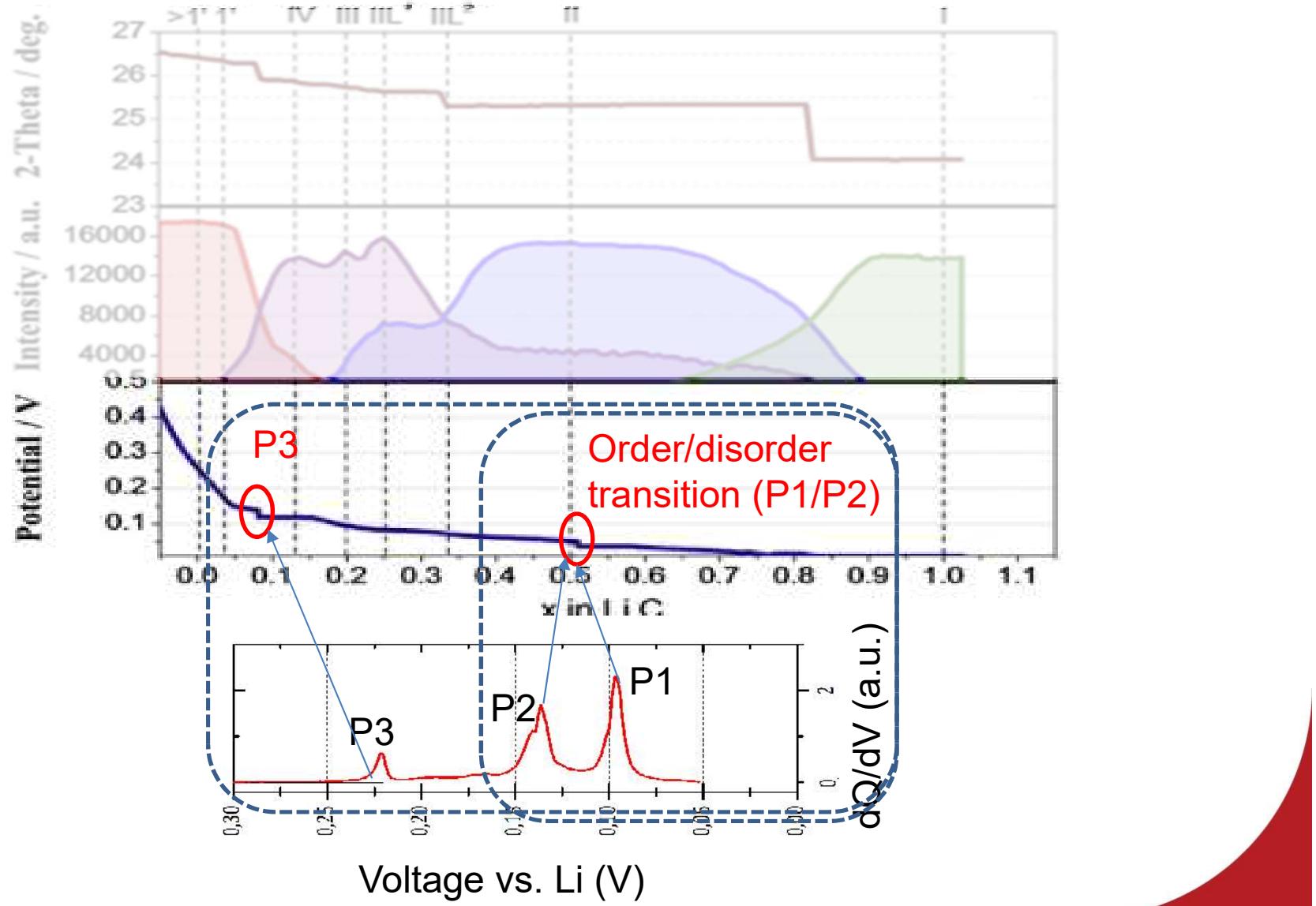


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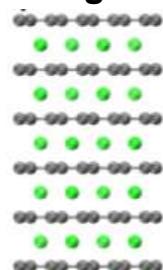
In-situ XRD, 30°C, from N. Cañas et al., Carbon 116 (2017) 255-263



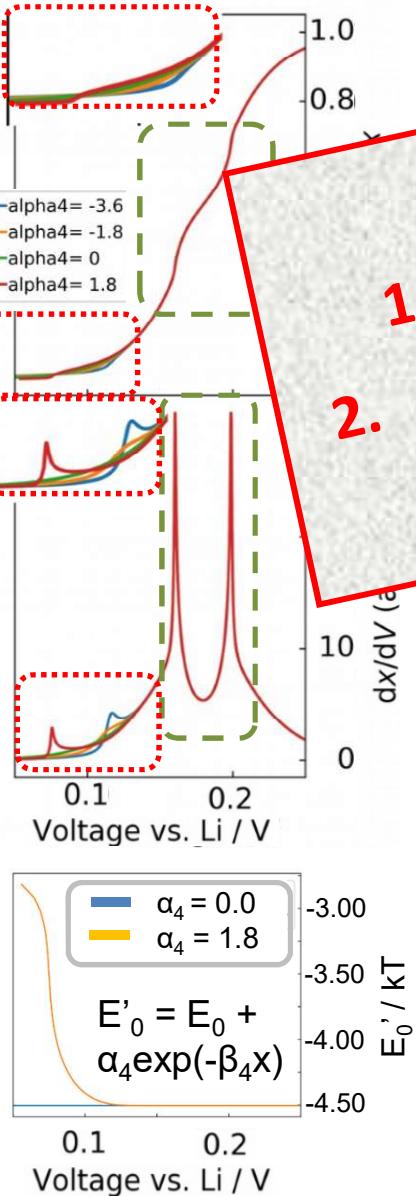
Transition at low Li occupancy

Stage I-
Stage II
transition

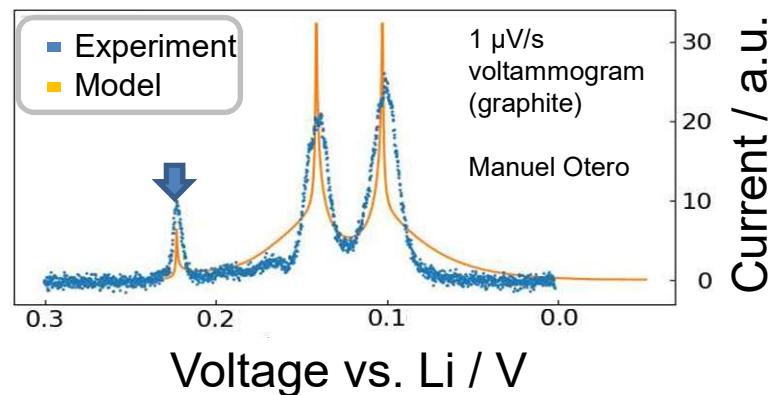
Stage I



Stage II



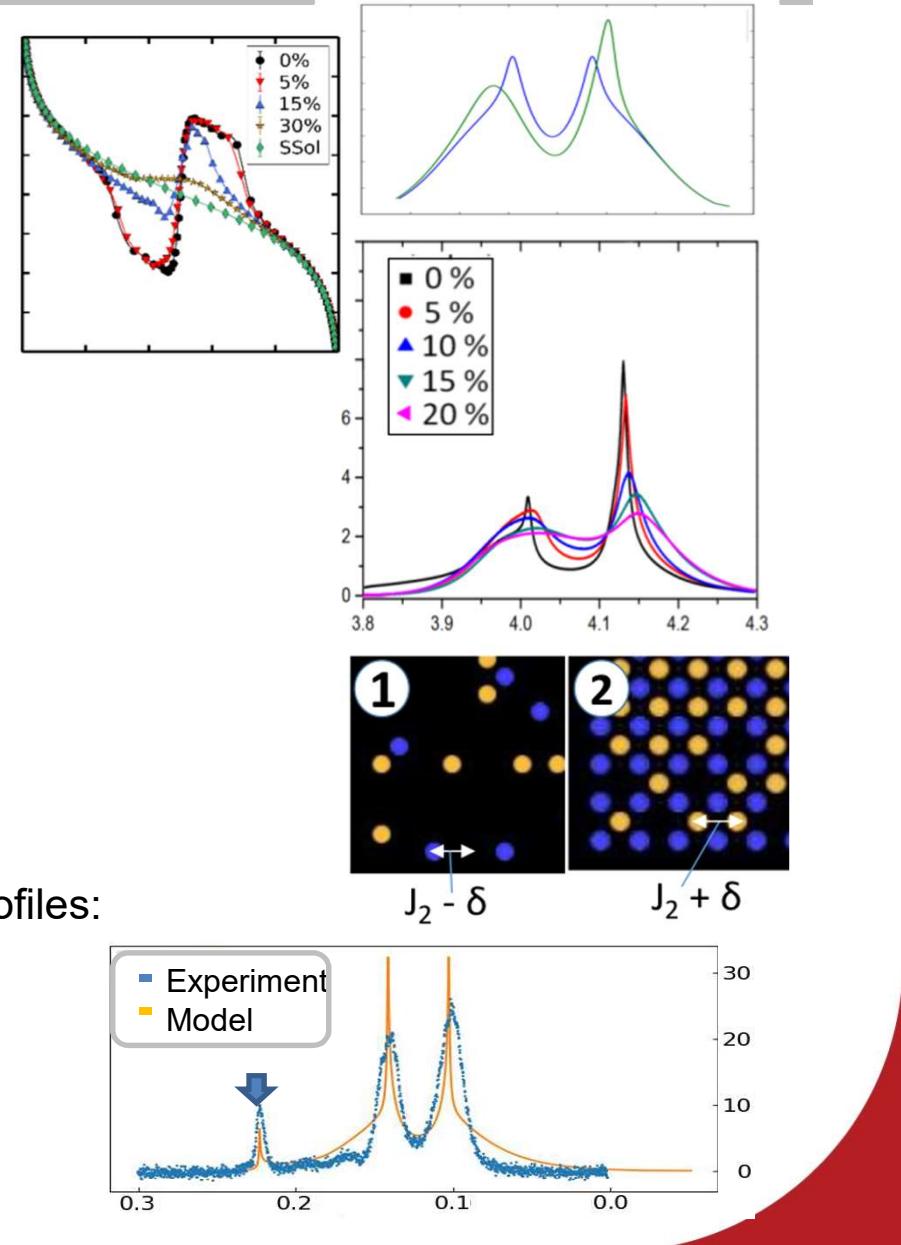
- Open questions:
1. Defect states with different E_0 ?
 2. Entropy and enthalpy information at different central temperatures.



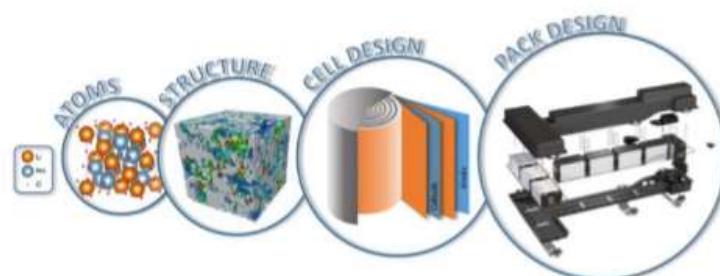
Optimised parameters: $\alpha_4 = 1.8 \text{ kT}$
 $\beta_4 = 77$

Summary and outlook

- Mean field: experiment/model validation with physically meaningful parameters
- Can recognise and quantify order/disorder transitions:
 - Effects on voltage, dQ/dV and entropy
- Defects pin Li sites:
 - Suppress ordered phases
- Future and ongoing projects:
 - Li/graphite half cell characterisation:
 - controlling **temperature** and **particle size**.
 - **model validation**: role of surface versus bulk.
 - **Reduced order description** of voltage profiles:
in collaboration with Oxford.
 - Role of configurational entropy.
 - Reduced number of parameters.



Acknowledgements



STFCBATTERIES.ORG

Proof of Concept Award



Mobility Grant

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