ONR Electrochemical Materials Program review 2024

Improved non-invasive techniques to understand Li-ion battery performance

Blended electrodes

Matthieu Dubarry and David Beck

matthieu@hawaii.edu

UH Materials Science Consortium for Research and Education CoRE

SCHOOL OF OCEAN AND EARTH SCIENCE AND TECHNOLOGY UNIVERSITY OF HAWAI'I AT MĀNOA

HNEI Hawai'i Natural Energy Institute University of Hawai'i at Mānoa

Introduction

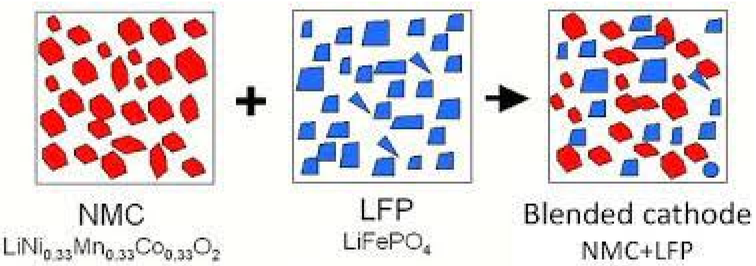
Noninvasive diagnosis & prognosis tools are needed to accelerate the deployment of Li-ion and Na-ion batteries.

Simple cells are well understood but the reality if often more complex.

Investigation of three types of blending:

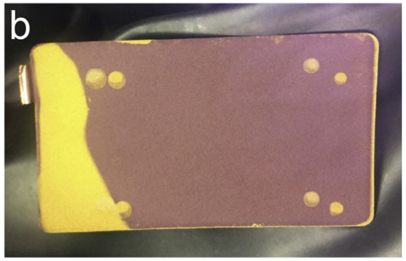
Blended electrodes

i.e. electrodes with two or more active materials (NMC/LMO, Graphite/SiOx…)



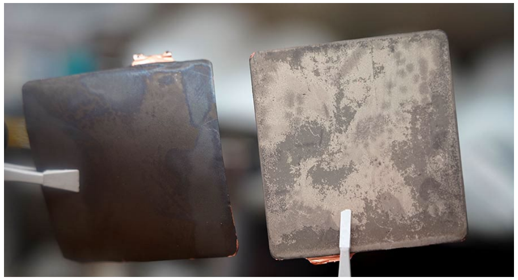
Inhomogeneities

An inhomogeneous electrode could be seen as a blend between electrodes not quite identical



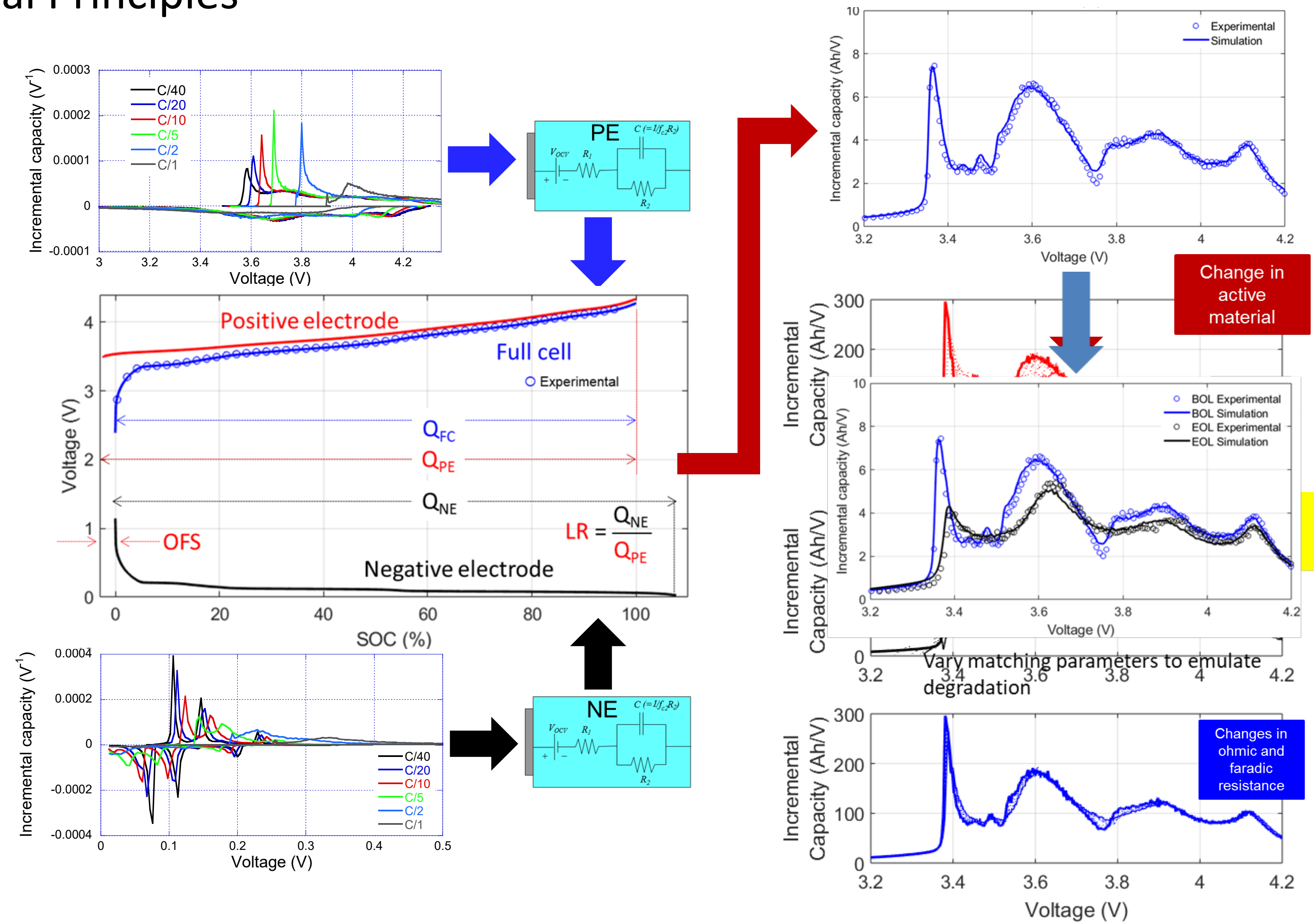
Plating

When plating occurs, the NE becomes a blend between the AM(s) and the charge carrier



Mechanistic modeling

General Principles



Dubarry M. et al. Journal of Power Sources 219 (2012) 204-216

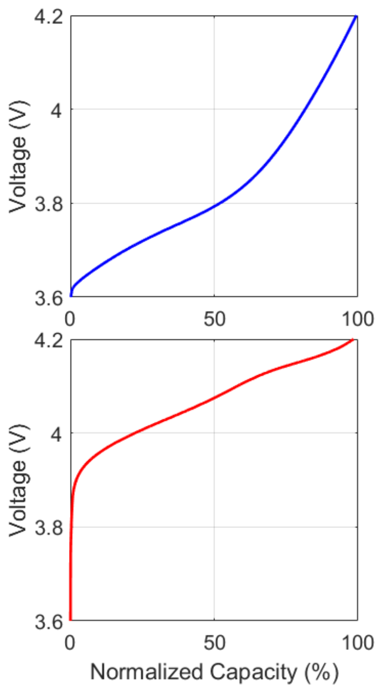
Mechanistic modeling
Blended electrodes

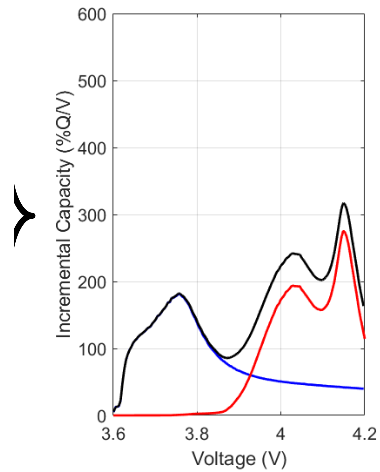
In a blended electrode, each dV must consider the dQ from each component.

Summing the dQ/dV = f(V) responses.

Calculate IC constant current response for each component and sum them

Proposed in 2012





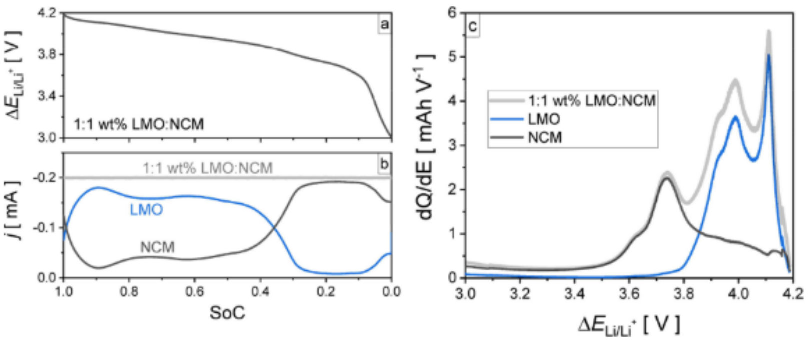
Is it realistic? If not, how should it be handled? Impact of chemistries?

Dubarry M. et al. Journal of Power Sources 219 (2012) 204-216

Beck D. and M. Dubarry Batteries – under review

Mechanistic modeling

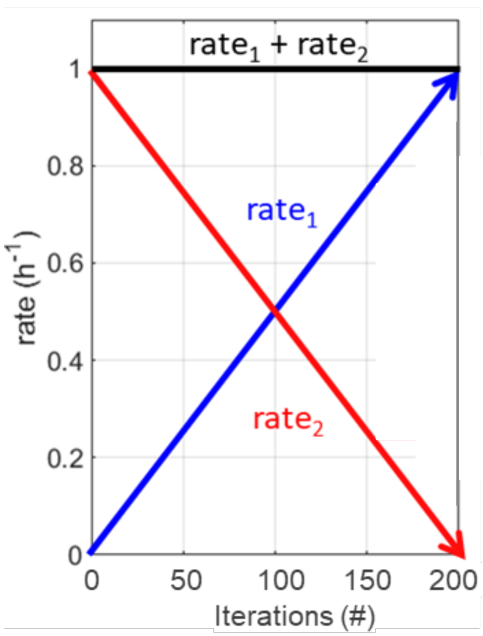
Blended electrodes



Clearly not that simple.
Simulation tools must adapt to chemistry

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

Need to implement a paralleling model to take that into account:

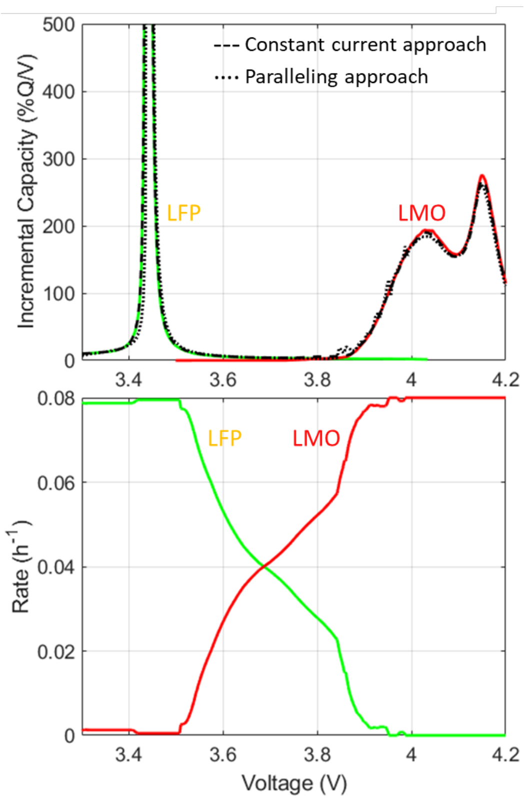


Accurate but x100 calculation time & noisy

Blended electrodes

Blend simulations: Constant current vs. paralleling

3 case figures: Separated, overlapping, and partially overlapping responses



Small differences at low rates. More significant for high-rate simulations

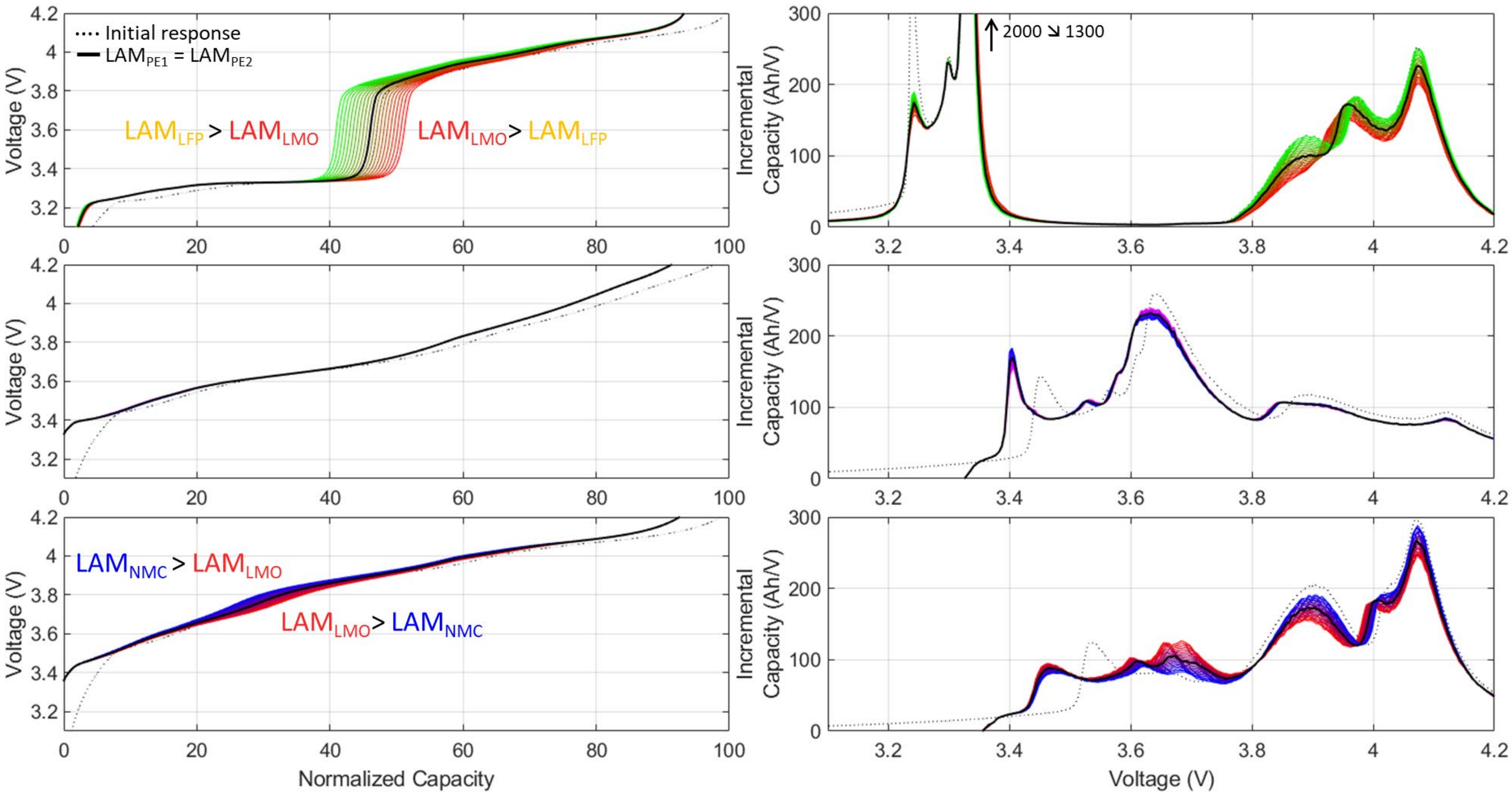
Beck D. and M. Dubarry Batteries – under review

Blended electrodes

Blend simulations: LAM_{PE} quantification

Many studies do not differentiate the components upon aging

BUT LAM_{PE} composition has a huge impact on electrochemical response:

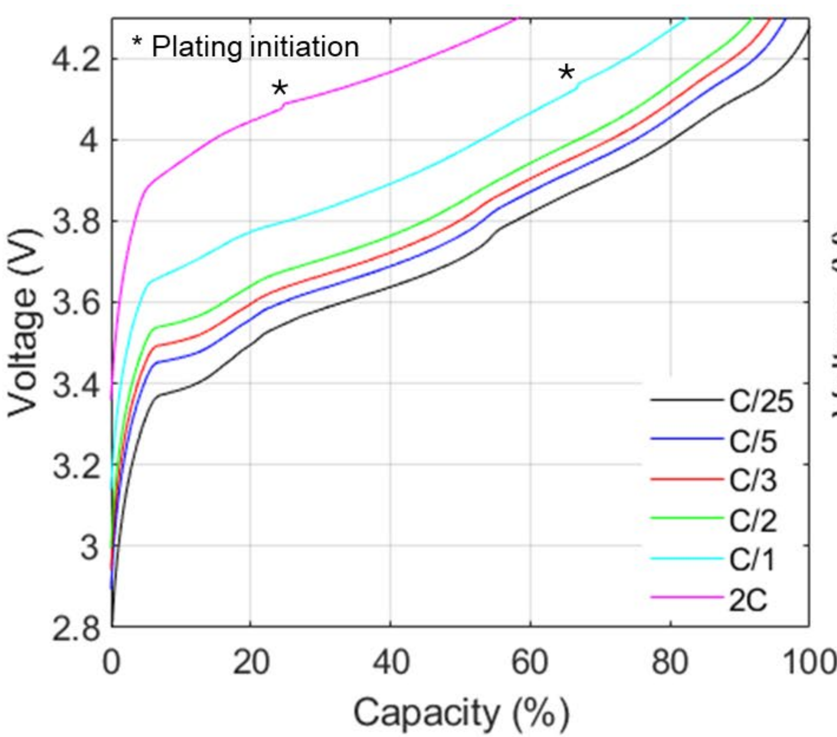


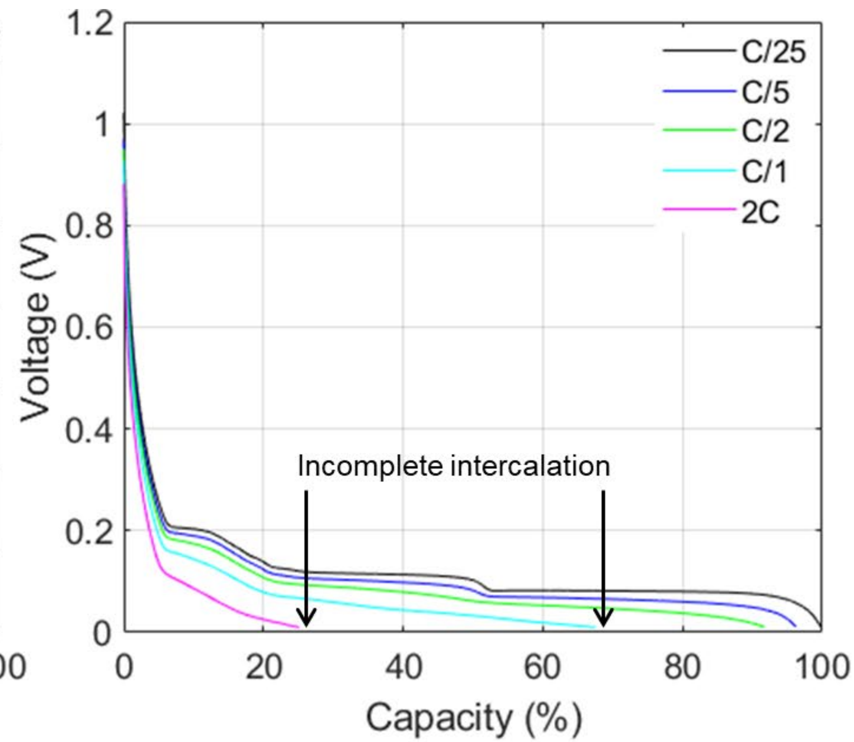
Beck D. and M. Dubarry Batteries 10(5), 159; doi: 10.3390/batteries10050159

Lithium and Sodium Plating

Plating modeling is available in the modeling framework

- BUT overly simplified with a 0V infinite plateau.
- Other problem is the lack of data for end-of discharges for high rates
  - Leads to inaccurate early plating predictions





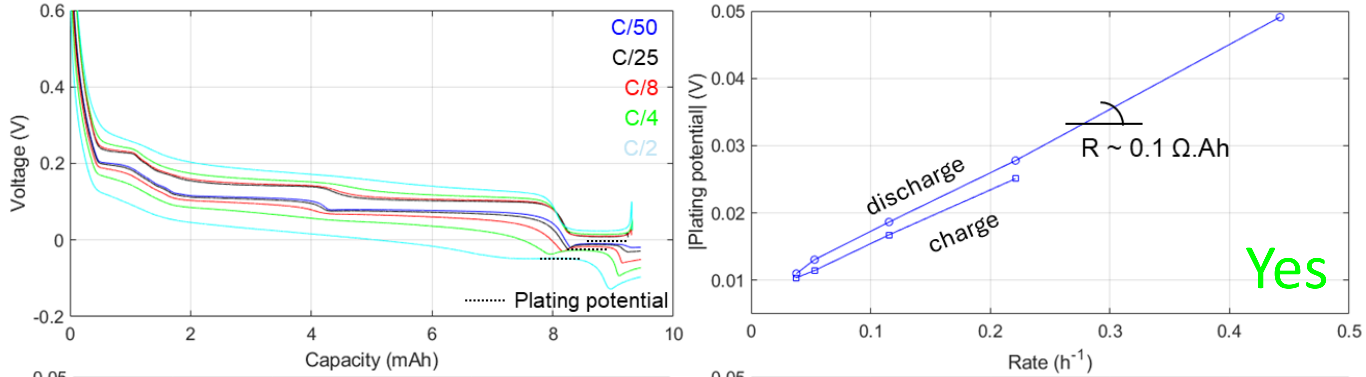
M. Dubarry et al., ACS Energy Letters– under review

Lithium and Sodium Plating

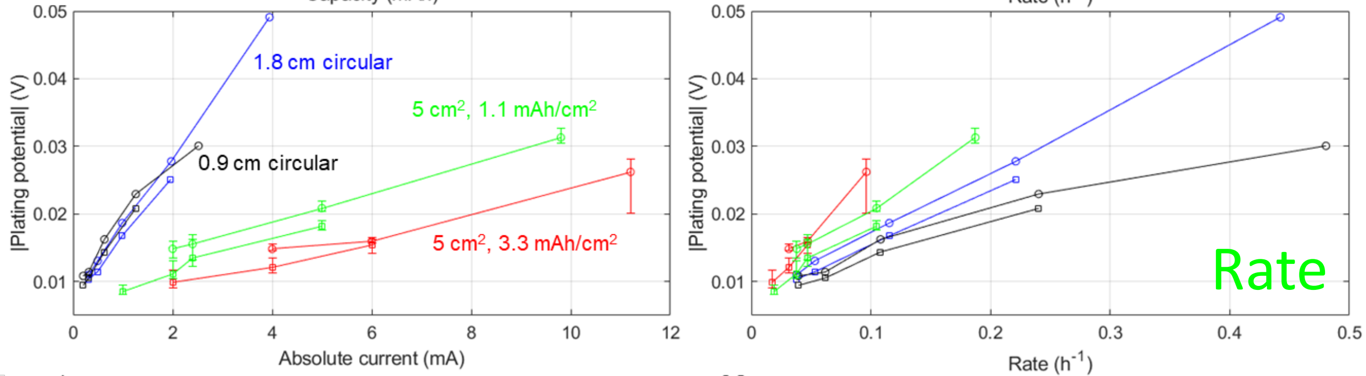
Collaboration with Coventry University

Experiments:

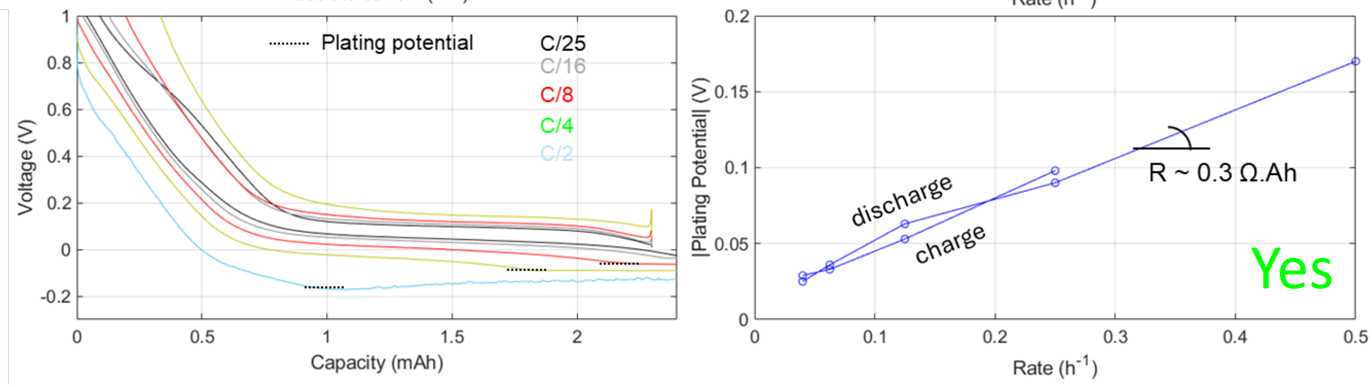
Is lithium plating potential rate dependent?



Is it rate or current dependent?



Is it the same for sodium plating?



M. Dubarry et al., ACS Energy Letters– under review

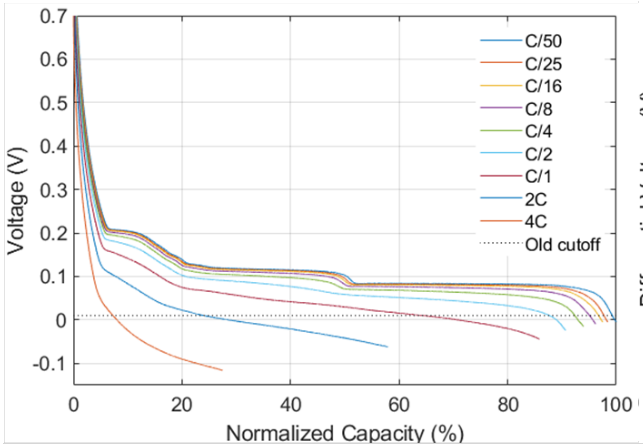
Mechanistic modeling

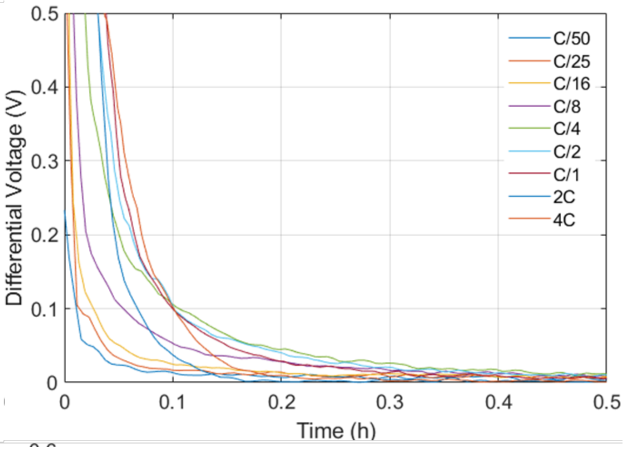
Lithium and Sodium Plating

Preliminary results:

RPTs can be extended with a rate dependent end of discharge cutoff

Rest dV/dt analysis showed no sign of stripping





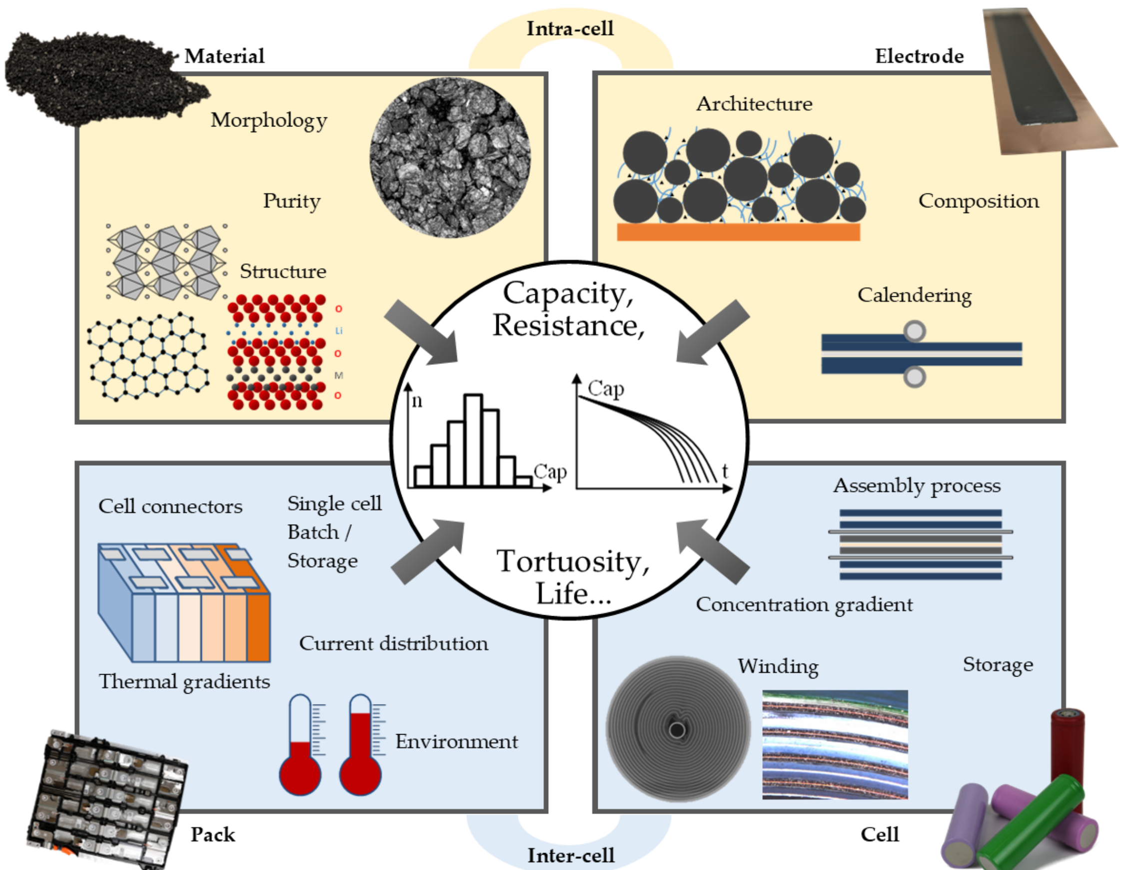
Better plating modeling with new parameter: the plating resistance

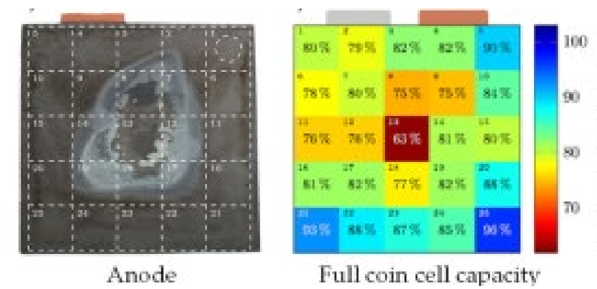
M. Dubarry et al., ACS Energy Letters– under review

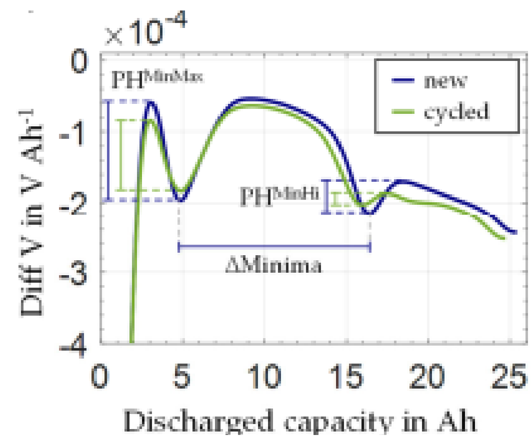
Mechanistic modeling

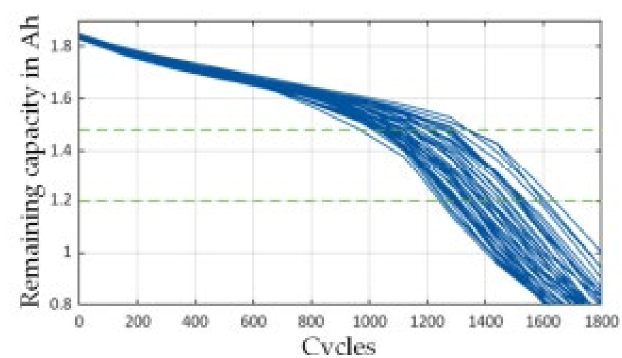
Inhomogeneous Electrodes

Inhomogeneities are a well-known issue







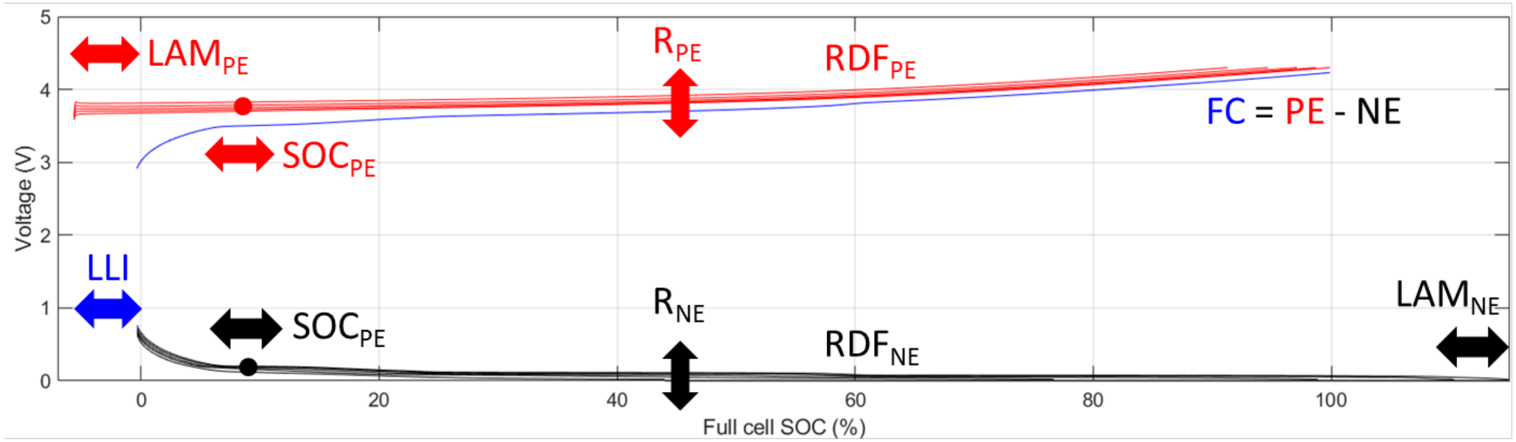


But their modeling isn't…

Beck, D. et al., Energies 2021, 14, 3276

Inhomogeneous Electrodes

Same strategy as for degradation: Inhomogeneity modes

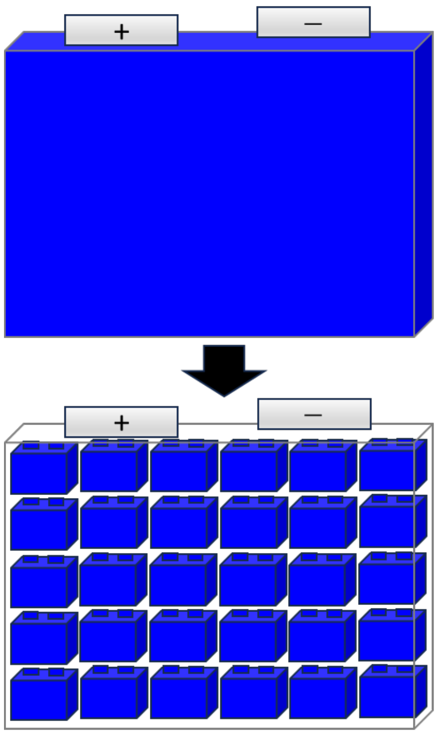


M. Dubarry, and D. Beck, Joule – under review

Inhomogeneous Electrodes

Paralleling should help but at which level?

Full cell level ? Electrode level? Or both?



M. Dubarry, and D. Beck, Joule – under review

Mechanistic modeling

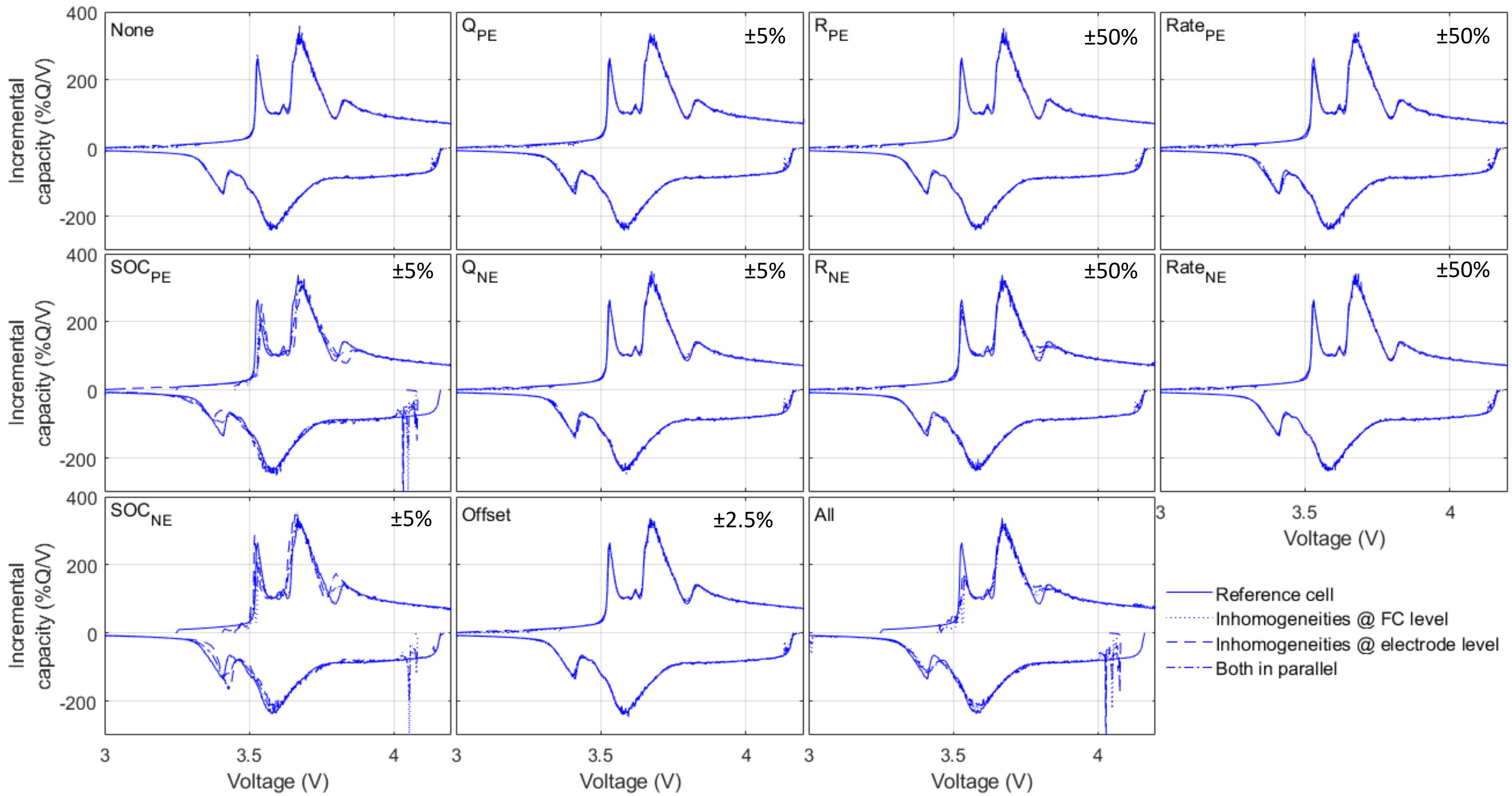
Inhomogeneous Electrodes

Summary

6/9 inhomogeneity modes have almost no impact on performance

BUT rate is affected, might influence degradation down the line…

3/9 inhomogeneity modes has impact. R_{NE} most resemble what reported in literature.



Mechanistic modeling

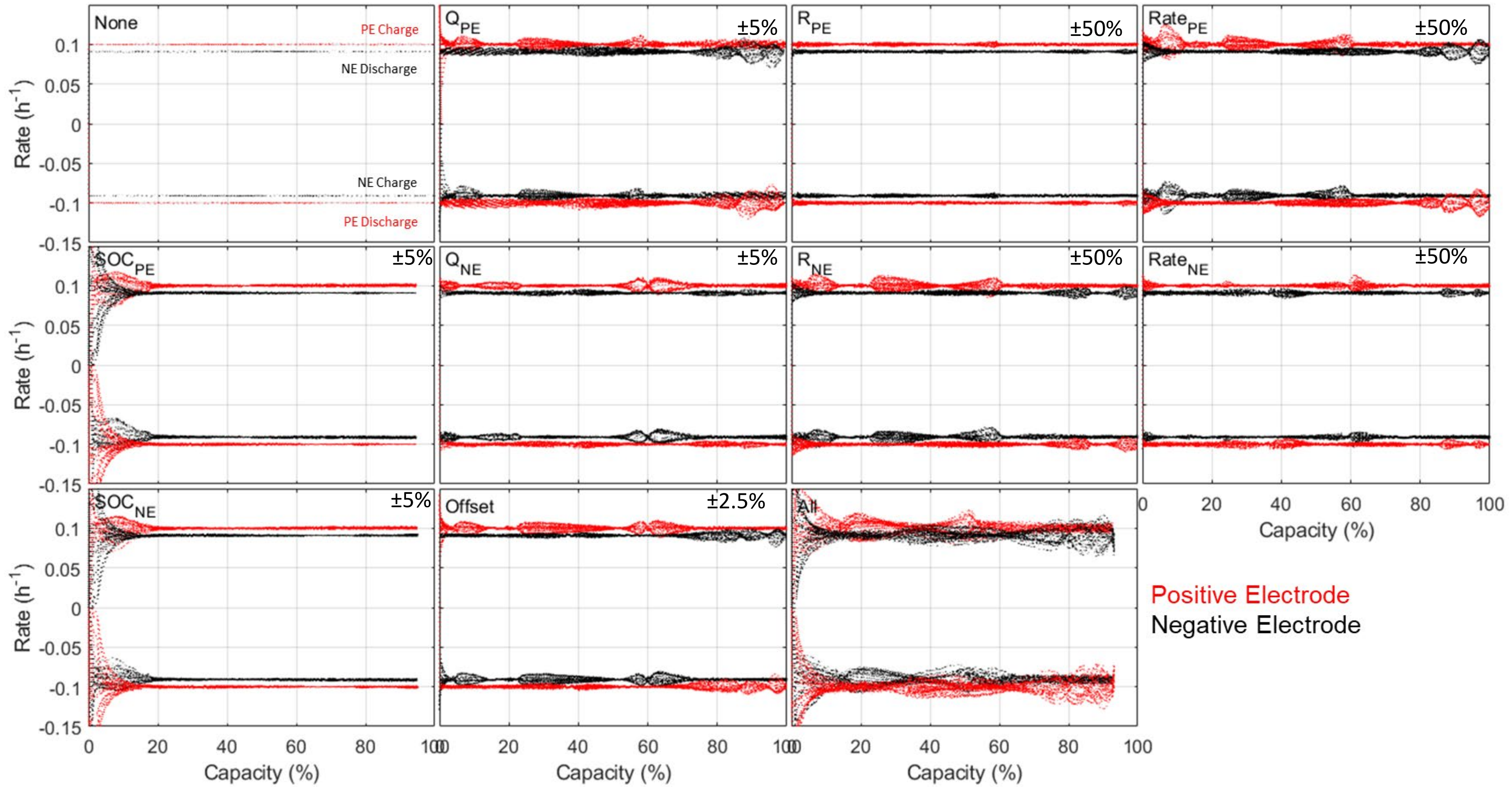
Inhomogeneous Electrodes

Summary

6/9 inhomogeneity modes have almost no impact on performance

BUT rate is affected, might influence degradation down the line…

3/9 inhomogeneity modes has impact. R_{NE} most resemble what reported in literature.



M. Dubarry, and D. Beck, Joule – under review

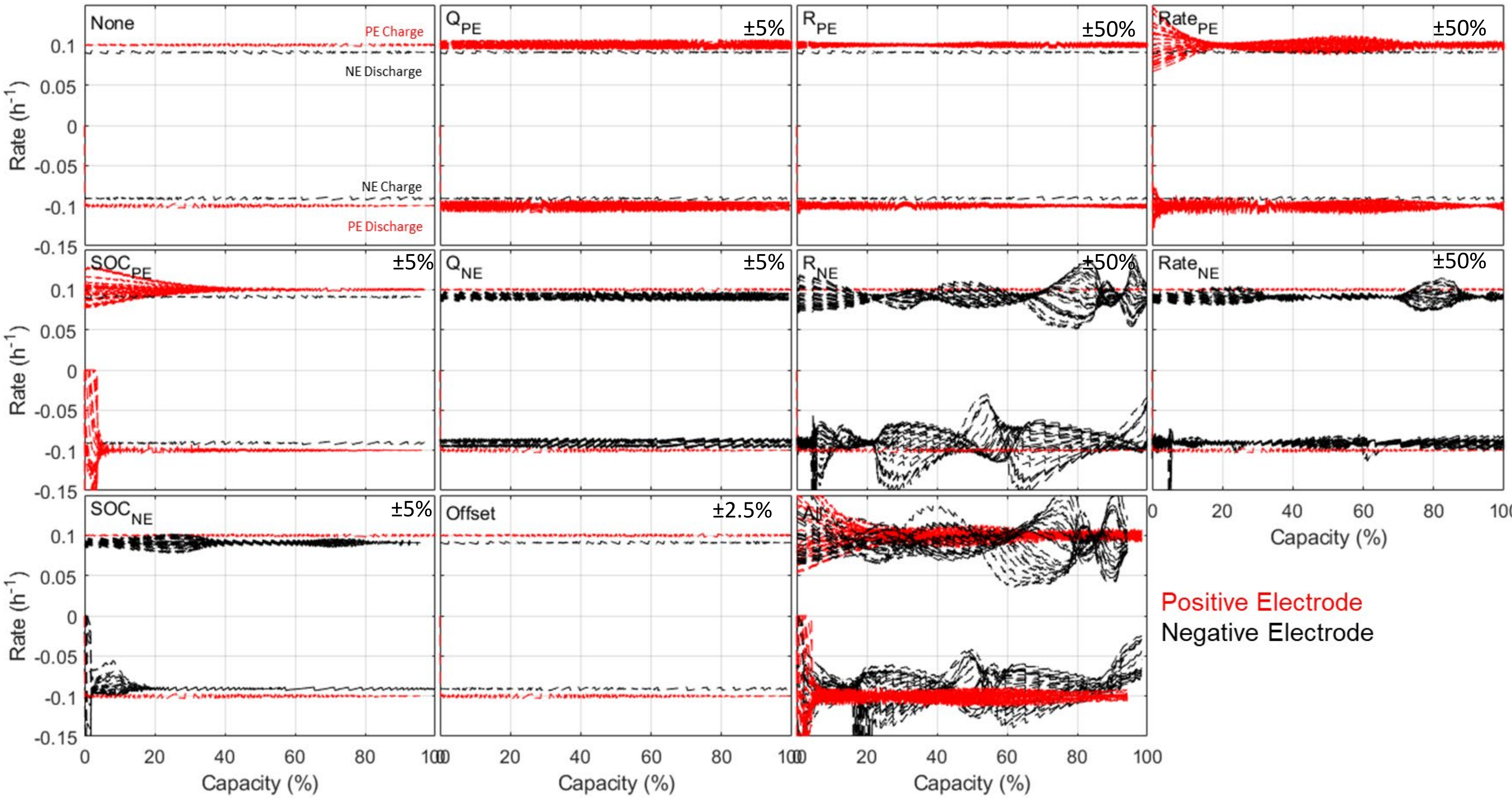
Inhomogeneous Electrodes

Summary

6/9 inhomogeneity modes have almost no impact on performance

BUT rate is affected, might influence degradation down the line…

3/9 inhomogeneity modes has impact. R_{NE} most resemble what reported in literature.



M. Dubarry, and D. Beck, Joule – under review

Inhomogeneous Electrodes

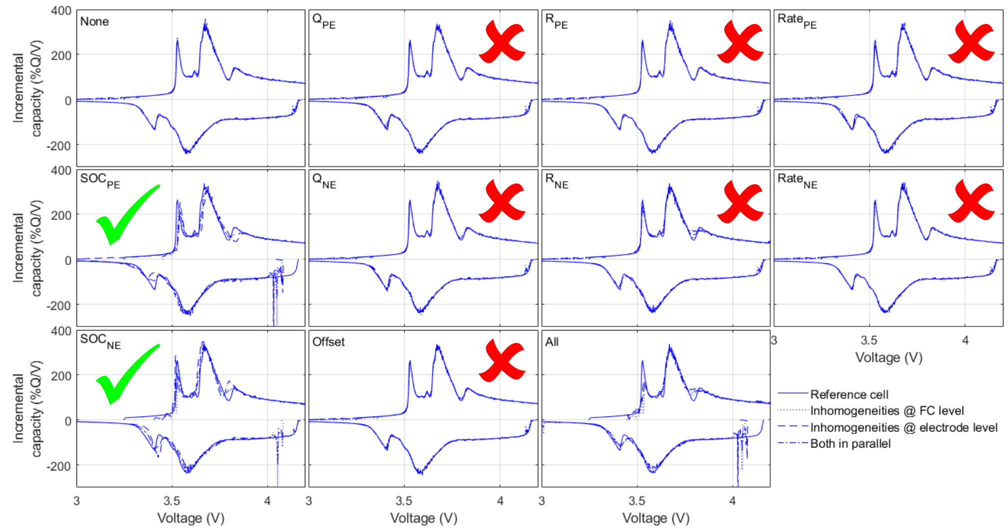
Quantification

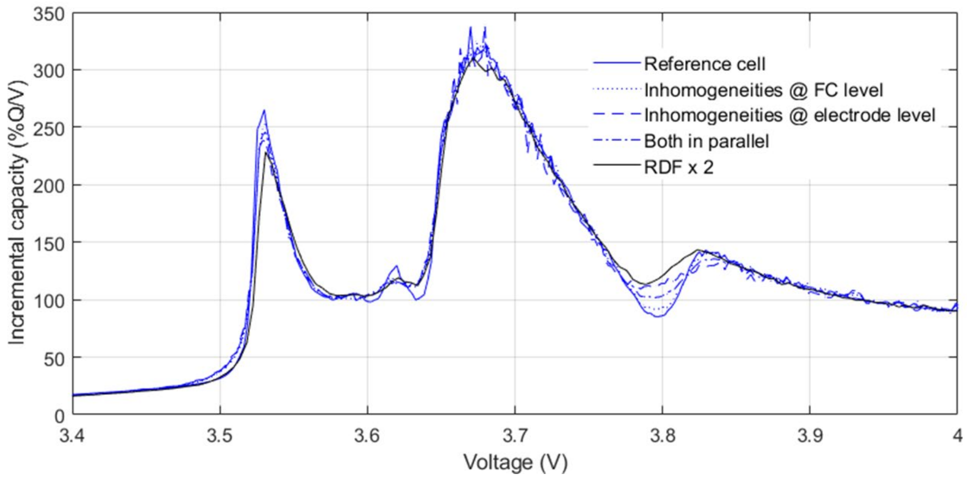
Impossible for 6/9 when mild randomly distributed variations

Might be possible at beginning of regime for the SOC ones

For R_{PE}, resemble impact of rate degradation factor

- Quantification impossible
- BUT simulation already implemented
- Close to experimental observations





HNEI Hawai'i Natural Energy Institute University of Hawai'i at Mānoa

Mechanistic modeling

'alawa

Validated

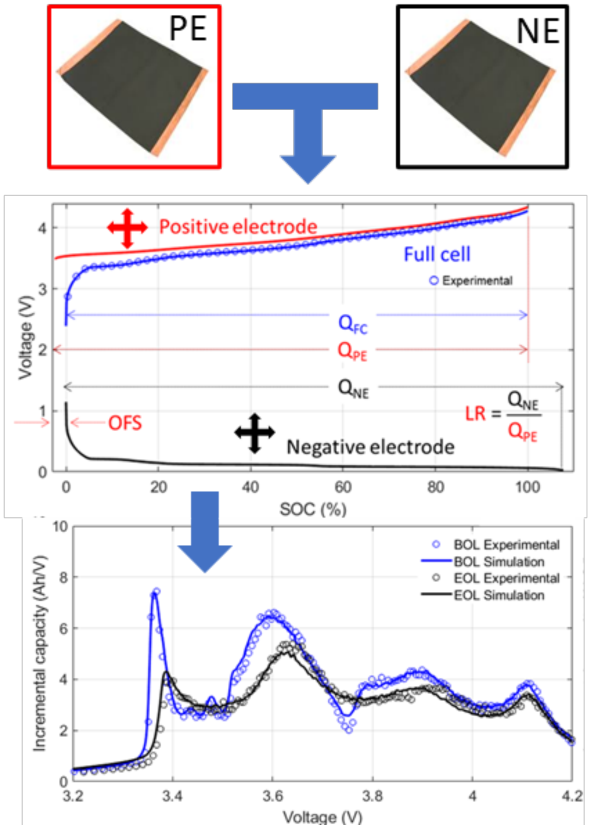
Degradation mode diagnosis
LLI, LAMs, Kinetics

Material based prognosis
With knee or not
Plating, reversible or not

Electrochemical responses
Constant current
Simple blends
Overdischarge
Overcharge

Big Data
Low rates
Feature of Interest Tracking

Mechanistic Modeling Approach



Under validation

Electrochemical responses
Na-ion and other chemistries
Advanced blends
Voltage fade
Inhomogeneous electrodes
Large battery packs
Dynamic duty cycles

Big Data
High rates
Temperatures
Blends
Non-continuous duty cycles

'alawa: Hawaiian for "to diagnose by insight"

Dubarry M. and D. Beck, Accounts of Material Research, In press.

Graphical user interface: the ‘alawa toolbox

‘alawa

~ 200 registered users from >115 organizations worldwide

Idaho National Laboratory

Sandia National Laboratories

BROOKHAVEN NATIONAL LABORATORY

AIST NATIONAL INSTITUTE OF ADVANCED INDUSTRIAL SCIENC AND TECHNOLOGY (AIST)

Honda Research Institute EU

BMW

UNIVERSITY OF OXFORD

Imperial College London

National Electric Vehicle Sweden

ATL

saft

Acknowledgments

All my students

Current and past Funding:

Office of Naval Research Science & Technology

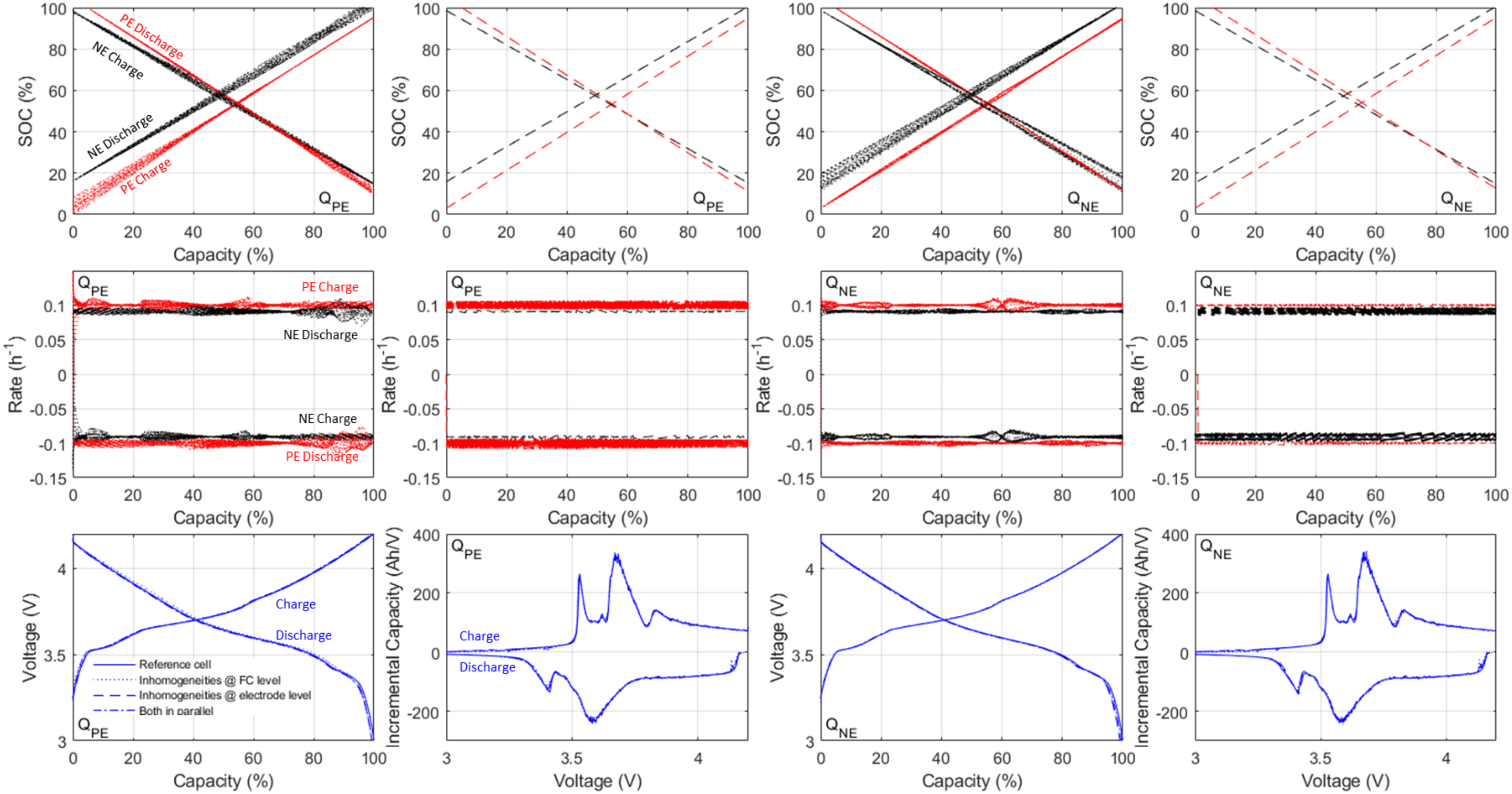
Mahalo for your attention! Questions ?

HNEI
Hawaiʻi Natural Energy Institute
University of Hawaiʻi at Mānoa

matthieu@hawaii.edu

Inhomogeneous Electrodes

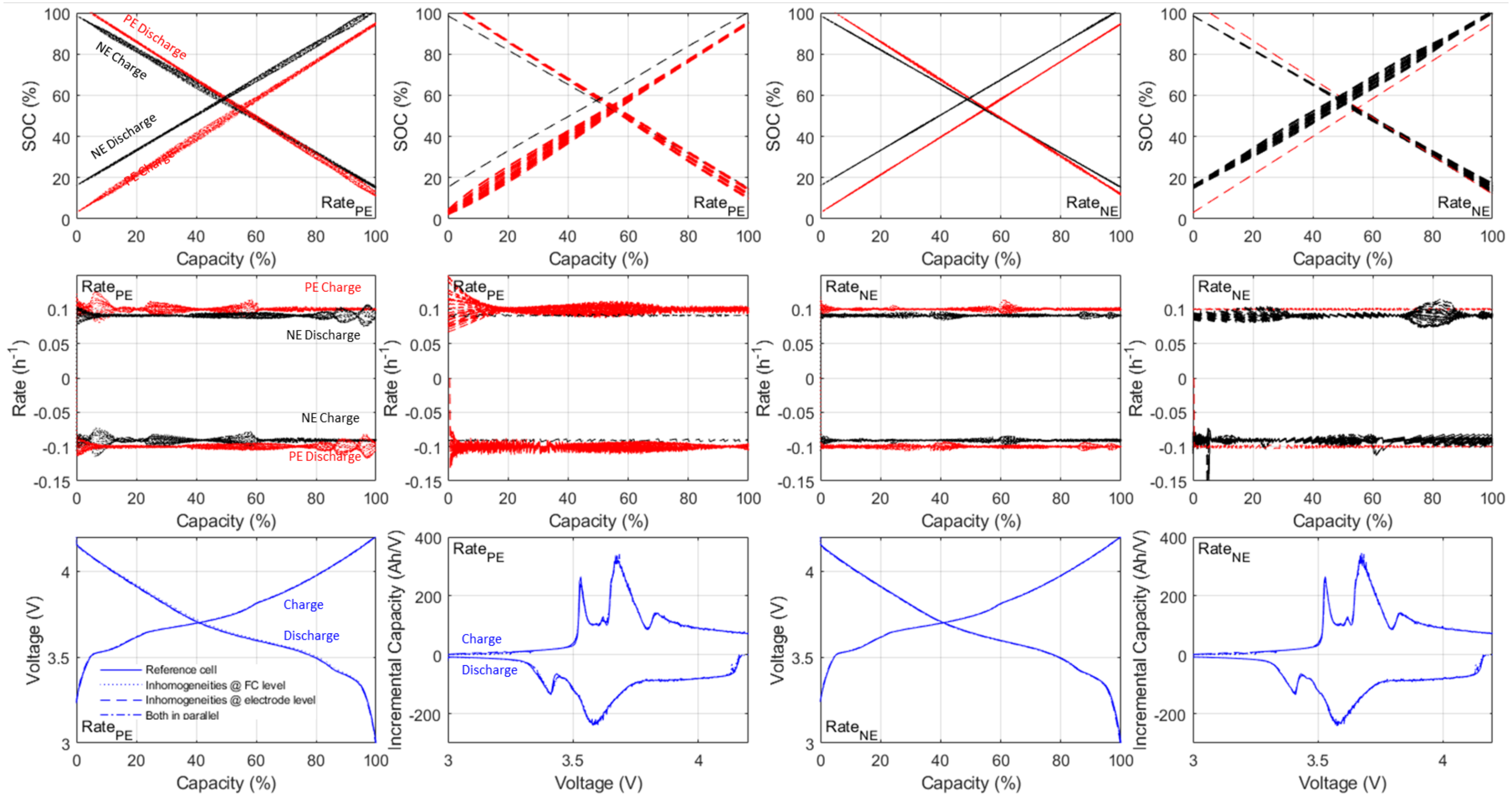
Inhomogeneity modes ±5% of randomly distributed Q_{PE} and Q_{NE}



M. Dubarry, and D. Beck, Joule – under review

Inhomogeneous Electrodes

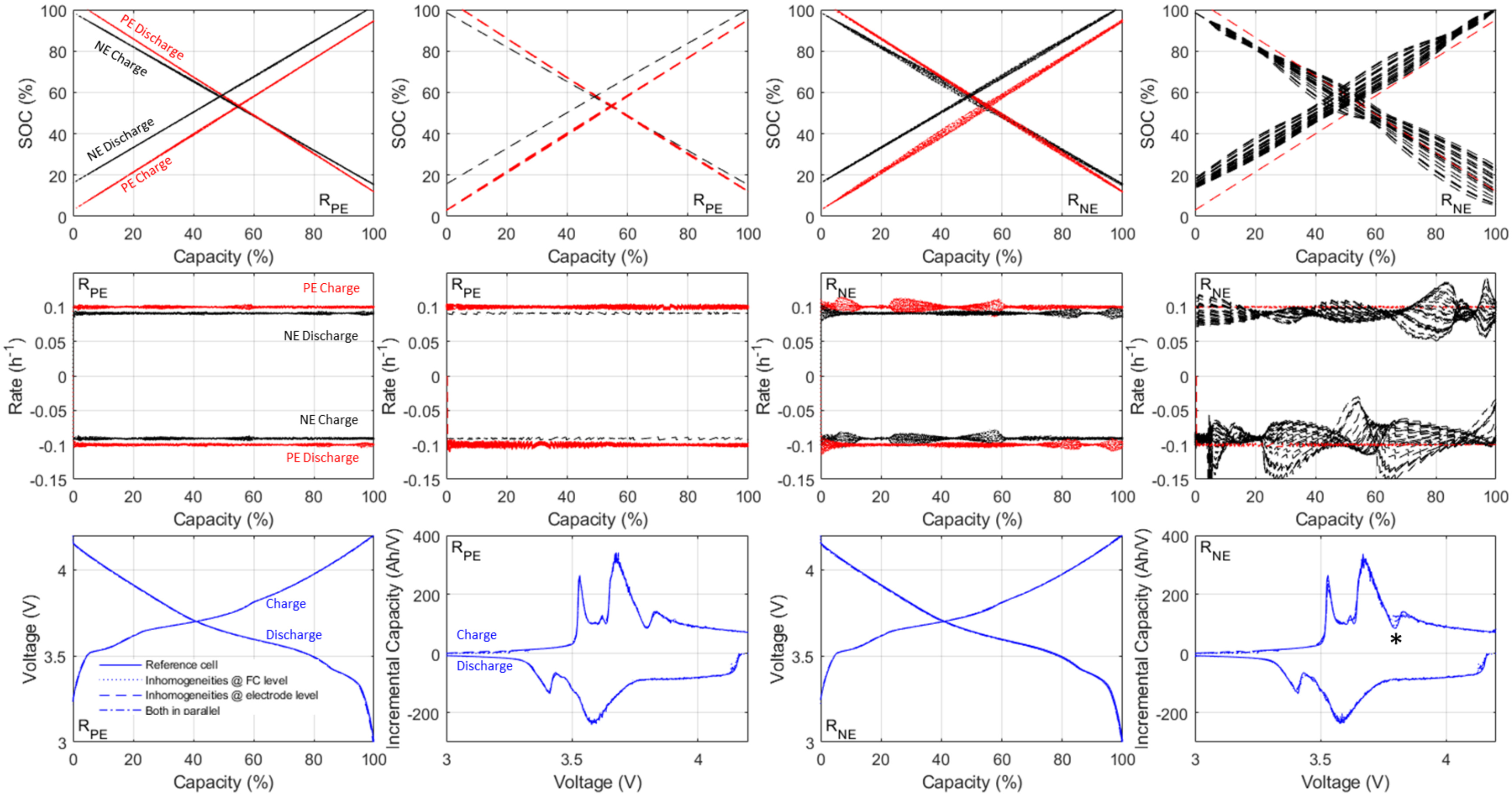
Inhomogeneity modes ±50% of randomly distributed $Rate_{PE}$ and $Rate_{NE}$



M. Dubarry, and D. Beck, Joule – under review

Inhomogeneous Electrodes

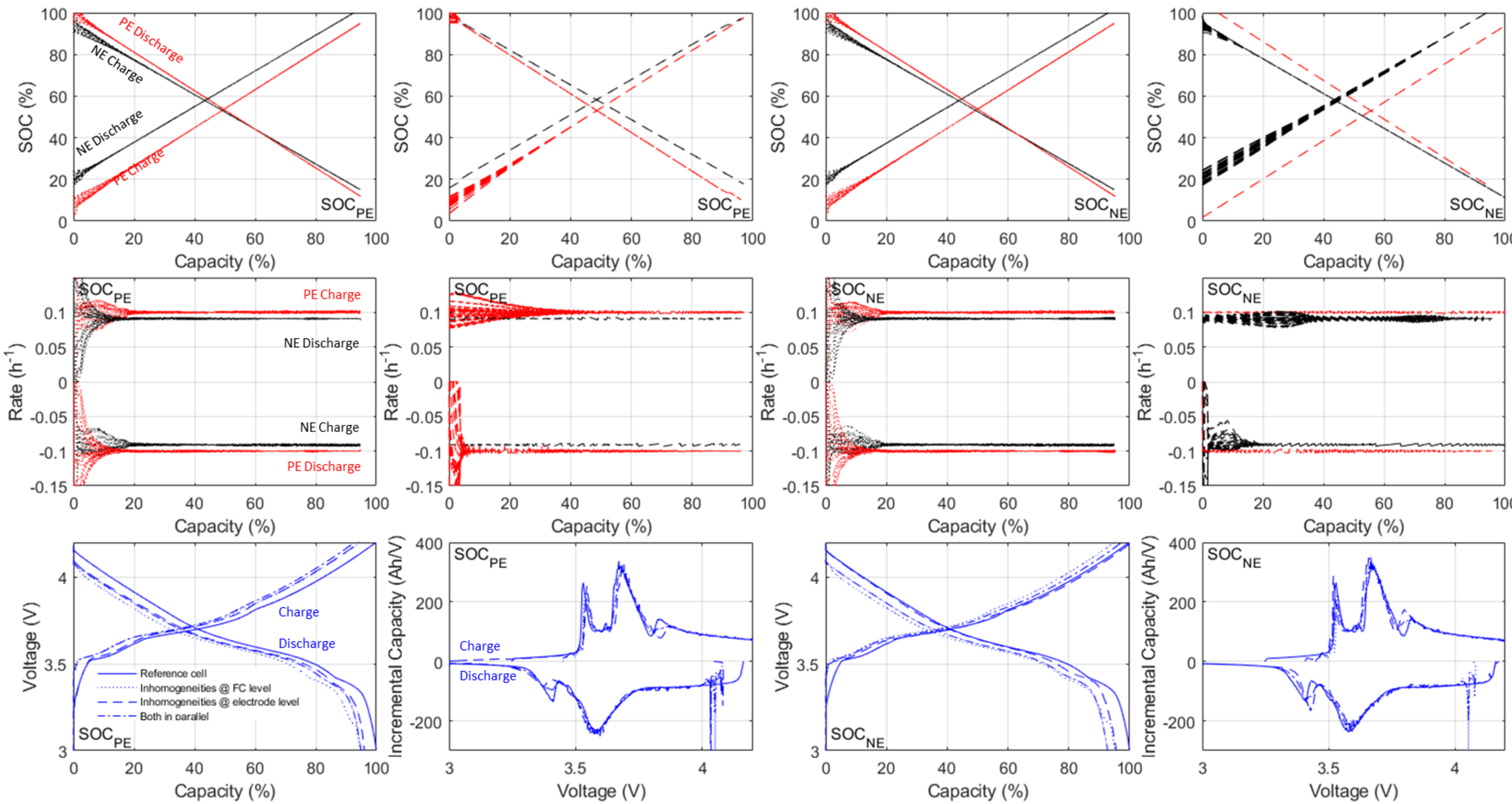
Inhomogeneity modes ±50% of randomly distributed R_{PE} and R_{NE}



M. Dubarry, and D. Beck, Joule – under review

Inhomogeneous Electrodes

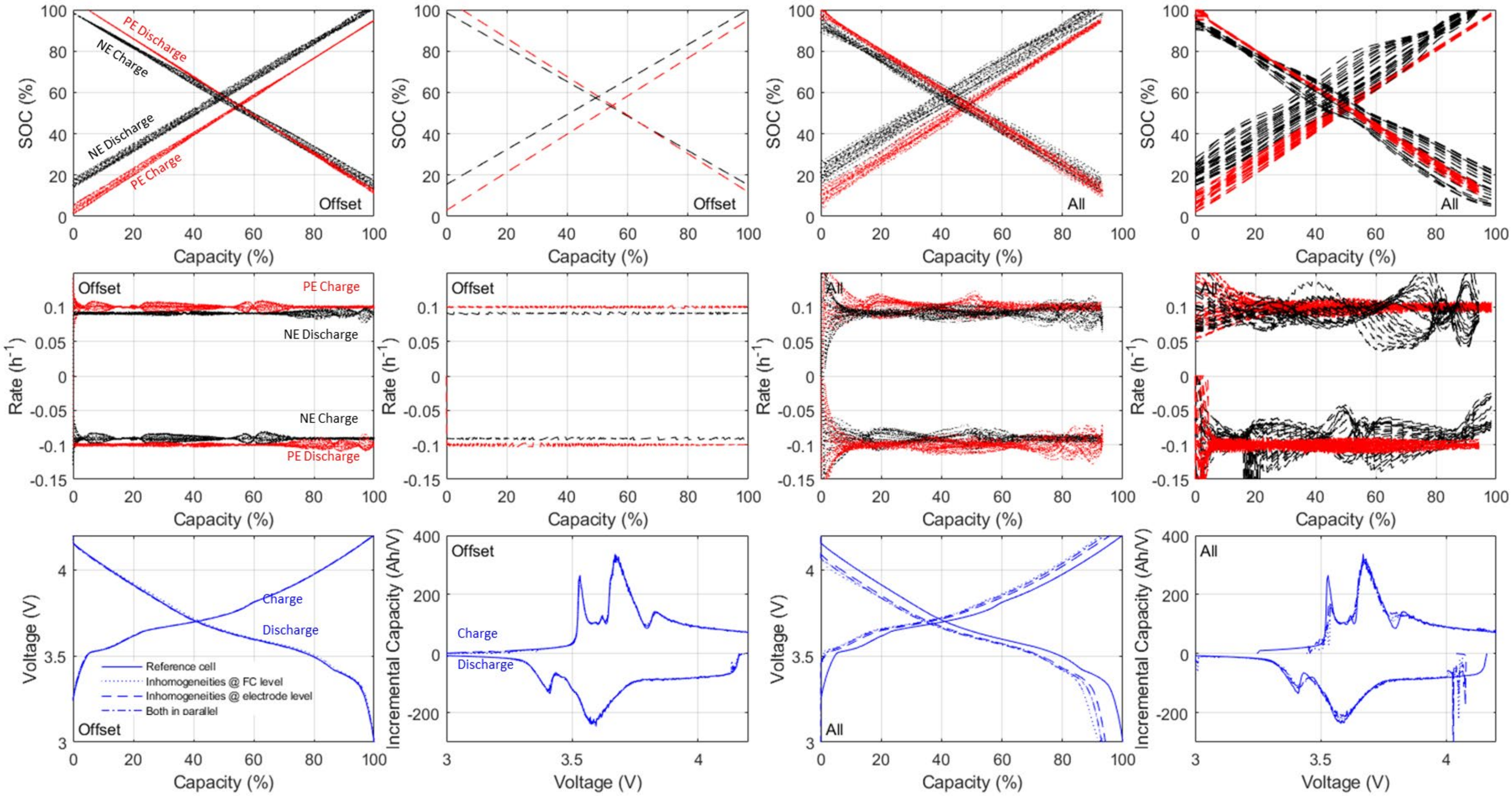
Inhomogeneity modes ±5% of randomly distributed SOC_{PE} and SOC_{NE}



M. Dubarry, and D. Beck, Joule – under review

Inhomogeneous Electrodes

Inhomogeneity modes ±2.5% of randomly distributed Offset and all together



M. Dubarry, and D. Beck, Joule – under review