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A New Insight into Blended Electrodes

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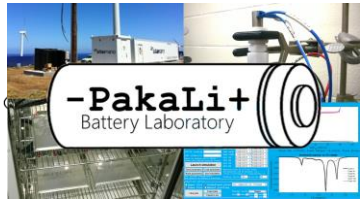


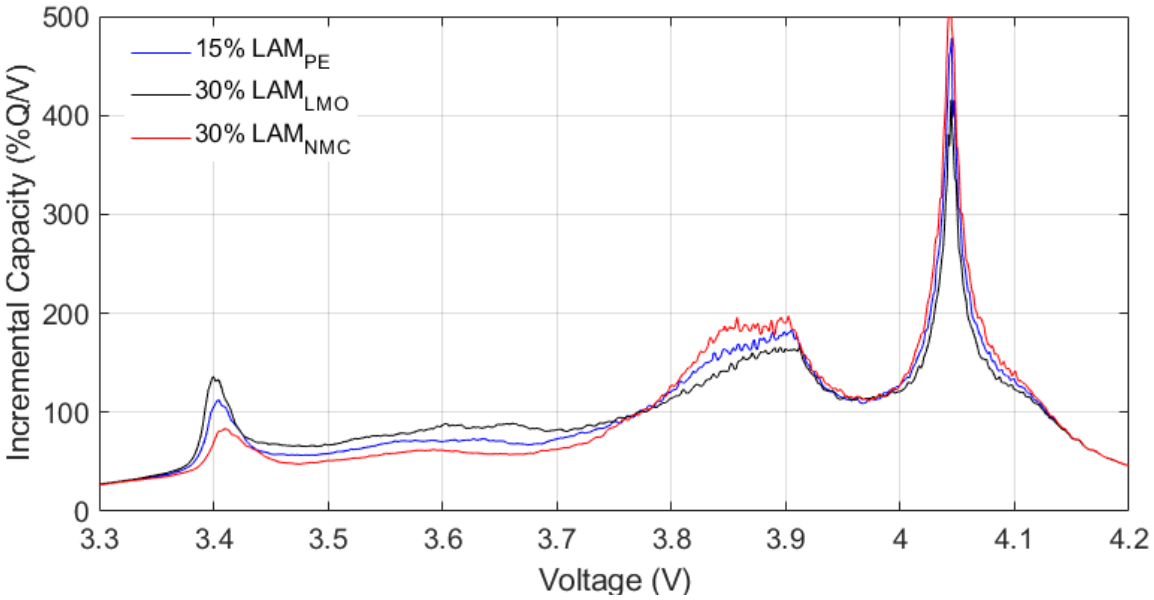
Objectives & Motivation

More and more commercial Li-ion batteries are using blends

- On the positive electrode (NMC+LMO, NMC+NCA,…)
- On the negative electrode (Gr+SiOx, Gr+HC,…)

Few efforts to integrate blending in diagnosis models & tools

- Electrodes are often treated as single material
- What if both components do not degrade at the same pace?
  - Example of a 50/50 {LMO/NMC} blend with 15% total LAM_{PE}:



Voltage responses are quite different

Diagnosis and prognosis tools need to take that into account

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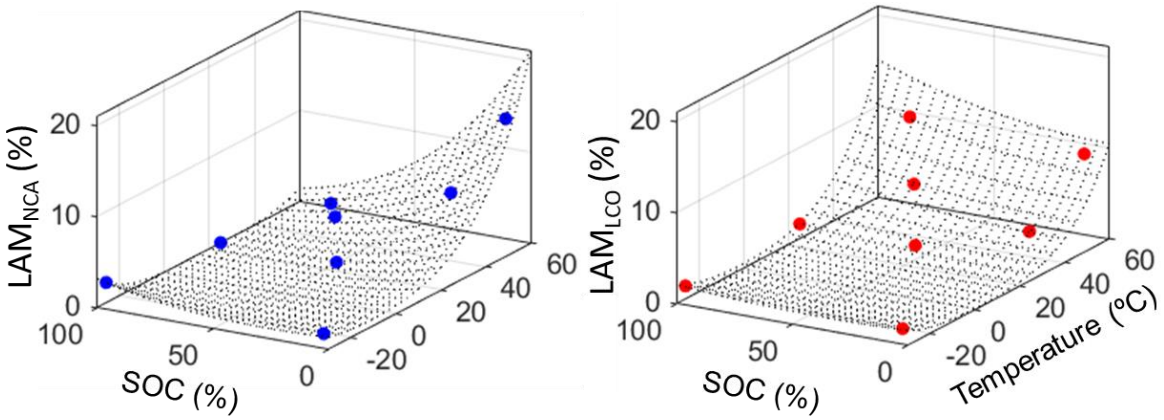
Mechanistic approach allows blends

Dubarry, M., et al. (2012) Journal of Power Sources **219**: 204-216
Schmidt, J. P., et al. (2013). Journal of Power Sources **239**: 696-704

- Calculate IC constant current response for each component and sum them



PE components were shown to degrade differently through aging of commercial cells both in cycling and calendar aging

Baure, G., et al. (2019) Journal of the Electrochemical Society **166**(10): A1991-A2001

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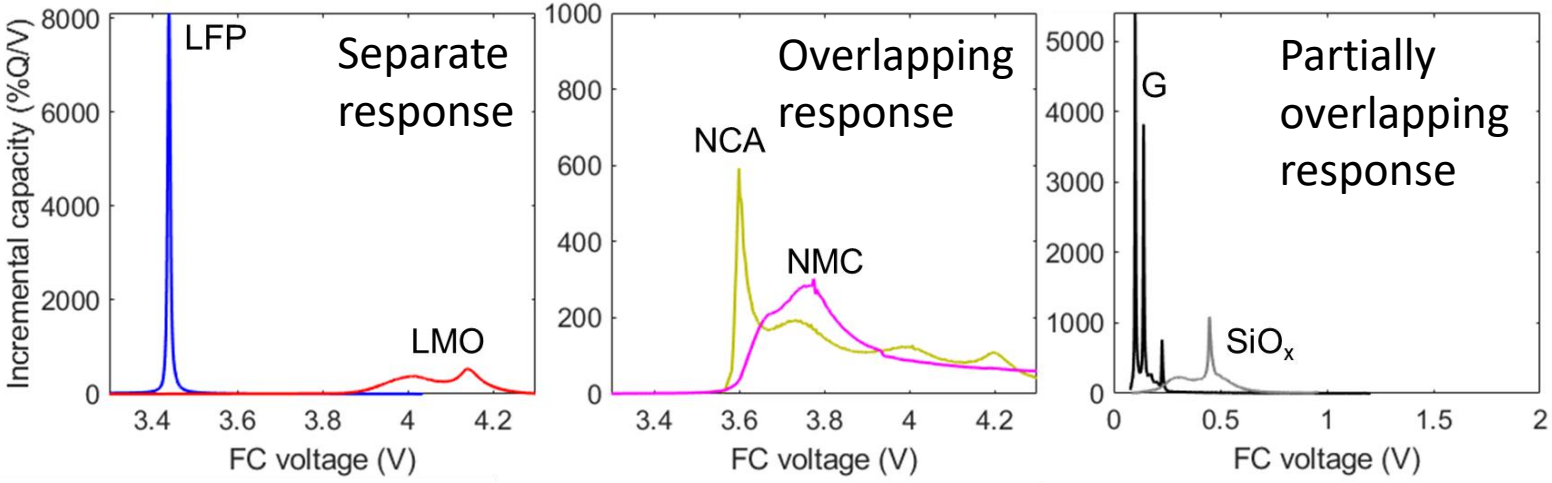
Mechanistic approach allows blends

- Calculate IC constant current response for each component and sum them
  - Is it realistic? If not, how should it be handled? Impact of chemistries?



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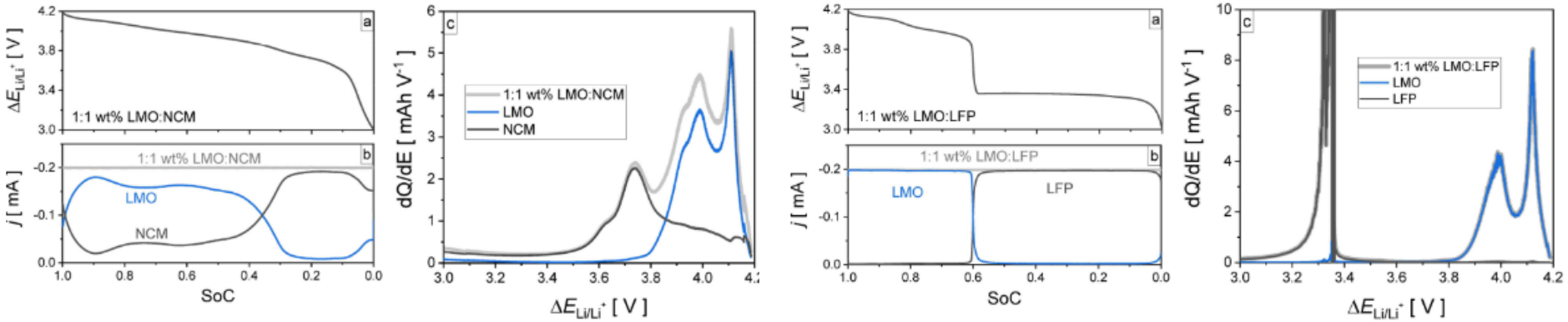


Heubner, C., et al. (2018), Journal of Energy Storage **20**: 101-108.
Liebmann, T., et al. (2019), ChemElectroChem **6**(22): 5728-5734.

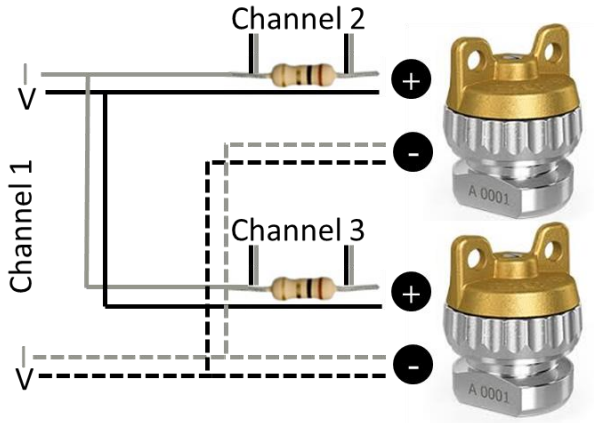
Clearly not that simple.
Simulation tools must adapt to chemistry

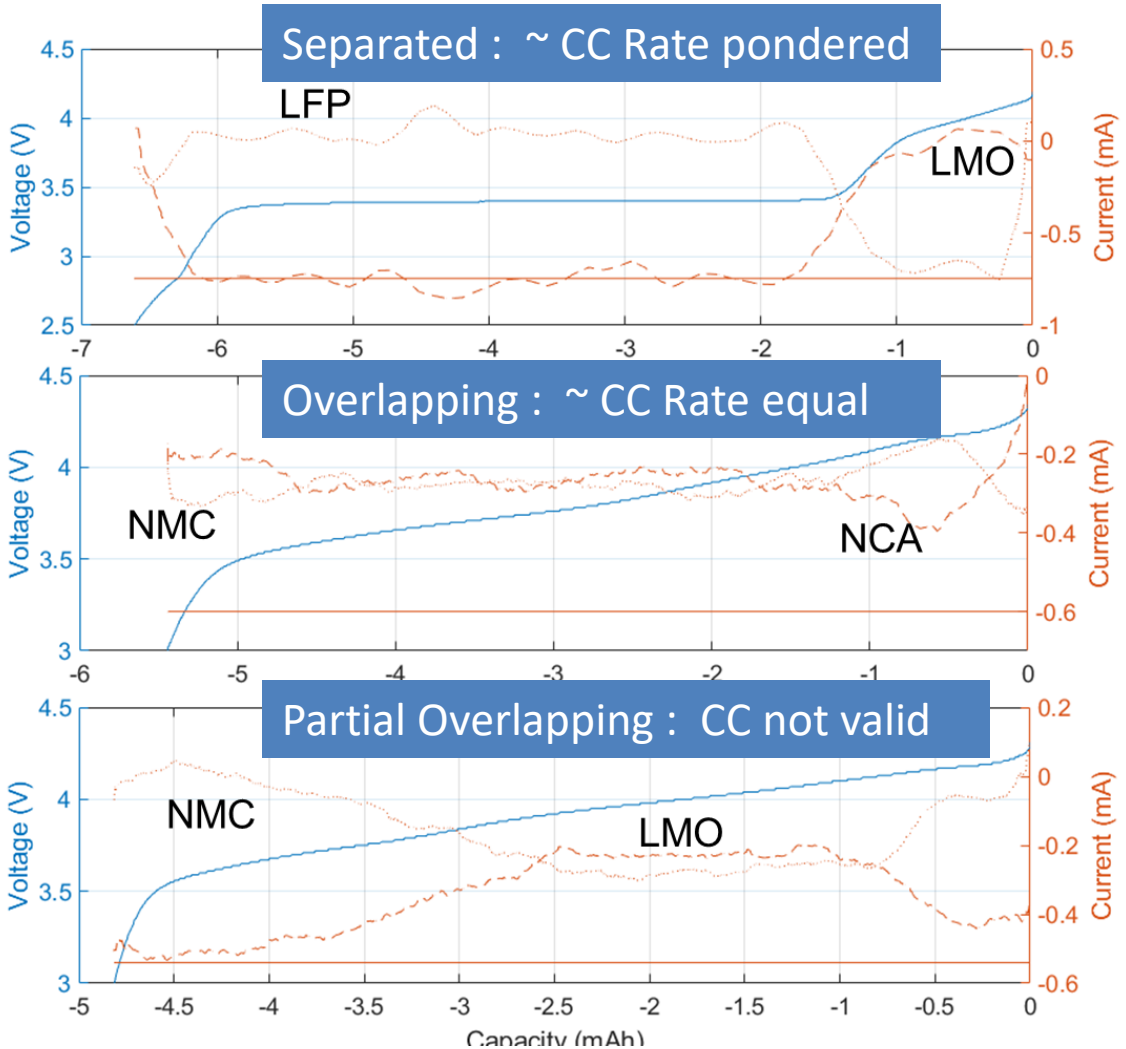
Results

HNEI validation experiments

Simple set up

- Deconstruct by using 2 half-cells
- Use the 4-points connectors
- Use resistance
  - No hall effect sensor small enough
  - 1/4W 1 Ω resistances

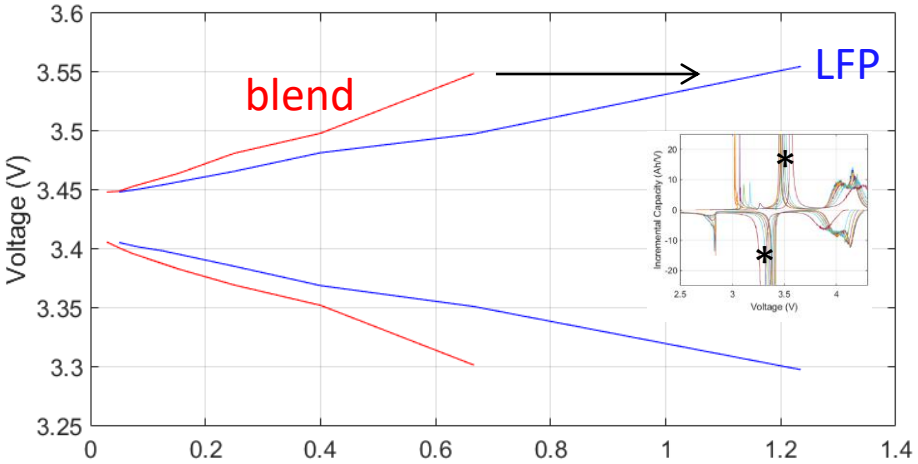




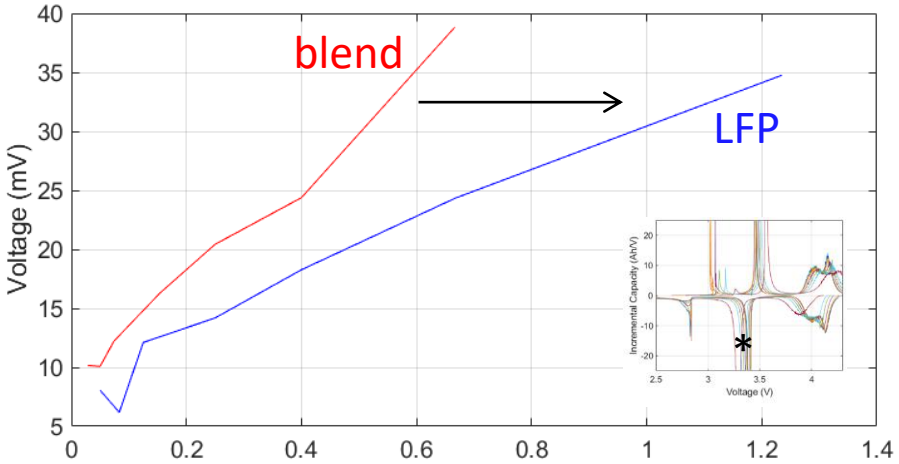
LFP-LMO: Separated Electrochemical Response

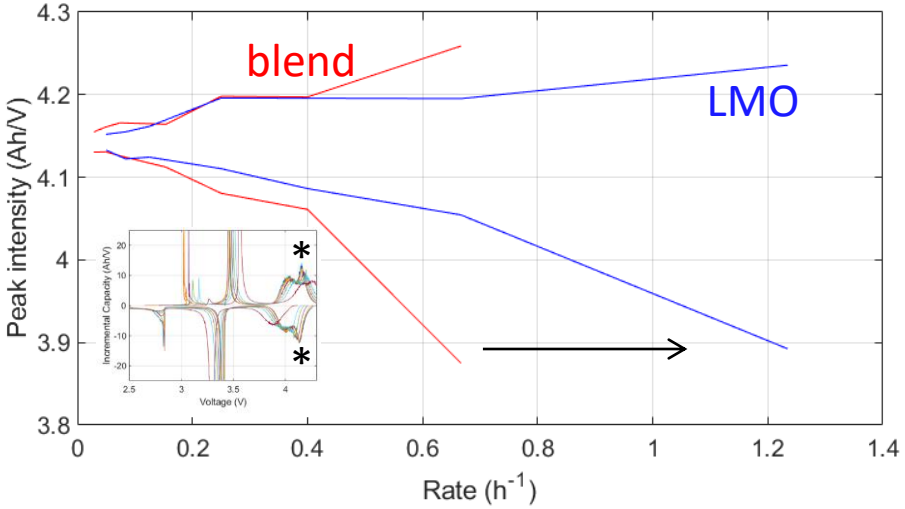
Verify local current on Features of interest

LFP Peak Maximum Voltage

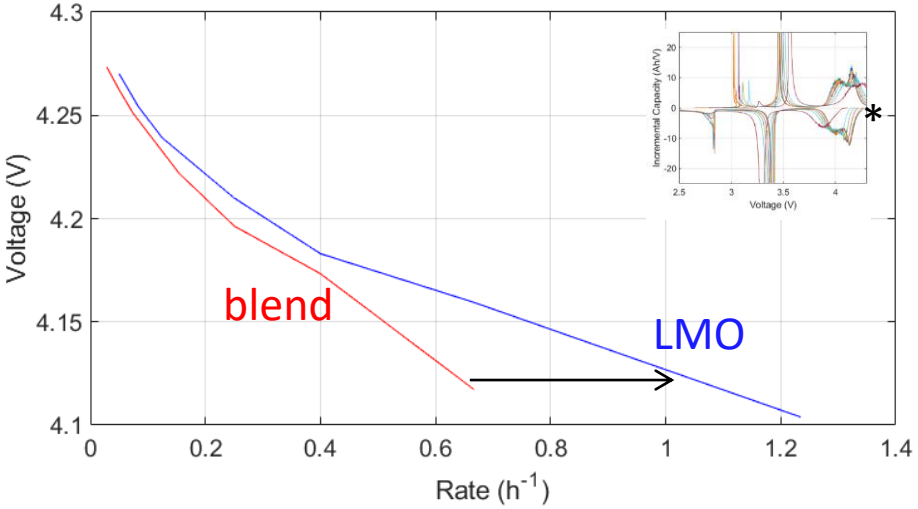


LFP Peak half width





LMO peak intensity



LMO initial voltage

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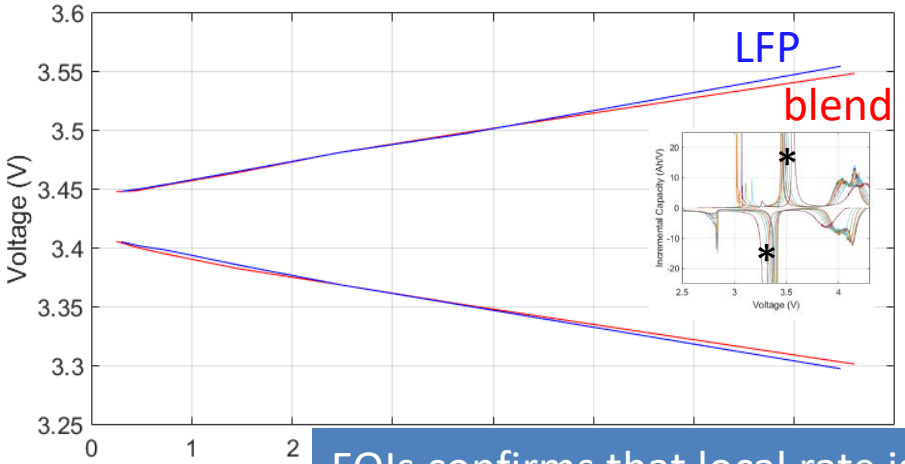

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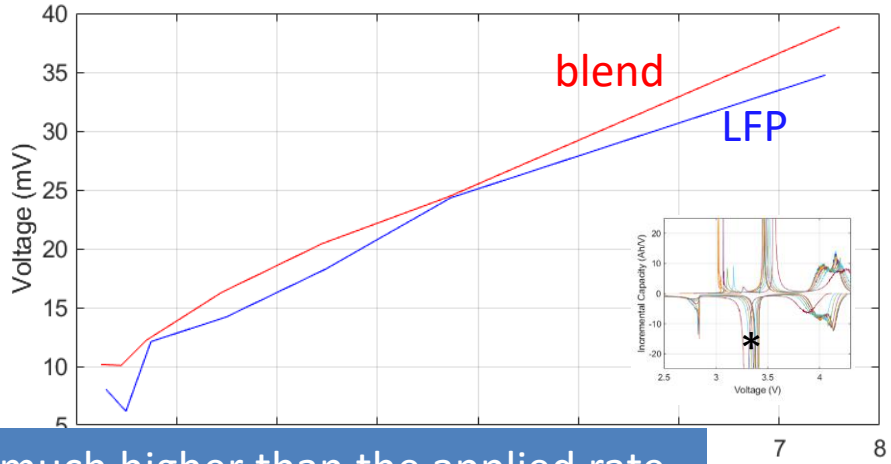
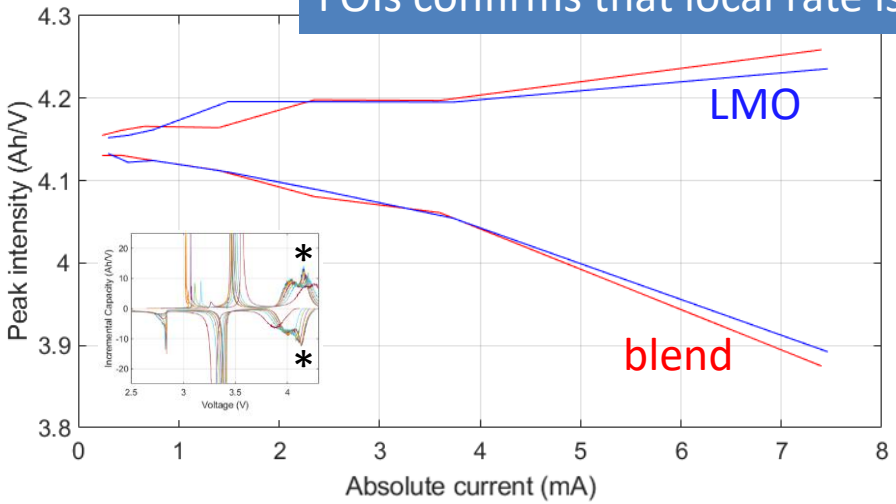


FOIs confirms that local rate is much higher than the applied rate



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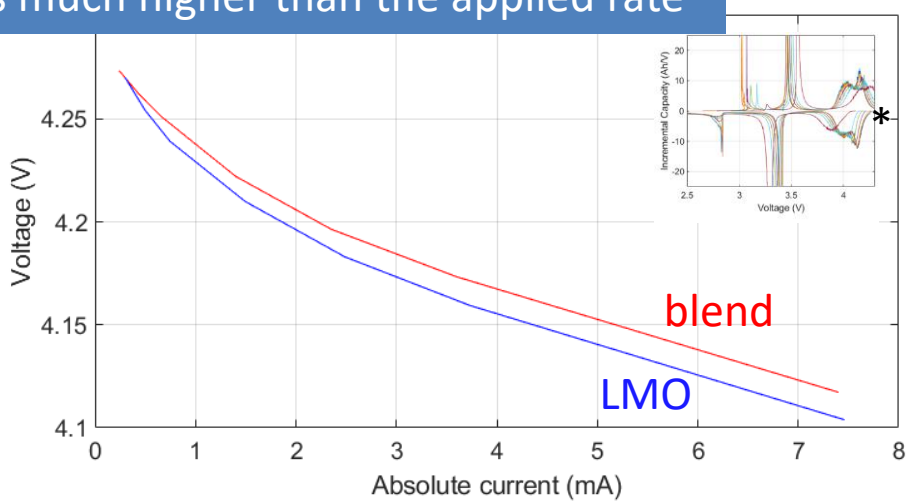


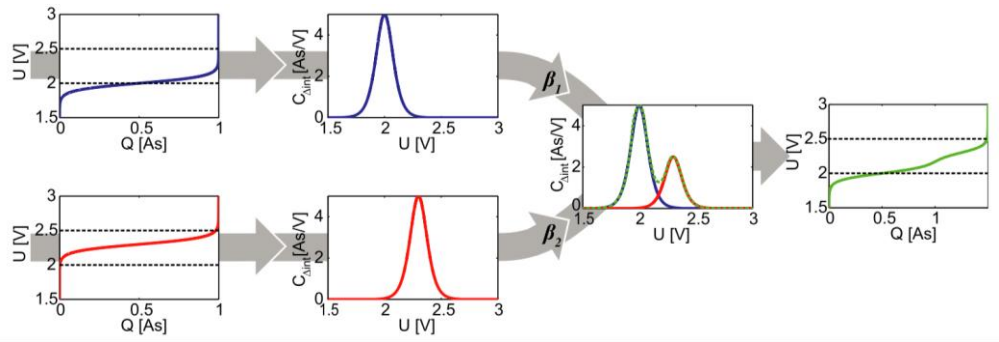
LMO initial voltage

Modeling: Use paralleling instead of CC sum?

Current procedure

Sum of IC response then integration

Dubarry, M., et al. (2012) Journal of Power Sources **219**: 204-216
Schmidt, J. P., et al. (2013). Journal of Power Sources **239**: 696-704

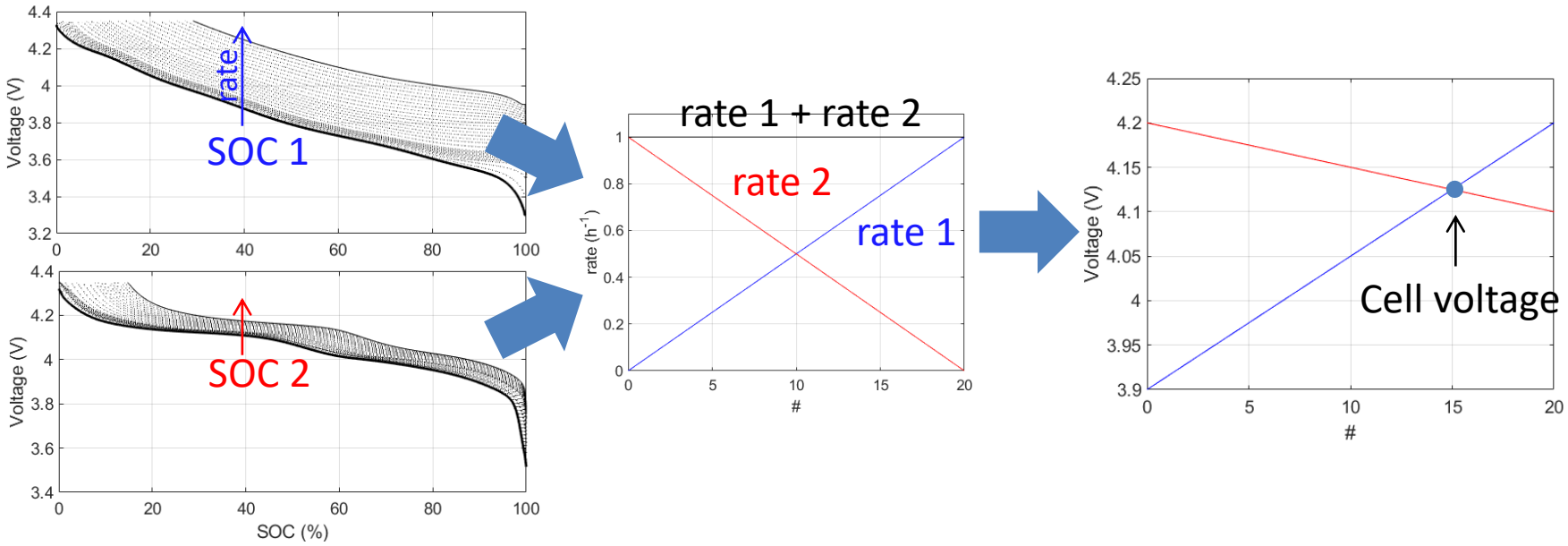


Use of paralleling model instead

Adapt model developed for packs to half-cells

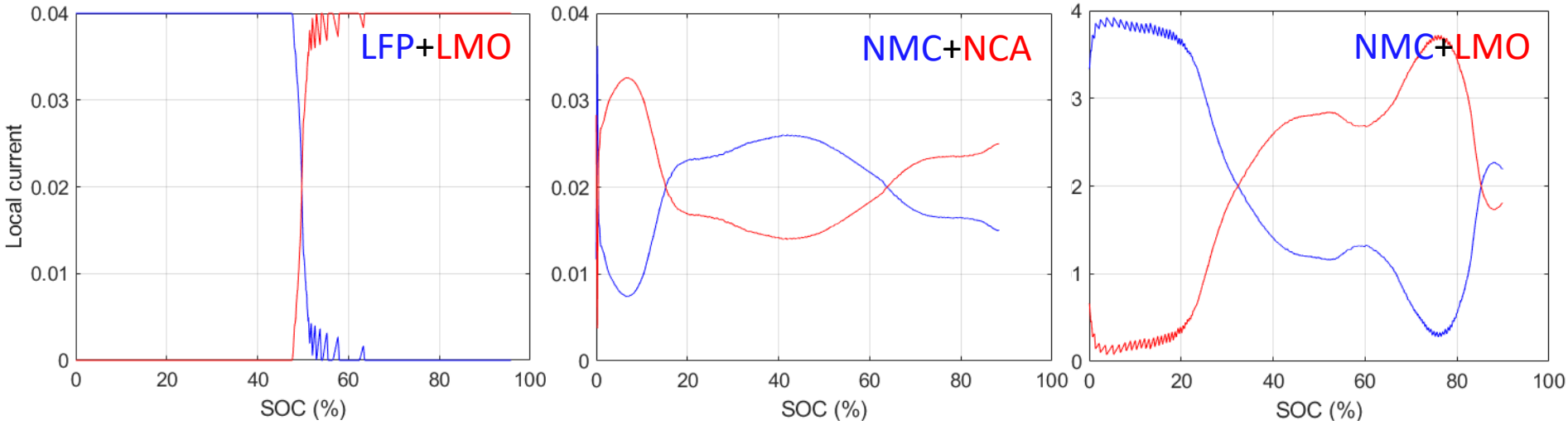
Dubarry, M., et al. (2016). Journal of Power Sources **321**: 36-46.

For all SOCs, look for intersection of ΔV vs. rate curves (with $\sum rate = rate_{req}$)



Use paralleling model

Preliminary modeling results



Model can be noisy

35 times slower than the CC option

Could be an issue for synthetic cycle generation

More validation in progress

Different approaches for paralleling modeling are under consideration

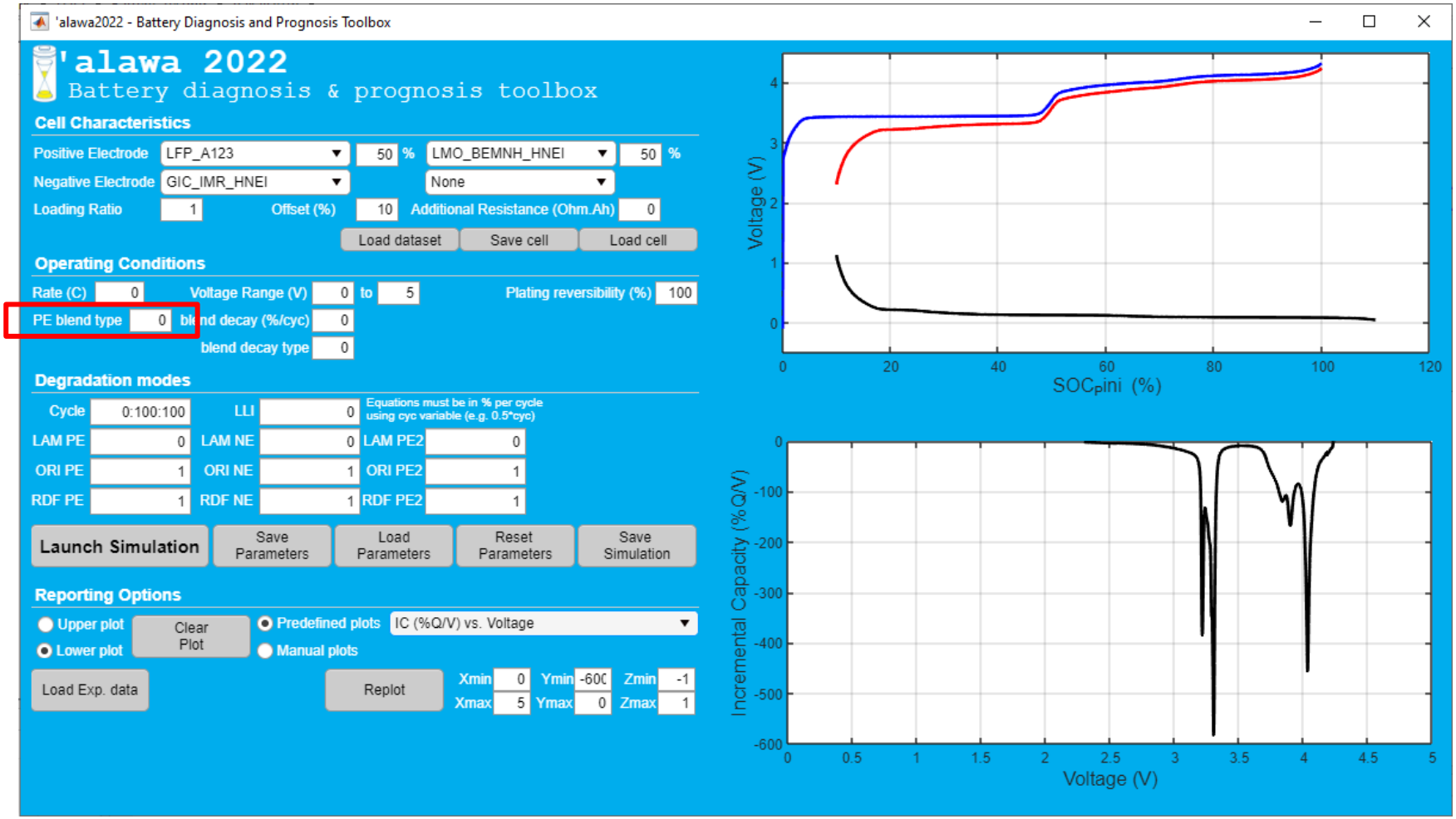
Calculating blended electrode response with paralleling model is capturing well the evolution of current on the different components of the blend

Improvement to the alawa mechanistic framework

New parameters added into framework: blend type

Choose between separated, overlapping, or partial overlap

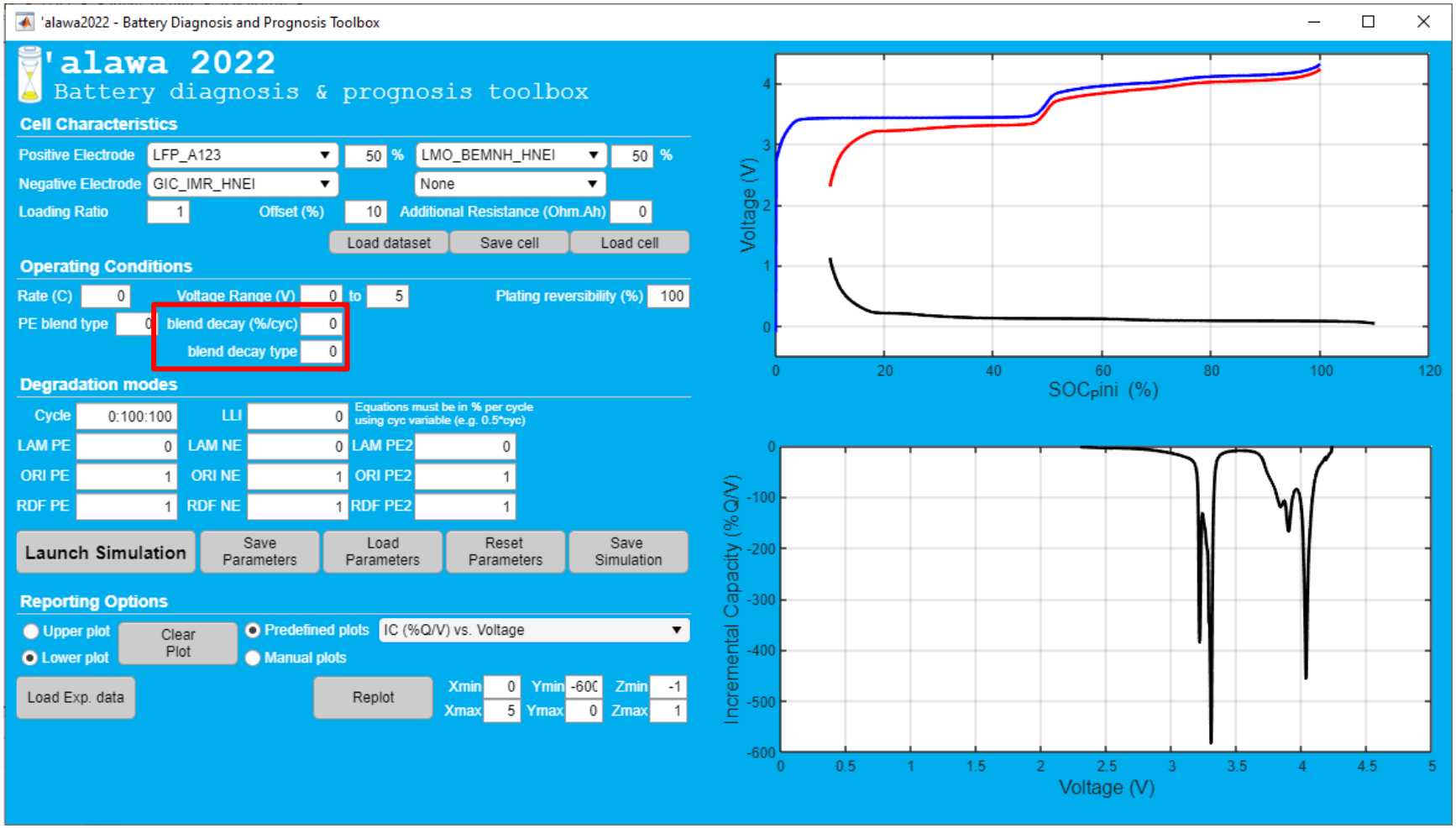
First two use CC method for speed. Last one use newly integrated paralleling model



Improvement to the alawa mechanistic framework

New parameters added into framework: voltage fade

Choose decay speed and type



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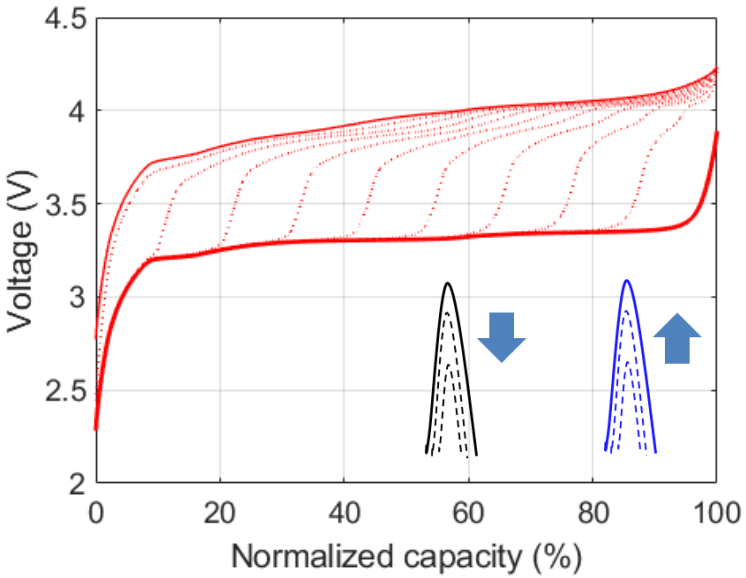
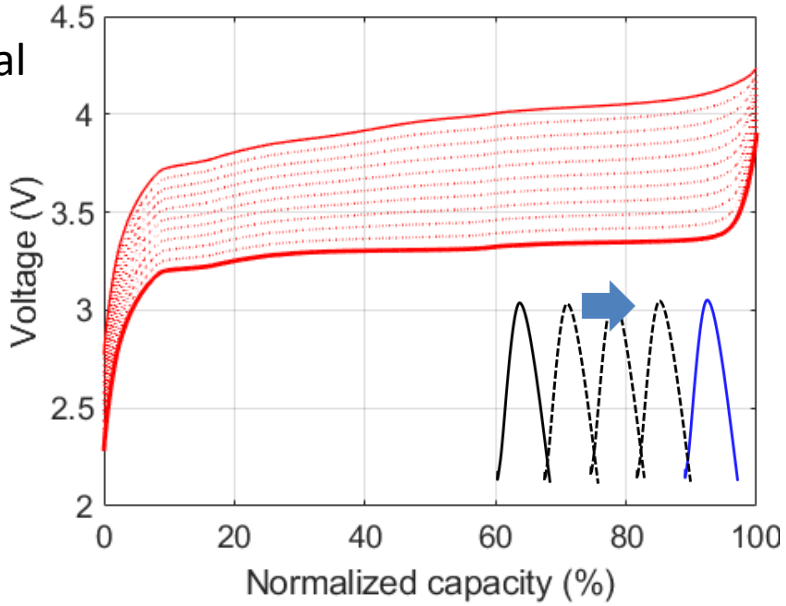
"Phase Transformation"

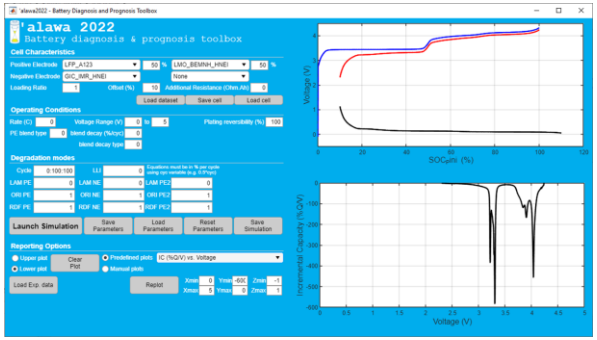


Hypothetical Example of LFP to LMO

"Solid Solution"



Dubarry, M., et al. (2012) Journal of Power Sources **219**: 204-216
Marco-Tulio Rodrigues et al., A02-0092, 239th ECS Meeting



β testing of 'alawa 2022 in progress.
Looking for before and after voltage fade data to integrate
Looking for feedback on what plots to integrate

Conclusions

Current distribution in blended electrode is complex

- Will depend on electrochemical response of each component
  - Separated: Local rate is multiplied since one phase is seeing all the current
  - Overlapping: Components are quasi equally dividing the current
  - Partially overlapping: Much more complex, current not constant

- Big implication for modeling and thus diagnosis and prognosis methods
  - To the very least, new parameter must be added to adjust the rate properly
  - Not accurate for partially overlapping: new approach needed, could be paralleling
    - But will increase calculation time which could be a problem for synthetic cycle generation.

- New parameters successfully implemented in HNEI mechanistic framework
  - New version of alawa framework in β testing, hoping for early 2022 release
  - β testers welcome

Acknowledgments

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Asia Pacific Research Initiative for Sustainable Energy Systems (APRISES)

Thank you, questions?

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