Electrochemical Modeling of LMR-NMC Materials and Electrodes

Project ID: ES189

Presented by Dennis Dees

Voltage Fade Team and CAMP Facility Team

2014 DOE Vehicle Technologies Office Annual Merit Review and Peer Evaluation Meeting

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Overview

Timeline

- Start: October 1, 2012
- End: Sept. 30, 2014
- Percent complete: 75%

Budget

- Voltage Fade project
- CAMP Facility project

Barriers

Development of a PHEV and EV batteries that meet or exceed DOE/USABC goals.

Partners

- ORNL
- NREL
- ARL
- JPL

Relevance

- The Argonne high energy composite layered lithium ion cathode $xLi_2MnO_3 \cdot (1-x)LiMO_2$ (M = Ni, Mn, Co), also referred to as lithium and manganese rich NMC material (LMR-NMC), is a cost-effective electrode material that offers the potential for capacities exceeding 250mAh/g, excellent cycle and calendar life, and outstanding abuse tolerance. However, the material currently possesses a voltage fade issue (and other related issues) that affects its long-term cycle life.

- The Voltage Fade Team is focused on the voltage fade phenomena and the CAMP Facility Team is working on optimizing these materials in prototype cells.

- This modeling effort supports both projects through the development and utilization of efficient simulation, analysis, and design tools for advanced lithium ion battery technologies.

- Further, these modeling tools are focused on correlating analytical diagnostic results with the electrochemical performance of LMR-NMC electrodes and cells.

  - Link experimental efforts through electrochemical modeling studies
  - Identify performance limitations and aging mechanisms

Approach and Milestones

- In general, the approach for electrochemical modeling activities is to build on earlier successful characterization and modeling studies in extending efforts to LMR-NMC materials and electrodes.

- Parallel modeling efforts are being pursued that diagnostically examine different aspects of LMR-NMC materials and electrodes.

- As the models mature, integration is planned to produce an enhanced overall model, but as the modeling efforts become increasingly integrated they also will become more complex and time consuming to utilize.

- The starting intercalation electrochemical cell model accounts for much of the LMR-NMC behavior and when combined with the analytical voltage fade model should be an effective tool for most transportation related applications.

- Milestones:
  - Develop a model describing the voltage hysteresis in LMR-NMC. (completed)
  - Develop a baseline voltage fade model for LMR-NMC. (completed)
  - Initiate integration of electrochemical material, electrode, and cell models for the LMR-NMC positive electrode. (completed)
  - Advance development of electrochemical models focusing on high energy lithium ion electrochemical couples. (ongoing)
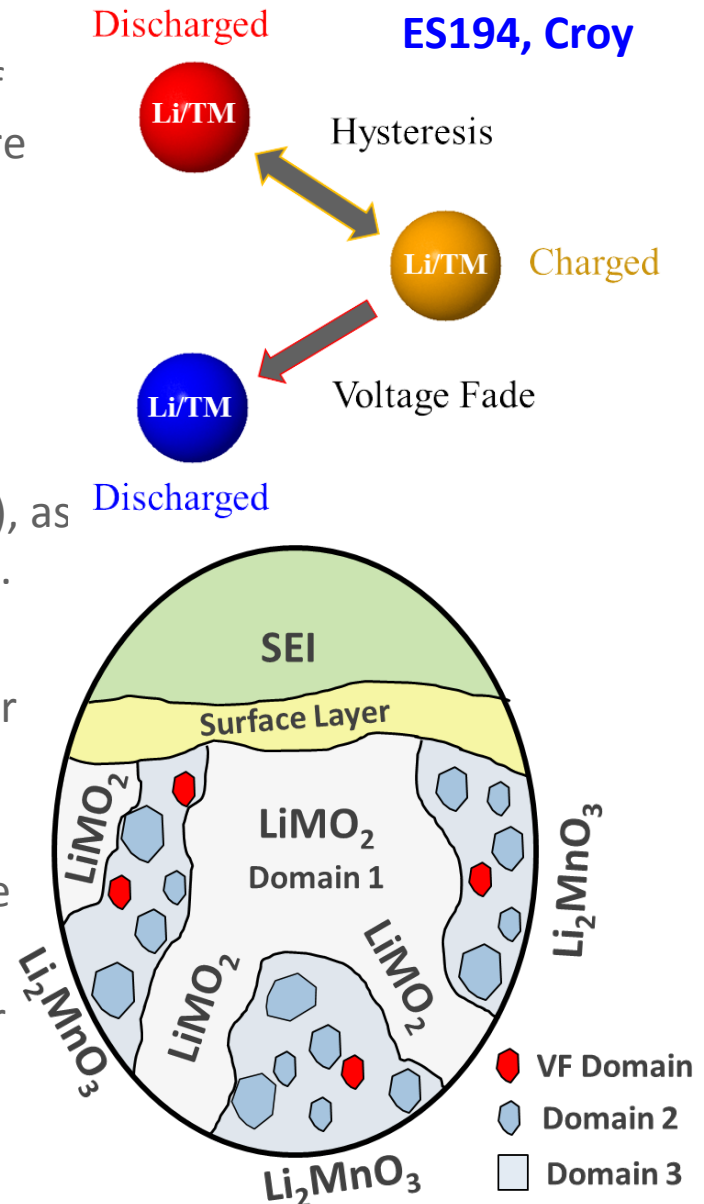
Technical Accomplishments and Progress

- Electrochemical model for intercalation active material electrodes and complex active material/electrolyte interfacial structure applied to LMR-NMC Electrodes.
    - Proven useful for examining LMR-NMC electrodes. Specifically addresses surface layer impedance, but treats bulk material as a solid solution.
    - Mostly a parameter fitting exercise using existing model applied to LMR-NMC electrode results obtained from micro-reference electrode cell.
- Developed simple analytical framework for simulating voltage fade in LMR-NMC electrodes.
    - Model projections qualitatively agree with experiment
- Developed electrochemical model of bulk LMR-NMC materials and electrodes.
    - Extends earlier work on volume-averaged, multi-phase, and phase-change active material electrodes.
    - Captures much of observed LMR-NMC voltage hysteresis behavior.
- Initiated development of electrochemistry model for LMR-NMC materials (i.e. unit cell kinetic mean field model) that specifically accounts for the movement of ions within the crystal lattice.

View of Activated LMR-NMC Material

- The activated LMR-NMC cathode material is made of nanometer scale $LiMO_2$ and Li_2MnO_3 domains that are highly integrated, but have unique electrochemical properties.

- The $LiMO_2$ domains (Domain 1) are considered to be relatively stable to changes in lithium concentration.

- The Li_2MnO_3 domains go through a slow reversible structural transition during cycling (Domains 2 and 3), as well as an irreversible structural change (VF Domain).

- The transition between Domains 2 and 3 generates the observed voltage hysteresis by the OCV curves for these domains being offset by a significant voltage.

- Further, the high voltage domain (3) is stable fully discharged, while the low voltage domain (2) is stable fully charged.

- LMR-NMC is also known to have a oxide surface layer that is different compositionally, structurally, and electrochemically from the bulk.

Discharged

ES194, Croy

Li/TM

Hysteresis

Li/TM Charged

Li/TM

Voltage Fade

Discharged

SEI

Surface Layer

$LiMO_2$

$LiMO_2$
Domain 1

Li_2MnO_3

Li_2MnO_3

$LiMO_2$

$LiMO_2$

Li_2MnO_3

- VF Domain
- Domain 2
- Domain 3

Description of Intercalation Electrochemical Model

- Phenomenological model developed for AC impedance and DC studies using same constituent equations and parameters

- Combines thermodynamic, kinetic, and interfacial effects with continuum based transport equations

- Complex active material / electrolyte interfacial structure

  - Film on active particles acts as an electrolyte layer with restricted diffusion and migration of lithium ions

  - Surface layer of active particle inhibits the diffusion of lithium into the bulk active material

  - Electrochemical reaction and double layer capacitance at film/layer interface

  - Particle contact resistance and film capacitance

- Volume averaged transport equations account for the composite electrode geometry

Transport through Cell Sandwich

$$\varepsilon \frac{\partial c}{\partial t} = \frac{\varepsilon}{\tau} \frac{\partial}{\partial x}\left(D \frac{\partial c}{\partial x}\right) + \frac{1}{z_+ \nu_+ F} \frac{\partial\left[\left(1 - c\bar{V}_e\right)\left(1 - t_+^o\right) i_2\right]}{\partial x}$$

$$i_2 = -\frac{\kappa\varepsilon}{\tau}\frac{\partial\Phi_2}{\partial x} - \nu RT \frac{\kappa\varepsilon}{F\tau}\left(\frac{s_+}{n\nu_+} + \frac{t_+^o}{z_+ \nu_+}\right)\left(1 + \frac{\partial \ln f_\pm}{\partial \ln c}\right)\frac{1}{c}\frac{\partial c}{\partial x}$$

$$\frac{\partial i_2}{\partial x} = F z_+ \sum_k a_k j_{kn} \qquad I = i_1 + i_2 \qquad i_1 = -\sigma_{eff}\frac{\partial\Phi_1}{\partial x}$$

Bulk Solid-State Diffusion

$$\frac{\partial c_{Sb}}{\partial t} = \frac{\partial}{\partial z}\left(D_{Sb}\frac{\partial c_{Sb}}{\partial z}\right)$$

Electrode SEI Reaction/Transport

$$\frac{\partial c_+}{\partial t} = D_+\left(\frac{\partial^2 c_+}{\partial y^2}\right) \qquad \eta_f = \frac{i_n \delta_f}{\kappa_f} + \frac{RT s_+}{nF}\ln\frac{c_+\big|_{electrolyte}}{c_+\big|_{active\ material}}$$

$$\frac{\partial c_{Si}}{\partial t} = D_{Si}\left(\frac{\partial^2 c_{Si}}{\partial y^2}\right)$$

$$i_n = i_0 \left(\frac{c_+}{c_{+,ref}}\right)^{\alpha_A}\left(\frac{c_{Ti} - c_{Si}}{c_{Ti} - c_{Si,ref}}\right)^{\alpha_A}\left(\frac{c_{Si}}{c_{Si,ref}}\right)^{\alpha_C}\left\{e^{\left[\frac{\alpha_A F \eta_K}{RT}\right]} - e^{\left[-\frac{\alpha_C F \eta_K}{RT}\right]}\right\}$$
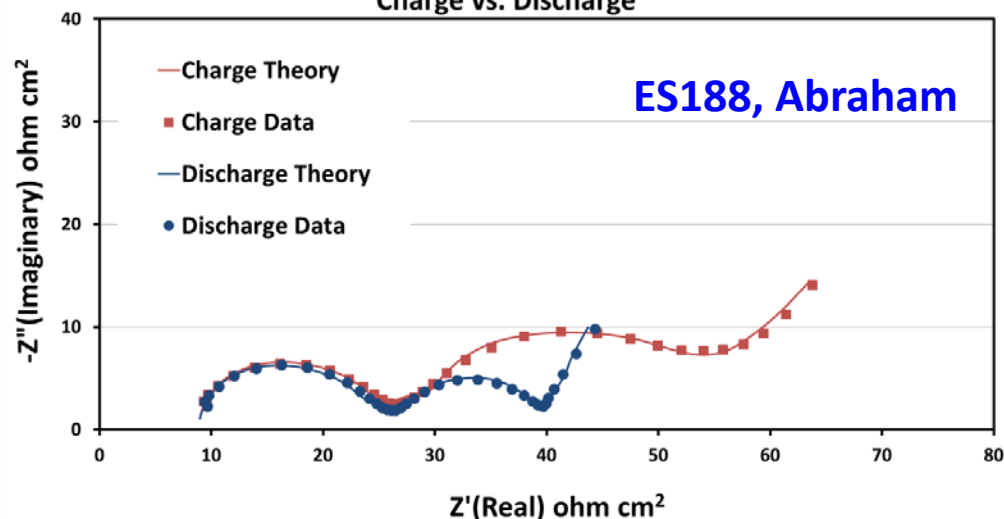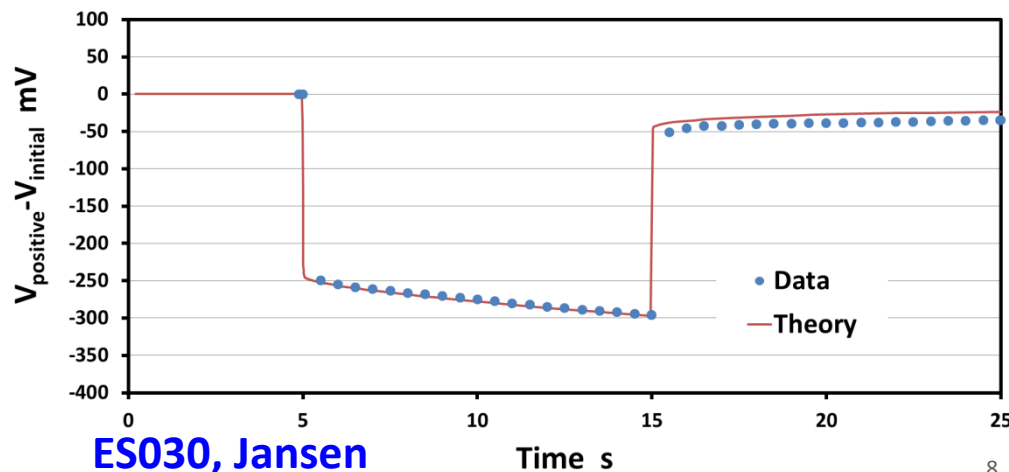
$$\eta_R = \sigma_P z_+ F j_n$$

Electrochemical Model can be Effectively Utilized to Study LMR-NMC Electrodes

- Adequate fits have been obtained for a wide variety of electrochemical studies (e.g. impedance, constant current discharge, and pulse power).

- AC impedance model analysis of reference electrode cell studies have been particularly useful for examining changes in transport and kinetic parameters with SOC, time, current direction, and age.

- Valuable for comparing LMR-NMC materials to other cathode materials.

- Voltage hysteresis requires separate open circuit voltage curves for charge and discharge that needs modification for voltage fade as the cell ages.

LMR-NMC Electrode Impedance (100kHz-10mHz) at 3.74 volts vs. Lithium Charge vs. Discharge

ES188, Abraham

- Charge Theory
- Charge Data
- Discharge Theory
- Discharge Data

Z'(Real) ohm cm^2

-Z''(Imaginary) ohm cm^2

LMR-NMC Electrode 10s 5C Discharge Pulse at 3.74 volts vs. Lithium

$V_{positive}-V_{initial}$ mV

Time s

- Data
- Theory

ES030, Jansen

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Recent Results from Intercalation Electrochemical Modeling Studies on LMR-NMC Electrodes

- Bulk (D_{sb}) and surface (D_{si}) lithium diffusion coefficients and kinetic exchange current density (i_o) fall off at low and high SOCs.

- D_{sb} decreases faster than D_{si} at low SOCs.

- Fall off with SOC faster than observed for other layered cathode materials.

- Steep fall off causes significant difference between charge and discharge ASIs in HPPC tests.

- Charge and discharge parameters correlate to electrode voltage better than lithium content.

- The long time constants associated with changes in the Li_2MnO_3 domain makes cycling history and wait times very important in determining parameters.
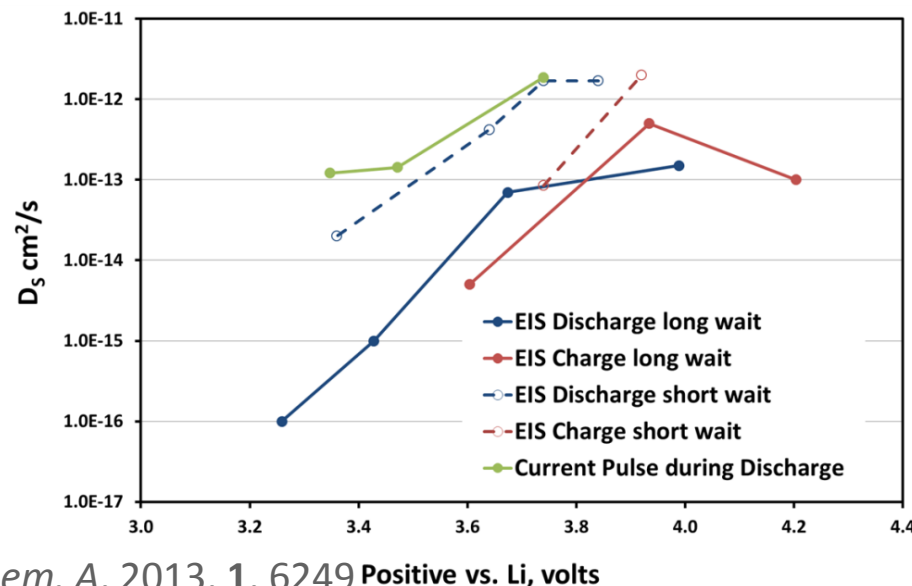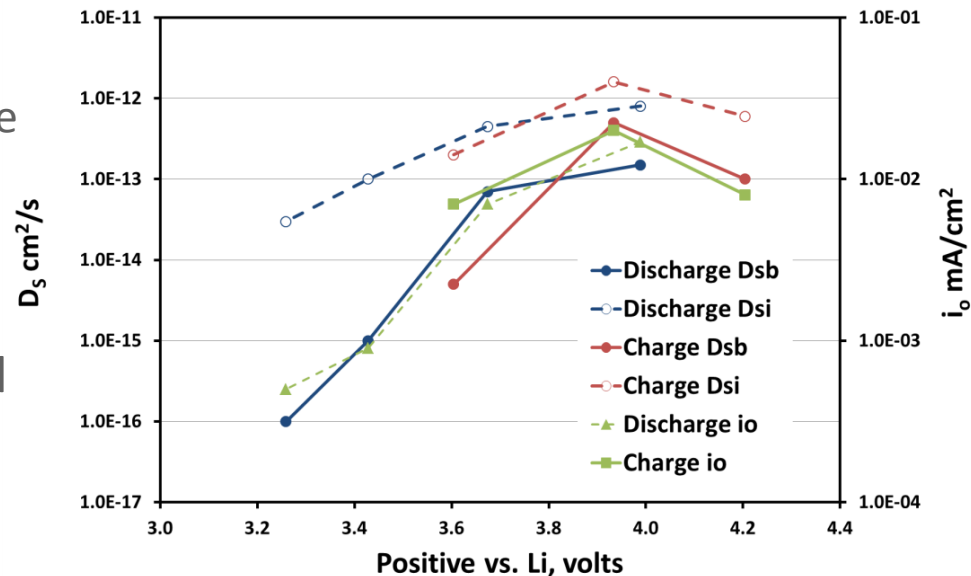
Also observed by Mohanty, *et.al., J. Mater. Chem. A*, 2013, **1**, 6249

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Simple Analytical Framework for Simulating Voltage Fade in LMR-NMC Electrodes

- Capture primary physics
  - Lithium concentration is driving force
  - Four regions in material: Q_{std}, Q_{hys}, Q_{vf}, Q_{unused}
  - Q_{vf} grows at expense of Q_{hys} (Croy et al JES 2014)
- Fit quasi-OCV curves analytically
  - Use thermodynamic-like functions
  - Q_{hys} changes from charge to discharge
  - Sum lithium contents at constant voltage
- Simple rate equations
  - Analytical solutions
  - On per cycle basis

$$-\frac{dQ}{d\tau} = kQ^n$$

- Consider two time constants
  - Voltage fade rate per cycle, k [=] cycle^{-1}
  - C-Rate used for cycling, $r_C := k$ [=] h^{-1}

Voltage function for each region: $U = U^o + \frac{RT}{\xi F}\left[ln\left(\frac{1-y}{y}\right) + \frac{\omega}{RT}y\right]$

$0.5Li_2MnO_3 \bullet LiNi_{0.5}Mn_{0.5}O_2$

Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$
5 mA/g, Li half cell
Data o
Model —

ES194, Croy

y in Li$_{1.2-y}$M$_{0.8}$O$_2$

Q_{vf} Q_{std} Q_{hys}

Q_{cycle}

Cell Voltage, V vs Li
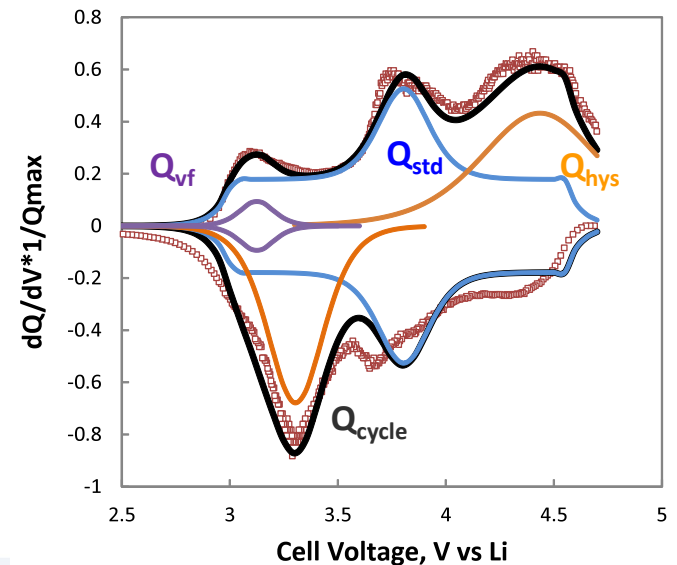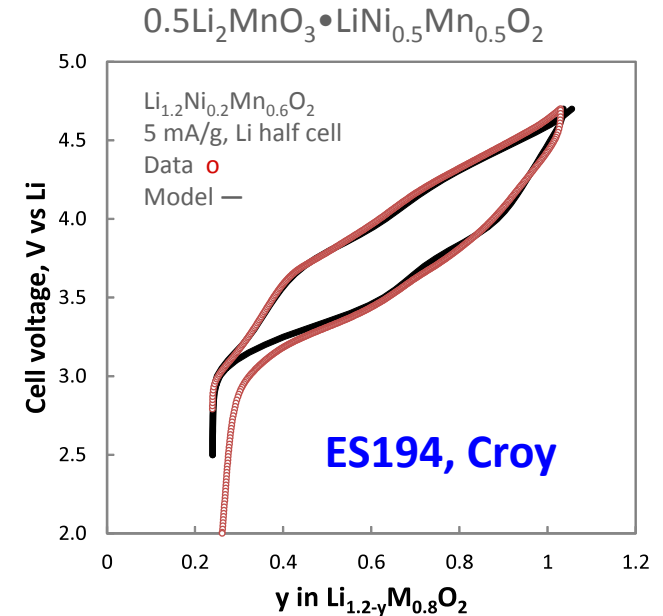
Kinetic model captures voltage fade

- Q_{vf} grows at the expense of Q_{hys}
- Voltage curves were deconvoluted per cycle
- Rate constant, k, fit to match change in Q_{vf}
- Best fit from 3rd order rate law **ES193, Iddir**
  - Tenuous connection to mechanism
  - Tri-vacancy required for TM migration

$$r_{vf} = \frac{dQ_{vf}}{dN} = -\frac{dQ_{hys}}{dN} = k(Q_{hys})^3$$
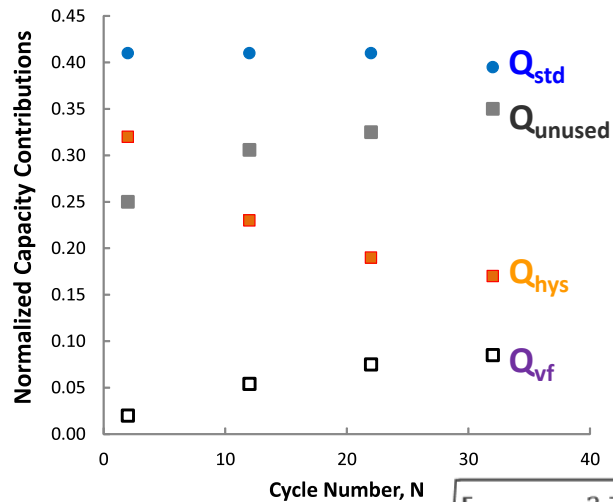
$$Q_{vf}(N) = Q_{o,vf} + Q_{hys} - \sqrt{\left[\frac{(Q_{hys})^2}{1 + 2kN}\right]}$$

$$U_{ave,c} = (Q_{std}U_{ave,std} + Q_{hys}U_{ave,hys,c} + Q_{vf}U_{ave,vf})/Q_{cycle}$$
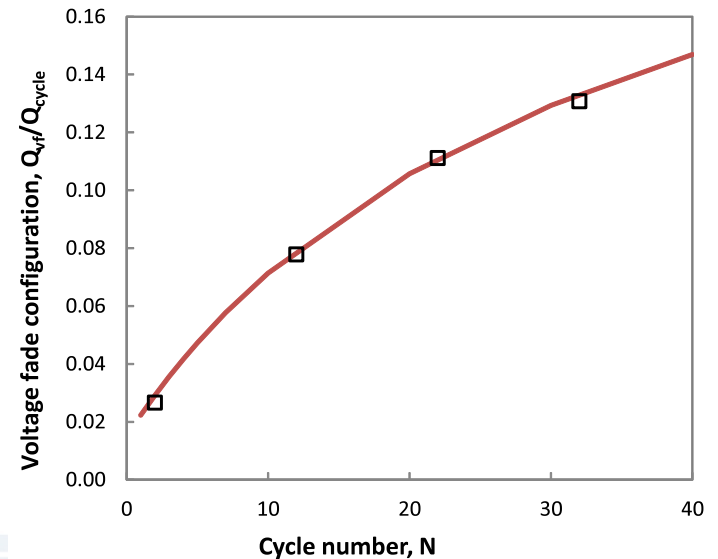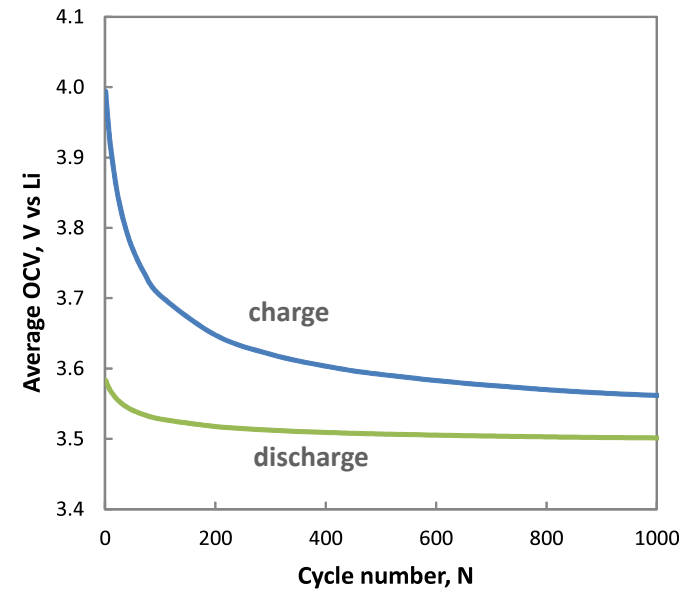
Faster rates & lower U_{max} limits Q_{hys} contribution

- Faster C-rate, r_C, for cycling limits capacity contribution from each region
  - Hysteresis $1/r_C^* \sim 7$ hrs
  - Standard $1/r_C^* \sim 1$ hrs
  - VF config $1/r_C^* \sim 1$ hrs

$$\gamma = \frac{Q_{hys,rC}}{Q_{o,hys}} = exp\left[-\frac{r_C}{r_C *}\right]$$

- Capacity accessed for cycle N, $Q_{hys,N}$, is also determined by the upper cut-off voltage, U_{max}

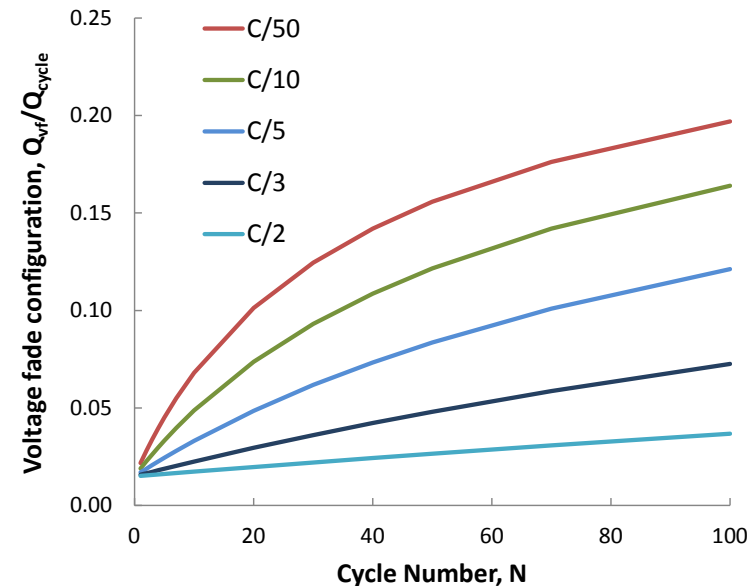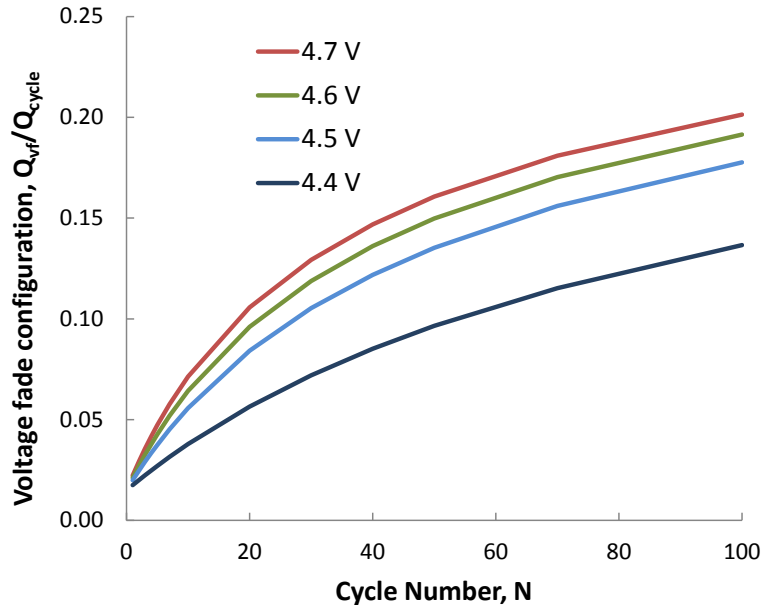$$\frac{1}{y_{min}} = \left[1 + exp\left(\frac{\xi F}{RT}(U_{max} - U^o)\right)\right]$$

- The less Q_{hys} accessed, the lower the rate of voltage fade

$$Q_{hys} = Q_{hys,o}\gamma(1 - y_{min})$$

ES188, Abraham

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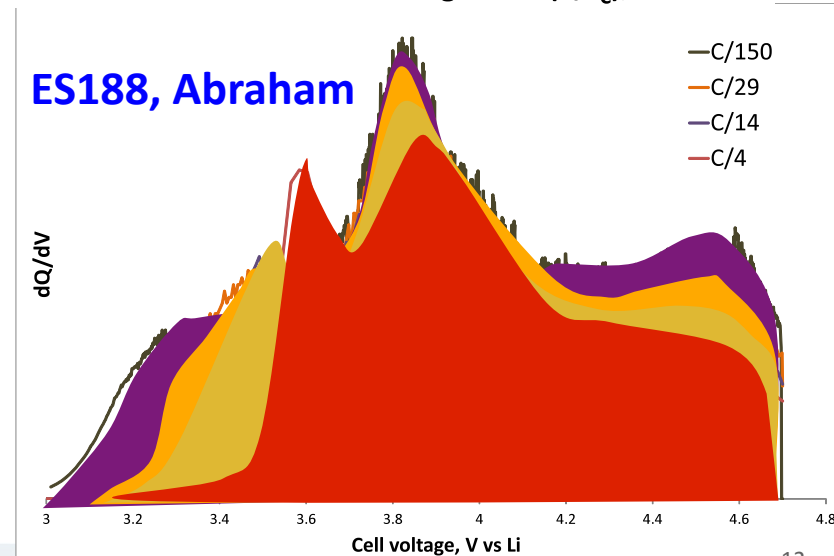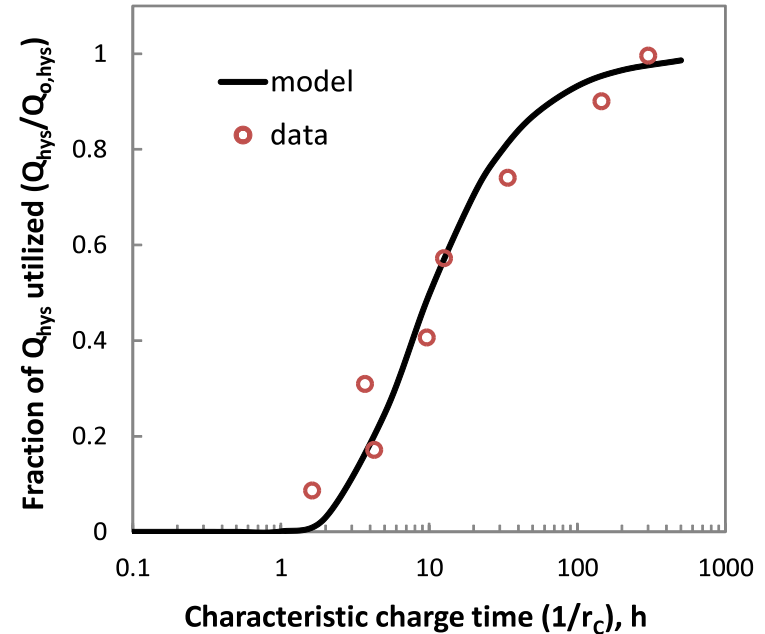
Model projections qualitatively agree with data

- Lower cut-off voltage, less voltage fade
- Faster cycling, less voltage fade

Bettge et al JES 2013

Long et al Unpublished 2014

ES188, Abraham
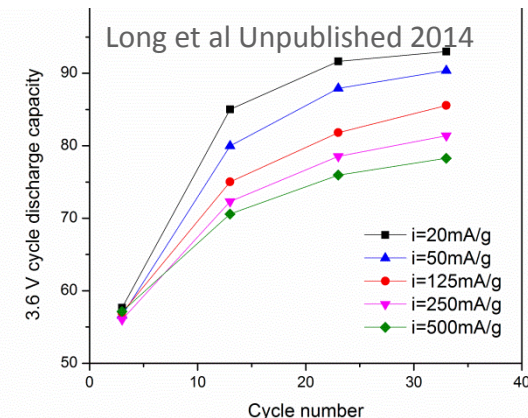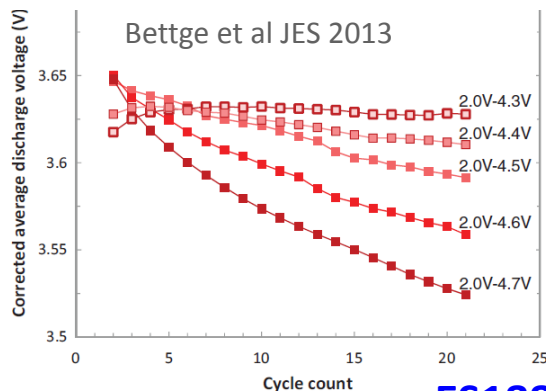
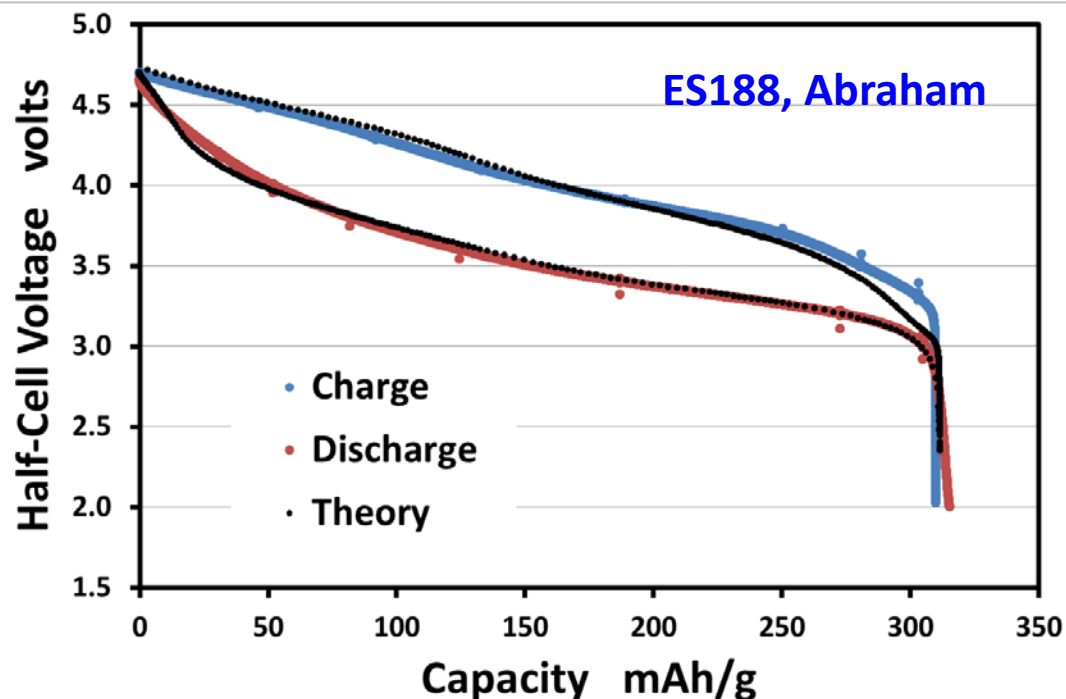# Electrochemical Model Describing the Bulk Lithium Transport and Structural Transitions in LMR-NMC

- Initial work has focused on the voltage hysteresis and to account for known phenomena occurring in and between the LiMO$_2$ domains (Domain 1) and the Li$_2$MnO$_3$ domains (Domains 2 and 3).

- A particle model was developed for LMR-NMC materials that includes lithium diffusion, domain transitions, and non-equilibrium lithium transport between domains.

  - Volume averaged expressions used to describe composite material
  - Avrami equation derived structural change relation
  - Lithium electrochemical potential driven mass transfer between domains

- A half-cell electrochemical model for intercalation electrodes was modified for LMR-NMC electrodes that includes the bulk phenomena for the active material.

- A fourth domain will be added to the model to account for voltage fade.

Bulk Transport and Structural Transitions

$$\frac{\partial \varepsilon_{S1} c_{S1}}{\partial t} = \nabla \cdot \left(\frac{\varepsilon_{S1} D_{S1}}{\tau_{S1}} \nabla c_{S1} \right) + a_{S21} N_{21} + a_{S31} N_{31}$$

$$\frac{\partial \varepsilon_{S2} c_{S2}}{\partial t} = \nabla \cdot \left(\frac{\varepsilon_{S2} D_{S2}}{\tau_{S2}} \nabla c_{S2} \right) - a_{S21} N_{21} + a_{S32} N_{32} - c_{S2} R_{23} + c_{S3} R_{32}$$

$$\frac{\partial \varepsilon_{S3} c_{S3}}{\partial t} = \nabla \cdot \left(\frac{\varepsilon_{S3} D_{S3}}{\tau_{S3}} \nabla c_{S3} \right) - a_{S31} N_{31} + a_{S23} N_{23} - c_{S3} R_{32} + c_{S2} R_{23}$$

$$\frac{\partial \varepsilon_{S2}}{\partial t} = R_{32} - R_{23} \qquad R_{ij} = k_{Sij} \Delta c_i^* \varepsilon_{Si} H \left(\Delta c_i^* \right)$$

$$N_{ij} = k_{\mu ij} \left[\mu_{Li}(i) - \mu_{Li}(j) \right] = k_{\mu ij} F \left[U_j - U_i \right] \qquad k_{\mu ij} = \frac{k_{Di} D_{Si} k_{Dj} D_{Sj}}{\left(k_{Di} D_{Si} + k_{Dj} D_{Sj} \right)}$$

LMR-NMC Particle Electrochemical Model Simulations
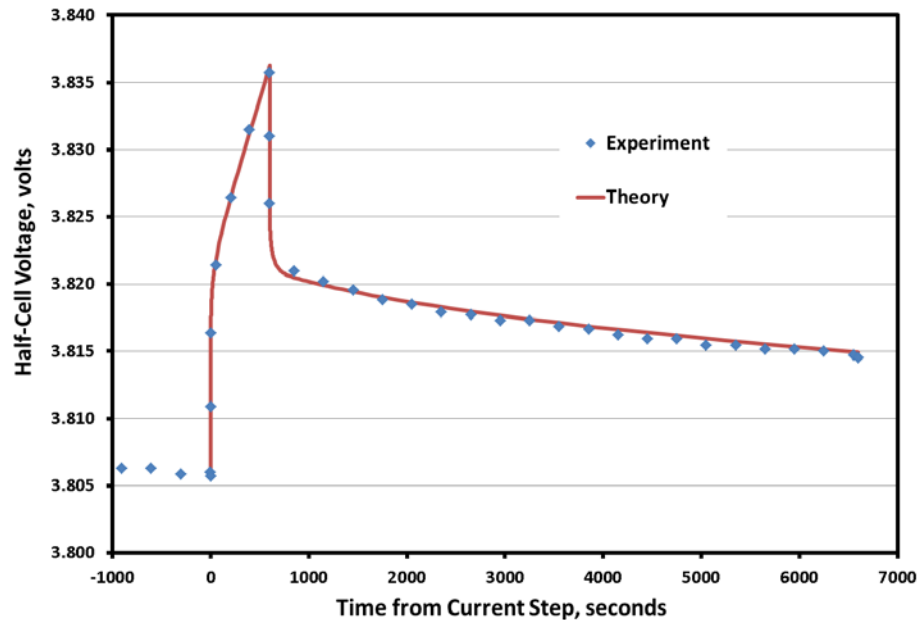
HE5050 LMR-NMC Half-Cell C/290 Cycling

- Particle model used to examine very slow cycling data in order to establish thermodynamics of LMR-NMC material and initial estimations of other transport and transition parameters.

- At these slow cycling rates there is a significant swing between domains 2 and 3.

- Increasing cycling rate reduces the transition between domains 2 and 3 in Li_2MnO_3 regions.

  - At C/1 there is little or no change in the volume fractions during cycling.
  - This is the reason why the intercalation model is valid to describe normal cycling.
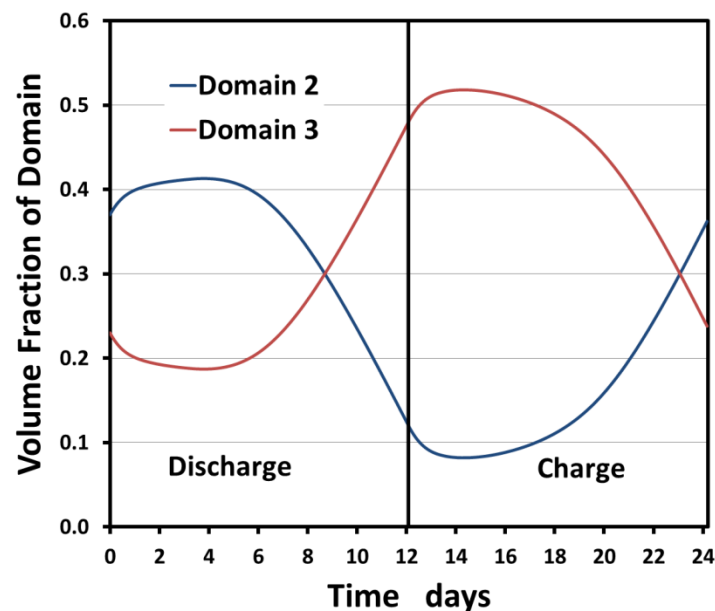
Half-Cell Electrochemical Model Parameter Refinement using LMR-NMC Galvanostatic Intermittent Titration Technique (GITT) Studies

- GITT voltage curves change dramatically with SOC.

- At long relaxation times the concentration gradients are relaxed and the slope of the curves is controlled by the domain transition rate and their OCV curves.

LMR-NMC GITT Experiment 10 min C/18 Charge Pulse and 100 min Rest

ES188, Abraham

- Particle model integrated into half-cell DC electrochemical model.

- Separating transport characteristics within and between individual phases from GITT data is a challenge.

- Generation of a complete parameter set is an iterative process.
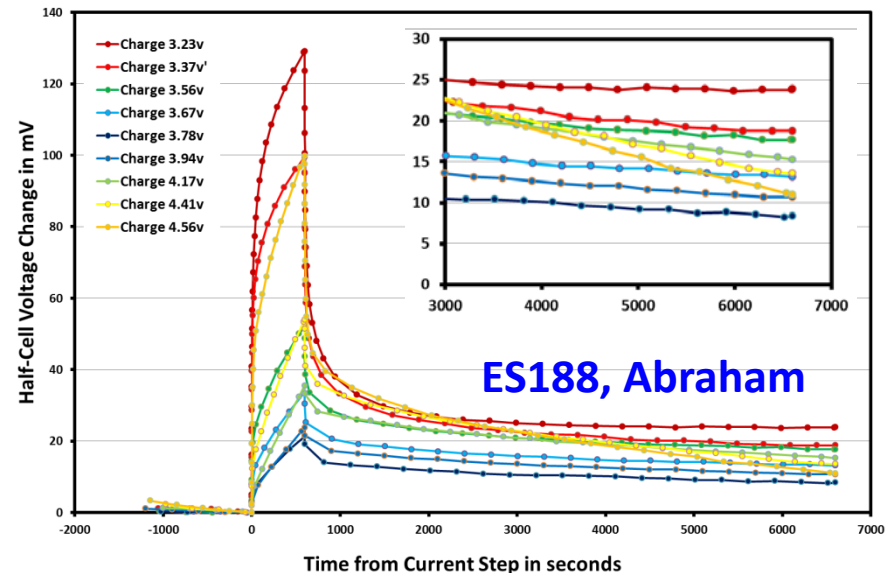
Electrochemical Model Captures Much of Observed LMR-NMC Voltage Hysteresis Behavior

- A portion of the voltage hysteresis is rate independent, which is built into the model by creating a voltage range where both unstable domains coexist (2 & 3). Model simulations exhibit significant voltage hysteresis even at a C/5000 rate.

- Time constant for previous cycling history impacting performance is extremely long.

- Hysteresis is lessened if LMR-NMC material is cycled in narrower voltage ranges from the top and bottom of charge.

- Early in the charge half-cycle if the cell is allowed to relax for long times the voltage will first drop and then rise as the domain transition (i.e. Domain 2 to Domain 3) starts to control the process.

LMR-NMC Simulations Conducted at a C/18 Rate.

ES194, Croy

Bettge, et.al., Unpublished, 2014
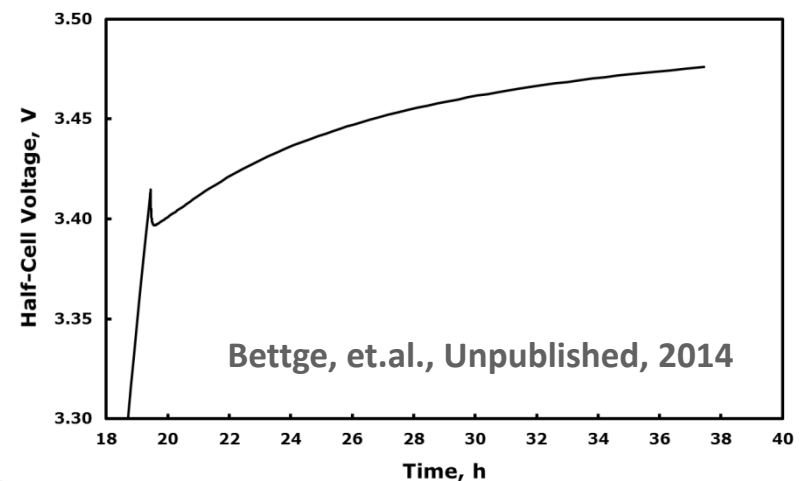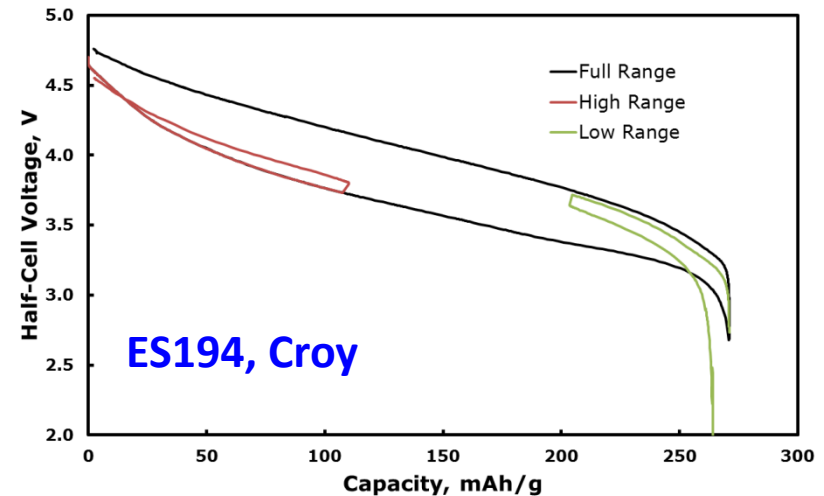
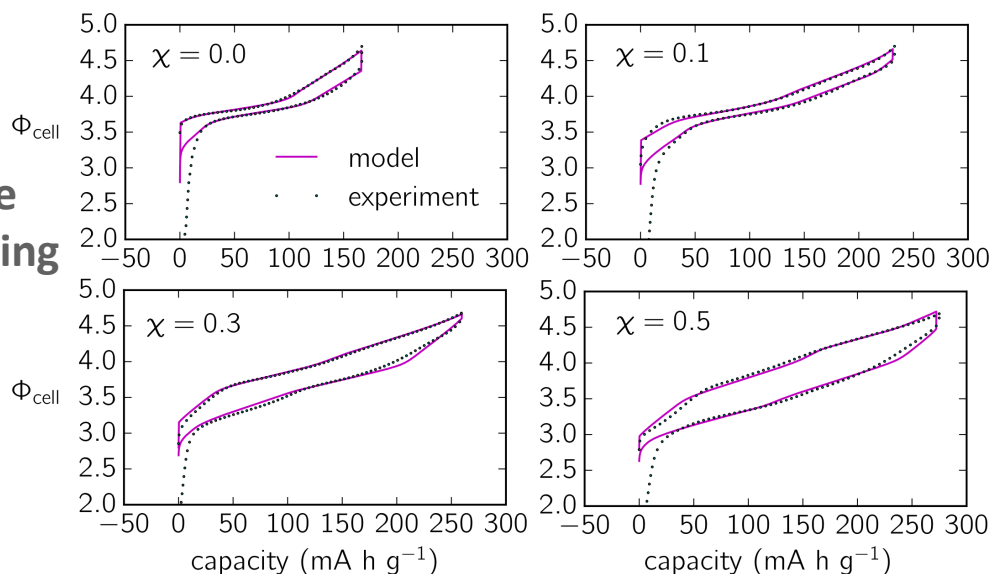# Electrochemistry Kinetic Model: Unit-Cell Approach for $\chi Li_2MnO_3 \cdot (1- \chi)LiMO_2$

- Model for LMR-NMC material that specifically accounts for the movement of ions within the crystal lattice.

- Initial work to develop model formalism has produced a unit cell kinetic mean field model (i.e. early steps to a lattice gas model).

- First comparison to experiments looks promising, however parameter rationalization requires attention.
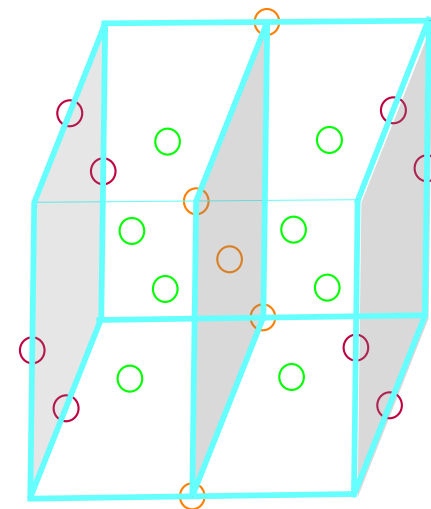
LMR-NMC Electrode Half-Cells Slow Cycling Compositional Dependence

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Φ_{cell}

$\chi = 0.0$

— model
⋯ experiment

$\chi = 0.1$

Φ_{cell}

$\chi = 0.3$

$\chi = 0.5$

capacity (mA h g^{-1})

capacity (mA h g^{-1})

○ site A

○ site B

○ site C

Remaining Challenges and Barriers

- The complexity of the electrochemical model for bulk LMR-NMC materials and electrodes makes parameter estimation for the individual domains a significant challenge, even with the relatively large data set and assumed simplifications.

- Parameter estimation for the bulk LMR-NMC electrochemical model will be further complicated by adding the voltage fade domain equations to the model.

- The electrochemistry model for LMR-NMC materials (i.e. unit cell kinetic mean field model) is in its early stages of development, determining a consistent set of parameters and establishing the correct level of complexity may present a challenge.

- As the integration of the individual models into a comprehensive full cell model moves forward, the added complexity of the multi-scale multi-time constant model may present a challenge numerically to solve.

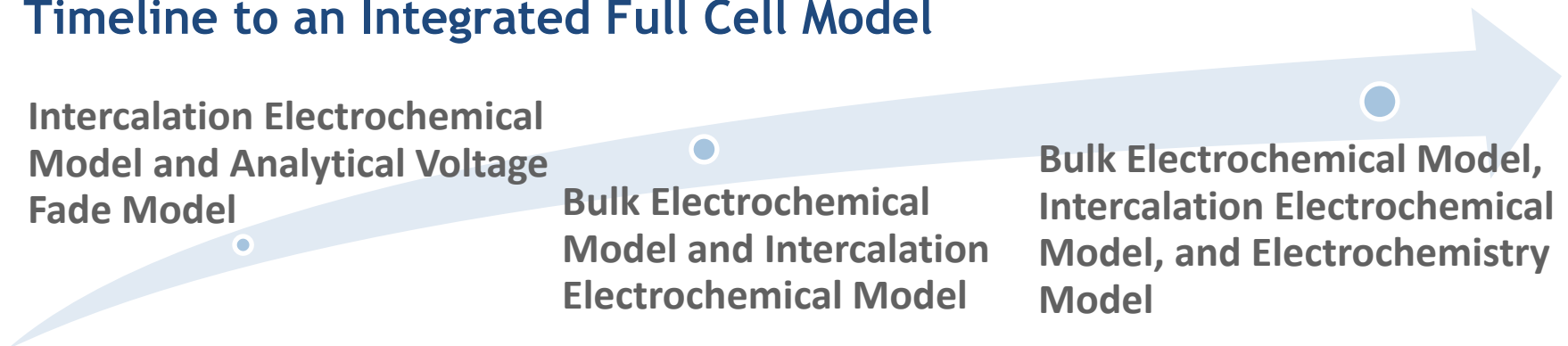# Responses to Previous Year Reviewers' Comments

- This effort is part of the Voltage Fade project and the CAMP Facility project. A separate presentation on this work was not given last year and no specific comments were found concerning this effort.

Future Plans

- Further examine LMR-NMC electrode testing and characterization results with electrochemical cell model with complex SEI structure.

- Improve fit of voltage cut-off and rate dependencies with simple analytical framework for simulating voltage fade.

- Continue parameter estimation for the electrochemical model of bulk LMR-NMC materials and electrodes. Add the voltage fade domain to the model.

- Continue parameter estimation and rationalization for electrochemistry model (i.e. unit cell kinetic mean field model) and revisit level of model complexity as needed.

- As the models mature, move forward with integration plan according to timeline.

- "Wrap up" Voltage Fade effort by end of FY2014. Contribute to final report and other publications.

Timeline to an Integrated Full Cell Model

Intercalation Electrochemical Model and Analytical Voltage Fade Model

Bulk Electrochemical Model and Intercalation Electrochemical Model

Bulk Electrochemical Model, Intercalation Electrochemical Model, and Electrochemistry Model

Summary

- This electrochemical modeling effort supports the Voltage Fade Team and the CAMP Facility Team through the development and utilization of efficient simulation, analysis, and design tools for LMR-NMC materials and electrodes in advanced lithium ion battery technologies.

- An existing electrochemical cell model for intercalation active material electrodes with complex SEI structure has proven useful for examining LMR-NMC electrodes. The model specifically addresses surface layer impedance, but treats bulk material as a solid solution.

- Developed a simple analytical framework for simulating voltage fade in LMR-NMC electrodes that qualitatively agrees with experiment.

- Developed an electrochemical model of bulk LMR-NMC materials and electrodes, which extends earlier work and captures much of the observed LMR-NMC voltage hysteresis behavior.

- Initiated development of electrochemistry model (i.e. unit cell kinetic mean field model).

- Future studies include extending and improving current modeling efforts, as well as model integration.

Acknowledgements and Collaborations

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CAMP Facility Operations and Collaborations ES030, Jansen
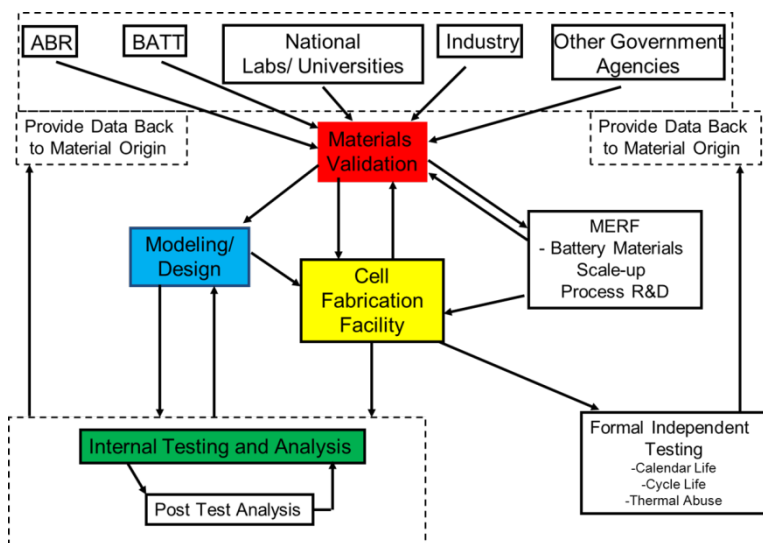
The Team ES161, Burrell
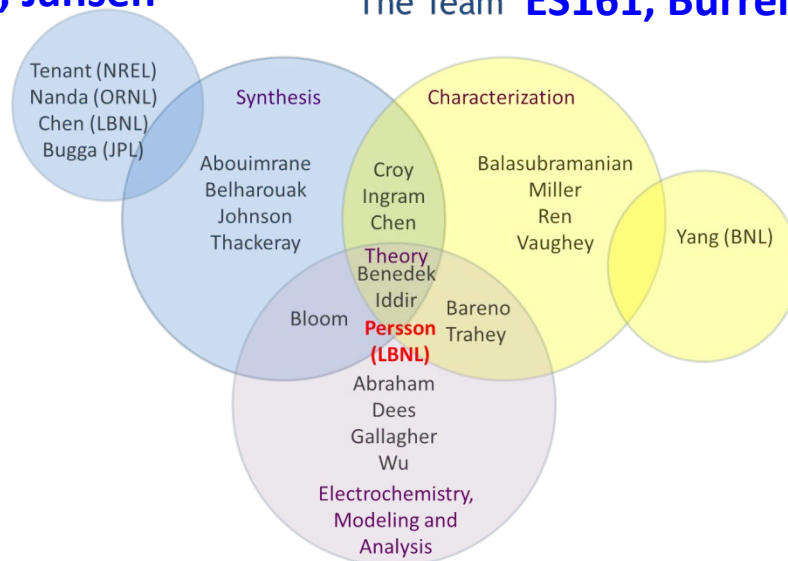
- Support for this work from DOE-EERE, Office of Vehicle Technologies is gratefully acknowledged
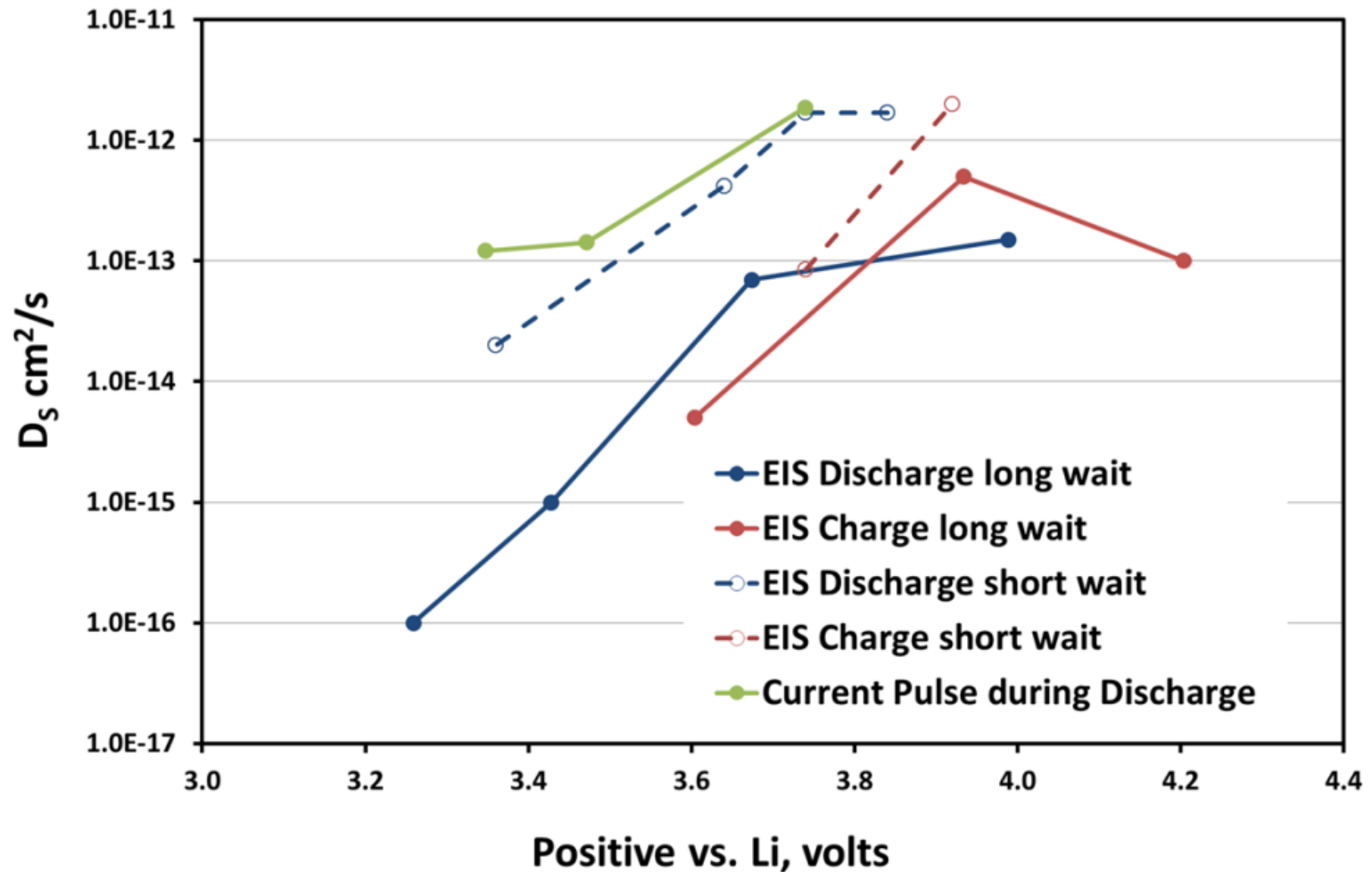 - David Howell, Peter Faguy & Tien Duong

Technical Back-Up Slides

Bulk (D_{sb}) and surface (D_{si}) lithium diffusion coefficients and kinetic exchange current density (i_o) obtained from EIS long wait studies.
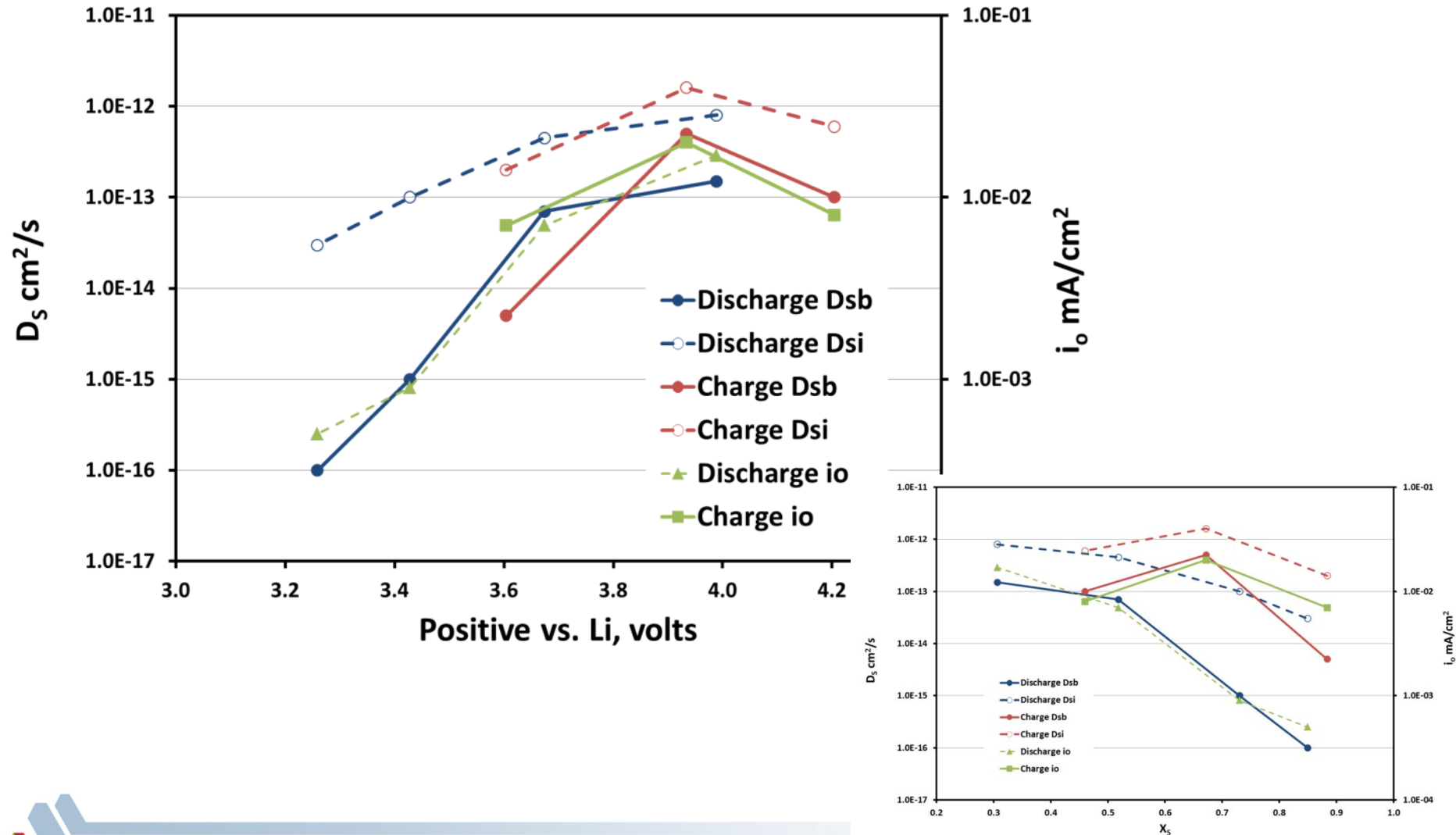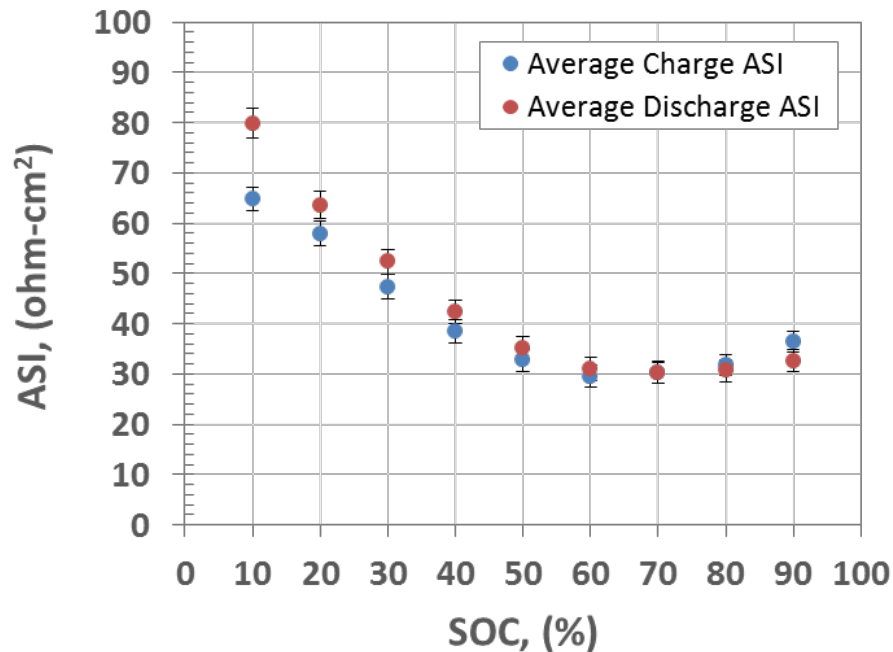
The long time constants associated with changes in the Li_2MnO_3 domain makes cycling history and wait times very important in determining parameters.
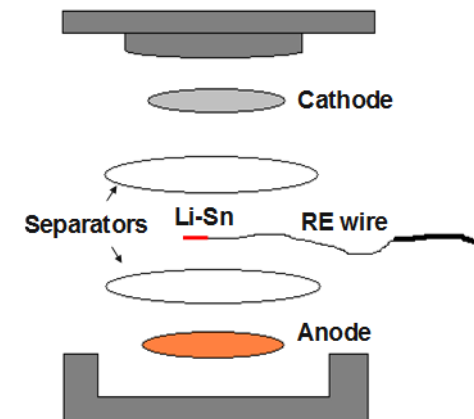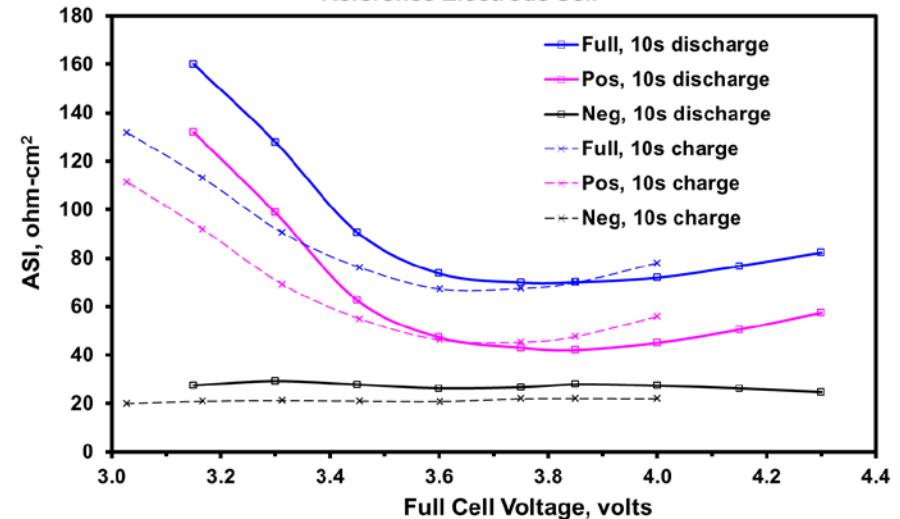
D_{sb} and D_{si} fall off at low and high SOCs, which cause significant difference between charge and discharge ASIs in HPPC tests.
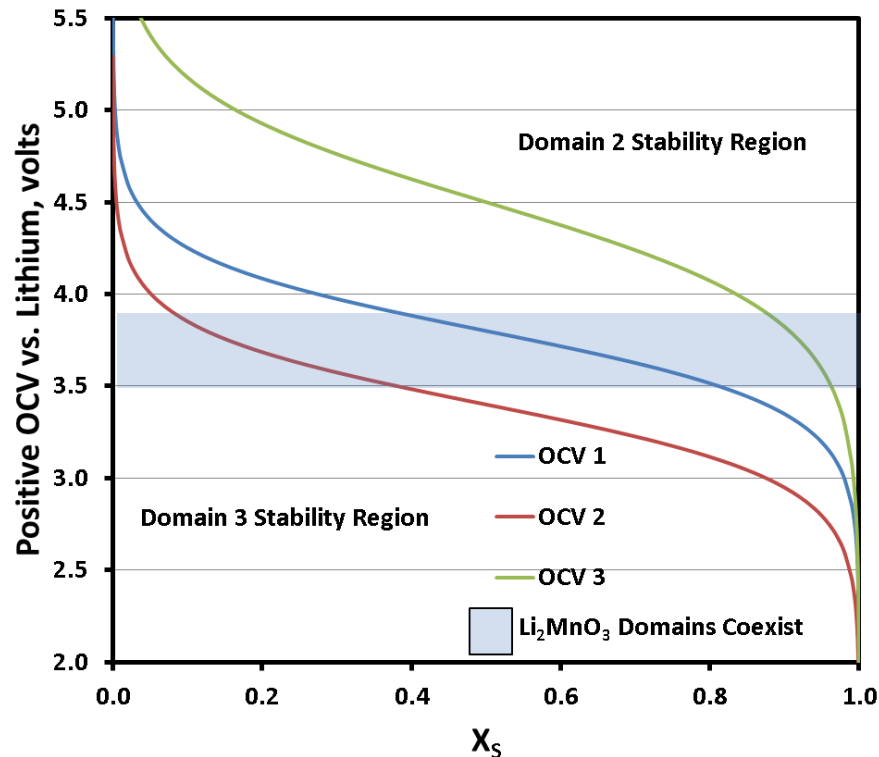

Average Charge and Discharge ASI for Full Pulse

10s Current Pulse ASI for LMR-NMC/Graphite Reference Electrode Cell

Key to an Accurate Model Simulation is the Open Circuit Voltage Curve for each Domain and the Stability Ranges for the Li_2MnO_3 Domains


- To create a voltage hysteresis it is important that the OCV curves for the unstable domains (domains 2 and 3) are offset by a significant voltage and that the high voltage domain is stable fully discharged, while the low voltage domain is stable fully charged.

- Simple thermodynamic expressions are assumed for all domains.

$$U_i = U_i^0 + \frac{RT}{\xi_i F} \ln\left(\frac{1 - x_{Si}}{x_{Si}}\right)$$

- Experimental observations indicate that a piece of the LMR-NMC voltage hysteresis is rate independent.

- Building a rate independent hysteresis component into the model requires the two Li_2MnO_3 domains to have a voltage range where both domains coexist.

Experimental observations indicate that a piece of the LMR-NMC voltage hysteresis is rate independent.

HE50505 LMR-NMC Electrode Half-Cell Cycling
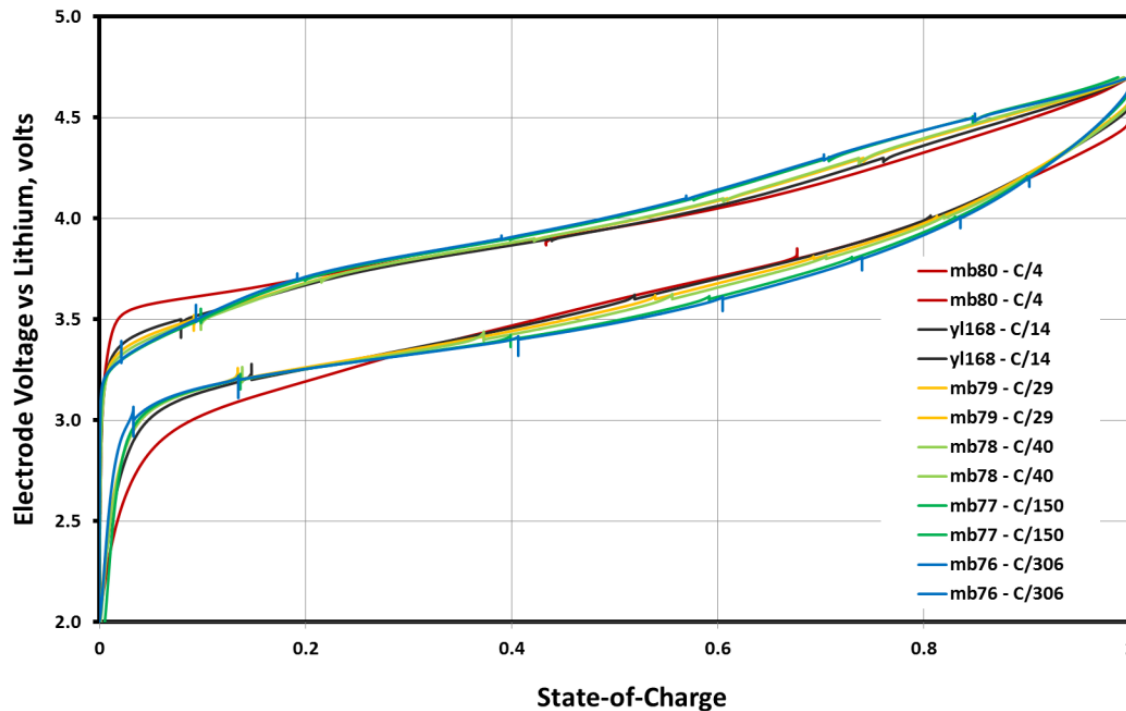
HE5050 LMR-NMC Electrode Half-Cell
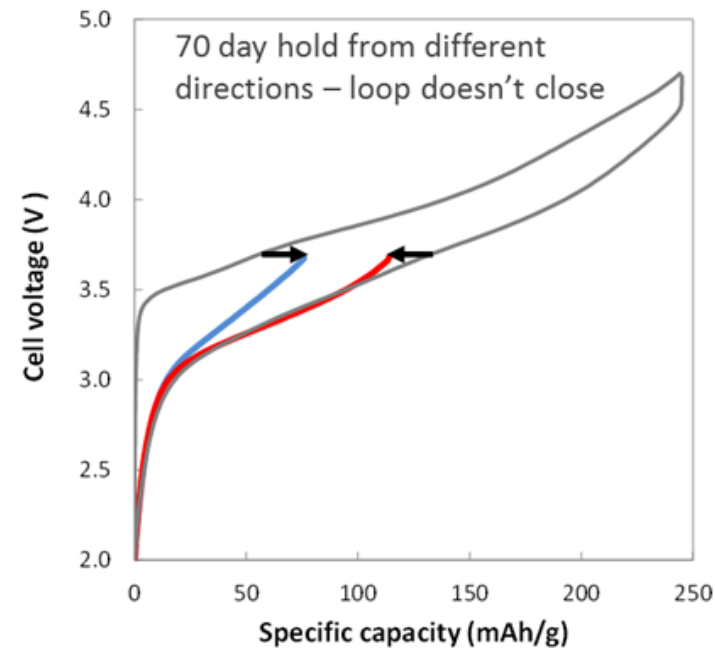
- Both slow cycling data and voltage hold experiment indicate that the voltage hysteresis will exist at all cycling rates.