# Phase Relations and Voltage Fade Response in LMR-NMC Materials

**Project Id: ES195**

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***In Collaboration with the Voltage Fade Team***

DOE Vehicle Technologies Program Annual Merit Review
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# Overview

**Timeline**

- Start: October 1, 2012
- End: Sept. 30, 2014
- Percent complete: 50%

**Budget**

- FY13: part of $4M

**Barriers**

- Calendar/cycle life of lithium-ion cells

**Partners**

- Voltage Fade Team at Argonne

# Project Objectives - Relevance

Voltage fade in lithium-, manganese-rich (LMR-NMC) oxides reduces energy density of lithium-ion cells on calendar–life and cycle–life aging

- Mitigating voltage fade will enable the use of these high–energy composite materials {$xLi_2MnO_3$ •$(1-x)LiMO_2$ (M=Ni, Mn, Co)} for PHEV and EV applications

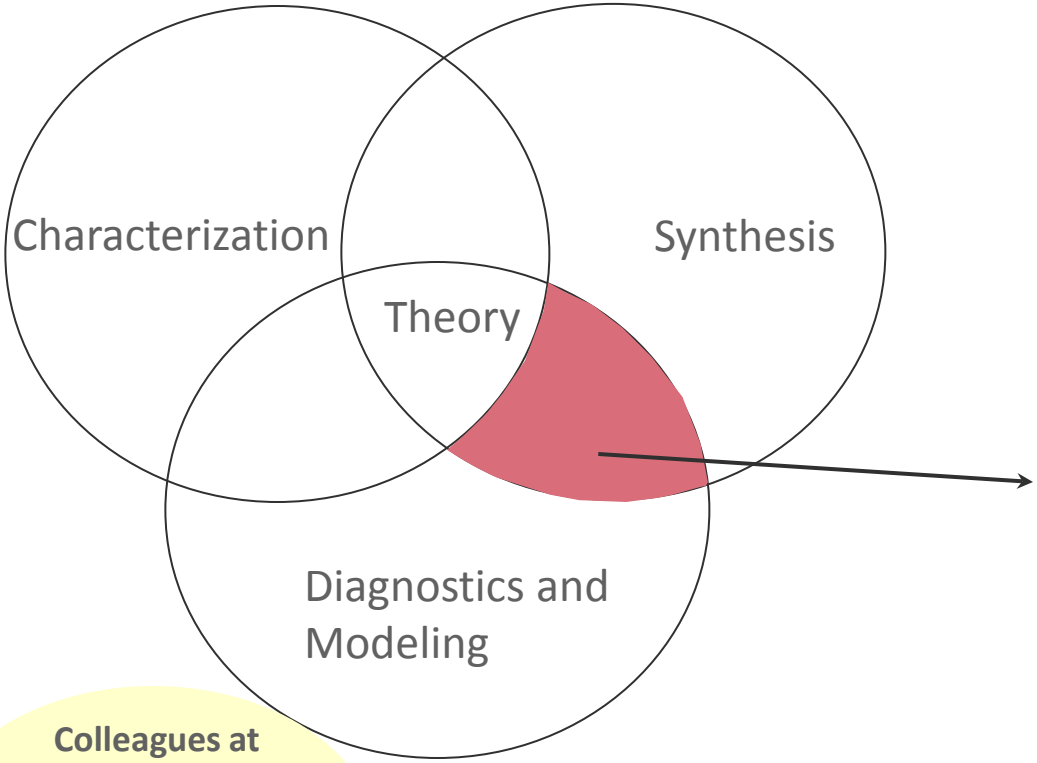
## Milestones

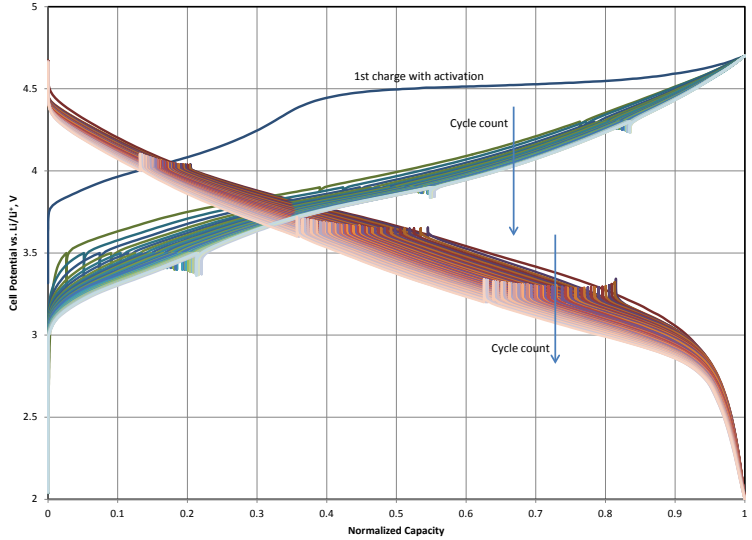
- Establish database to organize information from many partners January 2013
- Determine effect of composition and phase distribution on voltage fade. Use data to select an LMR-NMC oxide with minimal voltage fade September 2013

# Approach

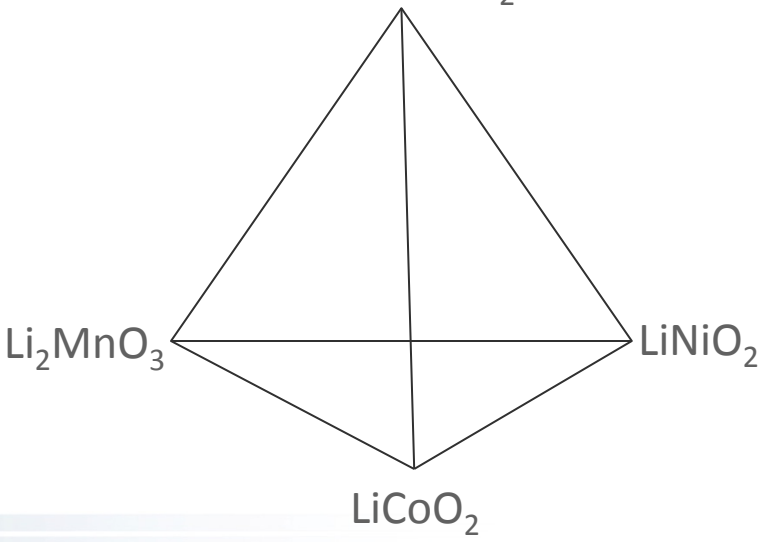
- **Use combinatorial synthetic methods to identify factors that contribute to voltage fade as part of a team effort**

A collaboration between



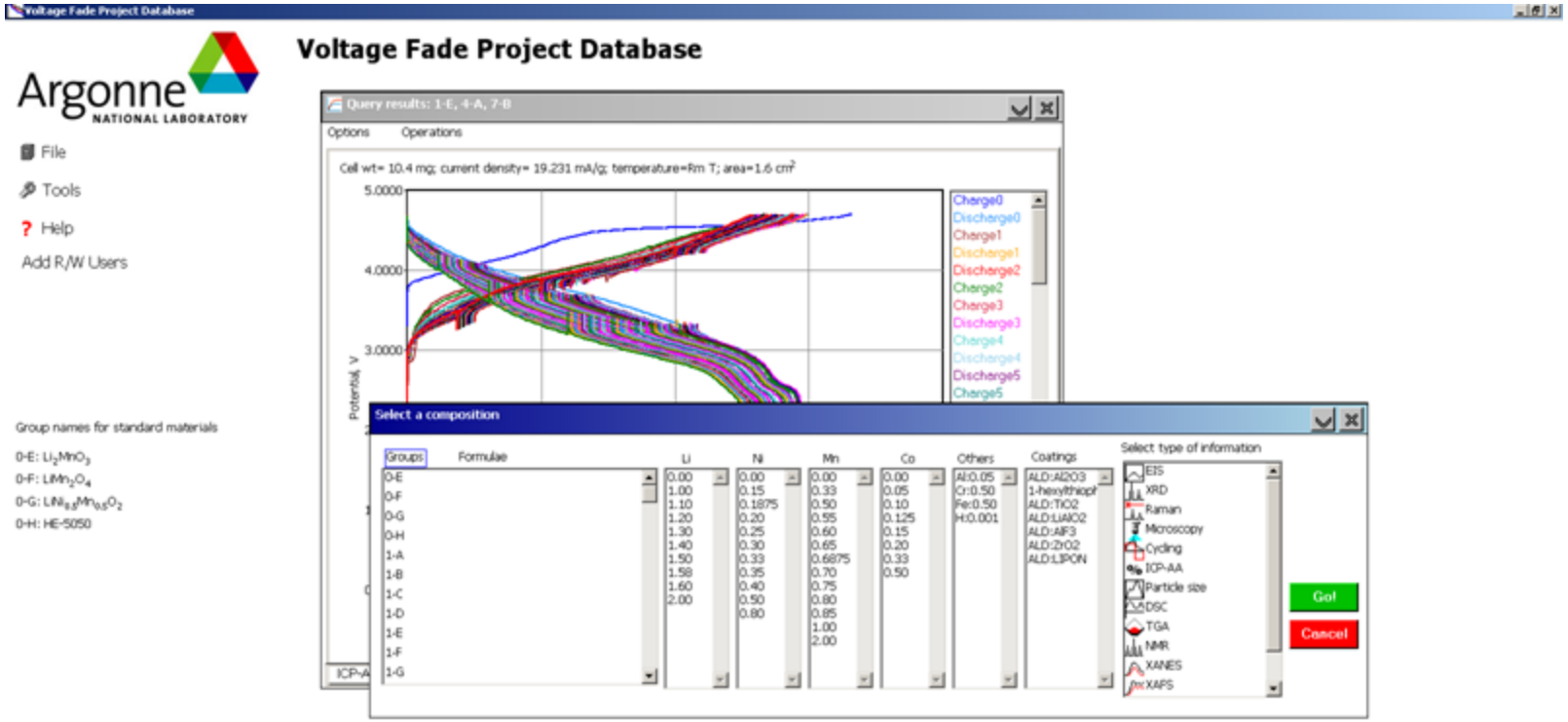

vs. ‘$LiMnO_2$’




**Colleagues at Oak Ridge, Pacific Northwest National, and National Renewable Energy Laboratories**

# Technical Accomplishments and Progress

- Established a user-friendly database for the collection and organization of information generated by team members (met milestone)
- Database is Windows-based and open for use



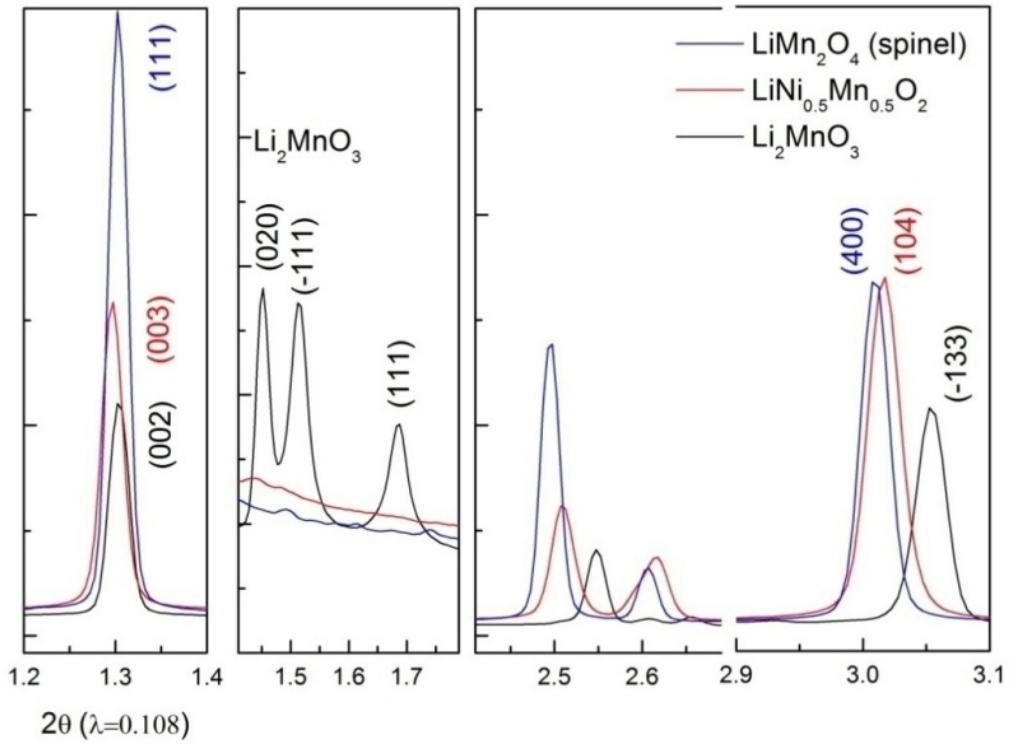
# Combinatorial Synthesis - Progress Characterization

| Group | Li | Ni | Co | Mn | Group | Li | Ni | Co | Mn |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1~1.6 | 0.15 | 0 | 0.85 | 12 | 1~1.6 | 0.25 | 0.2 | 0.55 |
| 2 | 1~1.6 | 0.15 | 0.05 | 0.85 | 13 | 1~1.6 | 0.3 | 0 | 0.7 |
| 3 | 1~1.6 | 0.15 | 0.1 | 0.75 | 14 | 1~1.6 | 0.3 | 0.05 | 0.65 |
| 4 | 1~1.6 | 0.2 | 0 | 0.8 | 15 | 1~1.6 | 0.3 | 0.1 | 0.6 |
| 5 | 1~1.6 | 0.2 | 0.05 | 0.75 | 16 | 1~1.6 | 0.3 | 0.15 | 0.55 |
| 6 | 1~1.6 | 0.2 | 0.1 | 0.7 | 17 | 1~1.6 | 0.35 | 0 | 0.65 |
| 7 | 1~1.6 | 0.2 | 0.15 | 0.65 | 18 | 1~1.6 | 0.35 | 0.05 | 0.6 |
| 8 | 1~1.6 | 0.25 | 0 | 0.75 | 19 | 1~1.6 | 0.35 | 0.1 | 0.55 |
| 9 | 1~1.6 | 0.25 | 0.05 | 0.7 | 20 | 1~1.6 | 0.4 | 0 | 0.6 |
| 10 | 1~1.6 | 0.25 | 0.1 | 0.65 | 21 | 1~1.6 | 0.4 | 0.05 | 0.55 |
| 11 | 1~1.6 | 0.25 | 0.15 | 0.6 | | | | | |

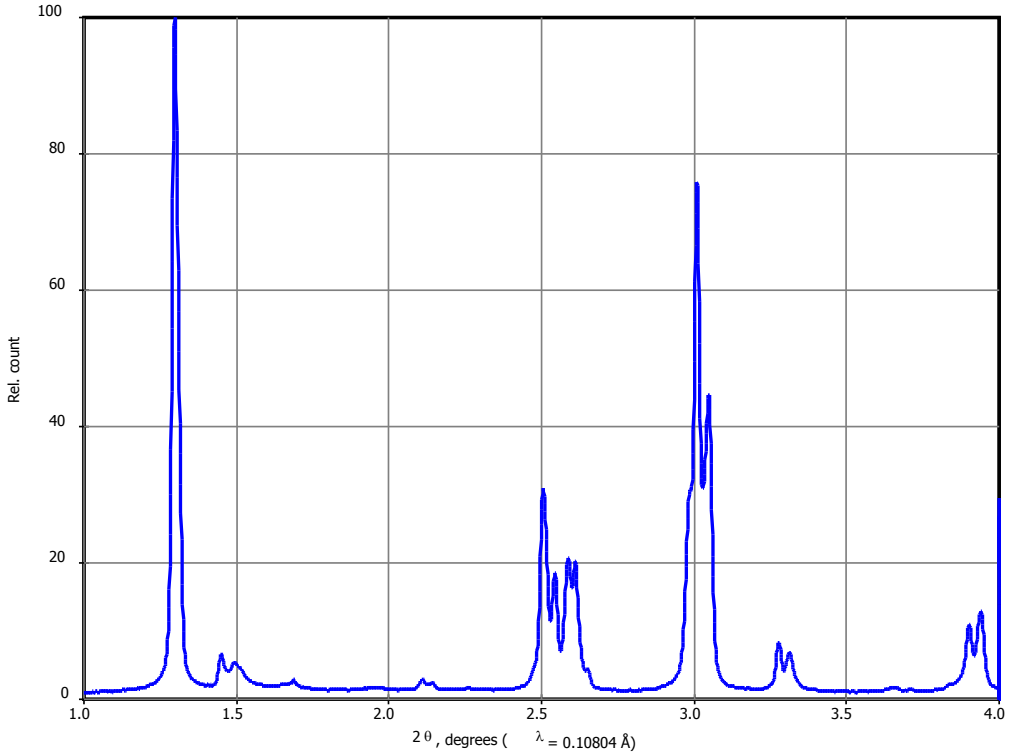
- 147 compositions were prepared by sol-gel methods, spanning the low-Co portion of the $Li_2MnO_3$-$LiCoO_2$-$LiNiO_2$-$LiMnO_2$ phase diagram
- In each group, the Li stoichiometry varied from 1 to 1.6 in steps of 0.1, labeled A, B,…, and G, respectively
- Each composition was characterized by XRD, elemental analysis, microscopy
- Electrochemical performance of selected compositions was studied in half-cells using a standard test protocol at room temperature

# X-ray Diffraction Patterns of Oxides Are Very Similar

- XRD patterns for $LiMO_2$ (R-3m), $Li_2MnO_3$ (C2/m), and spinel (Fd3m) phases are very similar to each other, but can be distinguished by using synchrotron X-rays with their higher spatial resolution

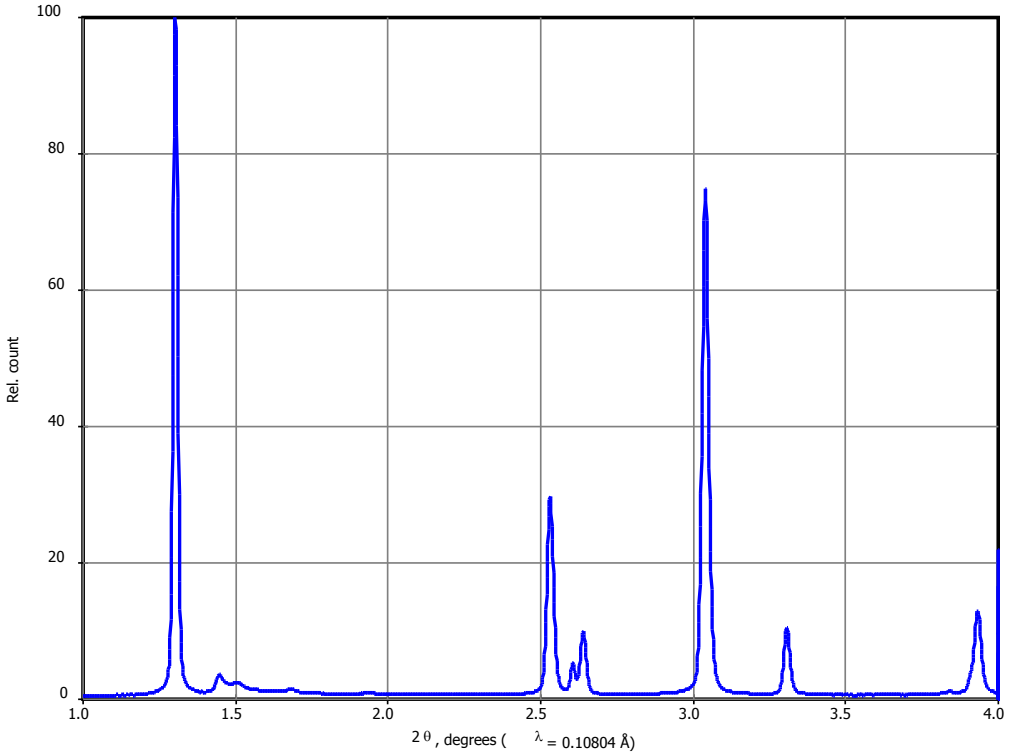


# XRD Results Indicate That the Phase Relationships Can Be Complex. 1



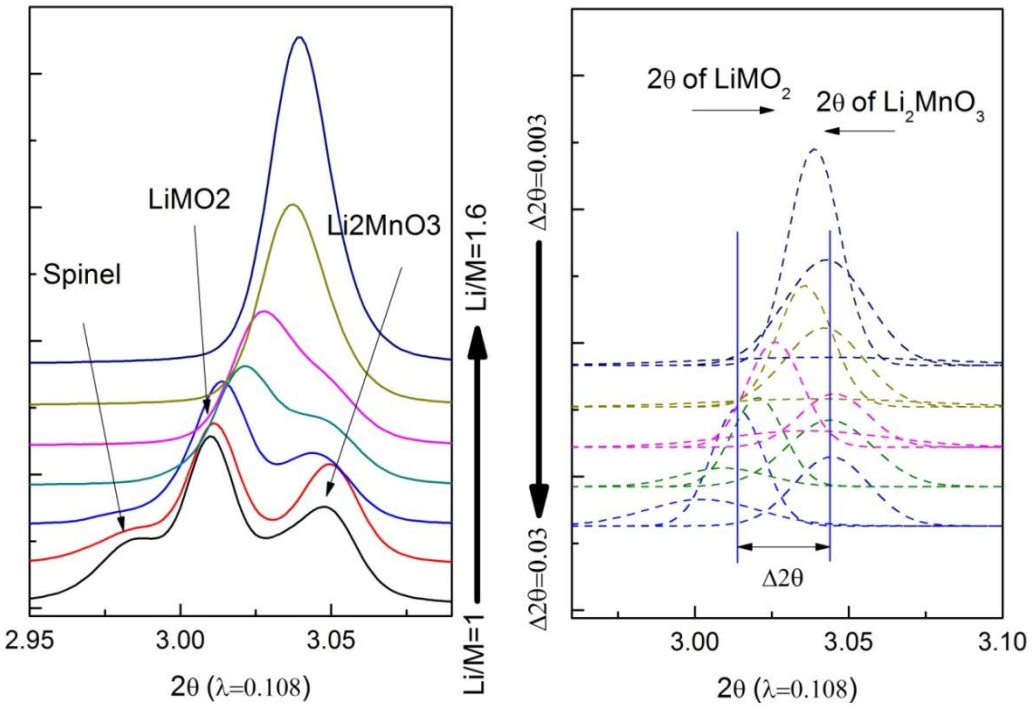

- XRD of low-Li materials showed evidence of spinel and/or excess $Li_2MnO_3$
- Complex pattern around 2θ~3.0° is consistent with presence of multiple phases

# XRD Results Indicate That the Phase Relationships Can Be Complex. 2



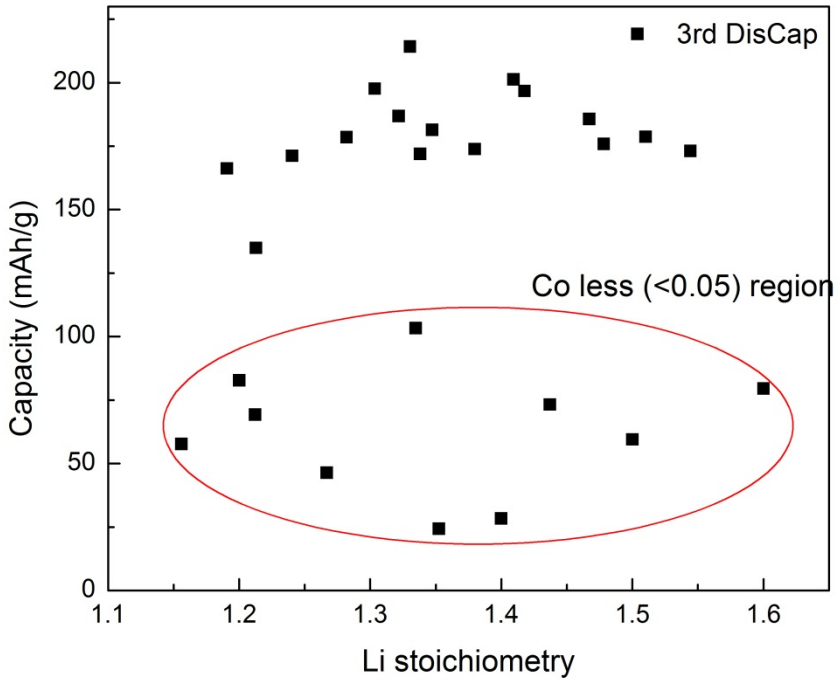

- Single peak at 2θ~3.0° is consistent with the presence of a composite phase

# Phase Distribution Is Sensitive to Li Concentration




- Nominal transition metal (M in $LiMO_2$) ratio: Ni=0.40; Mn=0.55; Co=0.05
- The reflection of the spinel (Fd3m) impurity was reduced; and the reflections due to $Li_2MnO_3$ (C2/m) and $LiMO_2$ (R-3m) were broadened, shifted, and, eventually, merged into each other. The data may indicate that interphase of domains of $Li_2MnO_3$ (C2/m) and $LiMO_2$ (R-3m) exist in the composite material as the domain sizes are reduced and become more integrated

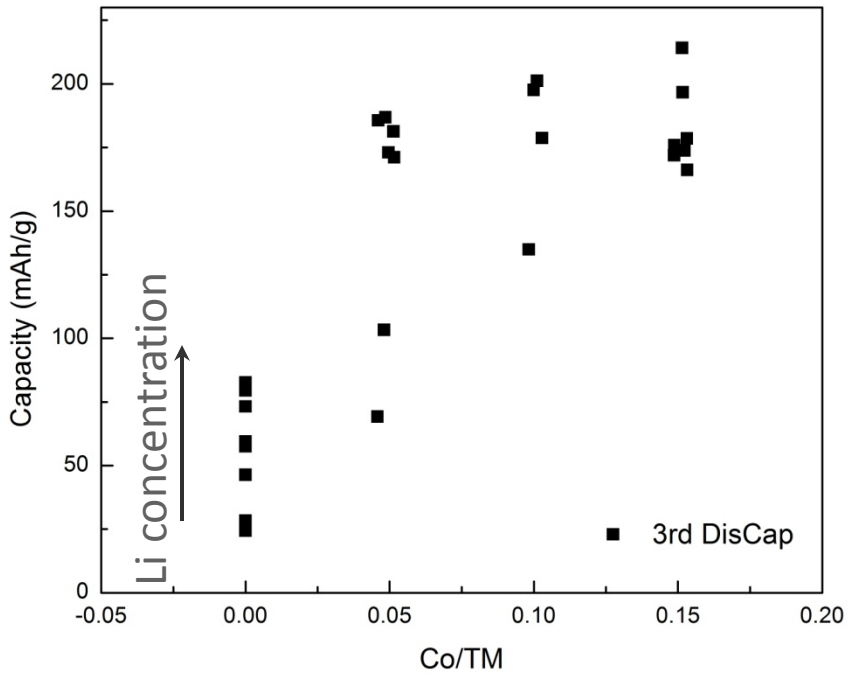
# Performance
# Effect of Li Stoichiometry on Capacity




- There were two distinguishable regions. The materials with lower capacities also contain less Co

# Effect of Co Stoichiometry on Capacity

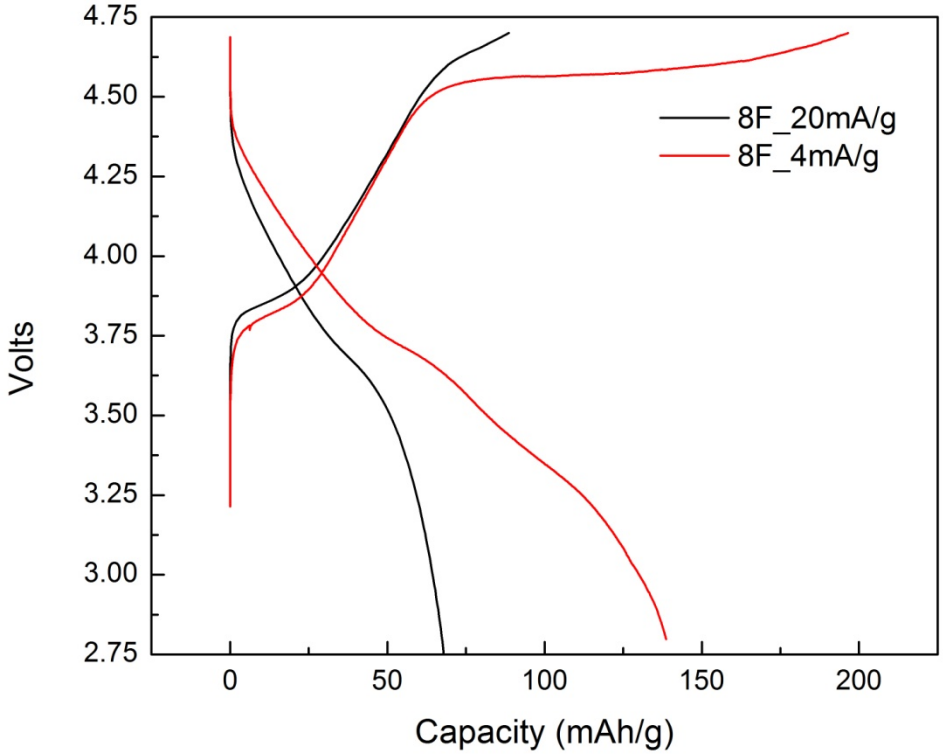
- Compositions with a high Co concentration tend to have higher capacities




» TM=(Ni+Co+Mn) and equals 1

# High-voltage Capacity Is Sensitive To Charge Rate

- No marked effect on capacity below 4.5 V
- Capacity between 4.5 and 4.7 V is sensitive to rate




- Six-fold increase in capacity between 4.5 and 4.7 V at lower rate
  - Co concentration may effect conductivity and/or the activation process

# Study the Relationship of Capacity to the Activation Process

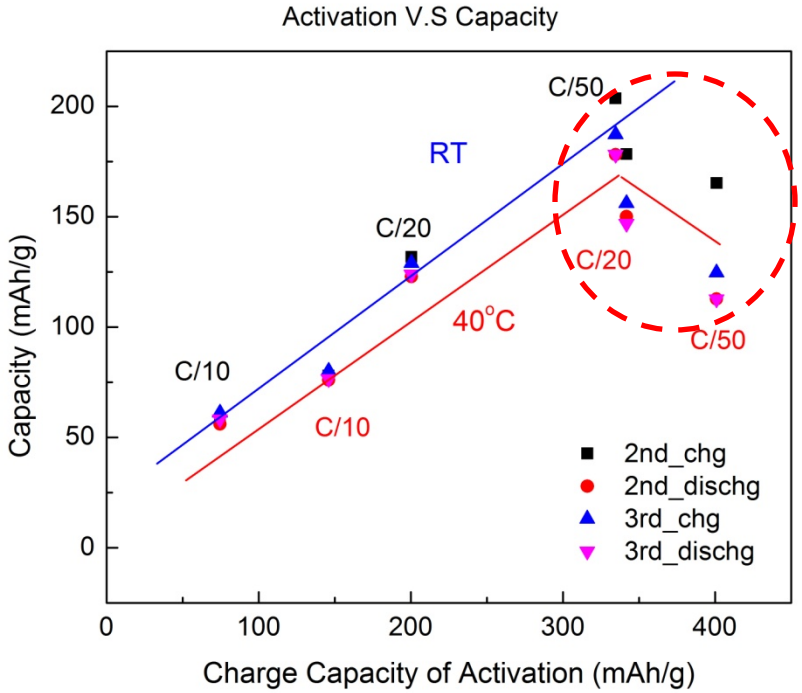
## Method:

- Activation: $Li_2MnO_3$ cathodes were charged to 4.8 V and then discharged to 2 V with different current, which are 15 mA/g (C/10), 7.5 mA/g (C/20), 3 mA/g (C/50), and at different temperature (RT, 40oC).
- Then, the capacity of activated $Li_2MnO_3$ was measured by the same voltage window, 2-4.7 V, with the same current, 15 mA/g, and at room temperature.

**Note:** All the capacity reported here is the "available" lithium sites after the activation. During the initial activation, theoretically, no capacity is measured below 4.5 V; the activation process above 4.5 V is needed for every "available" site.

# The Capacity Increases With The Degree of Activation

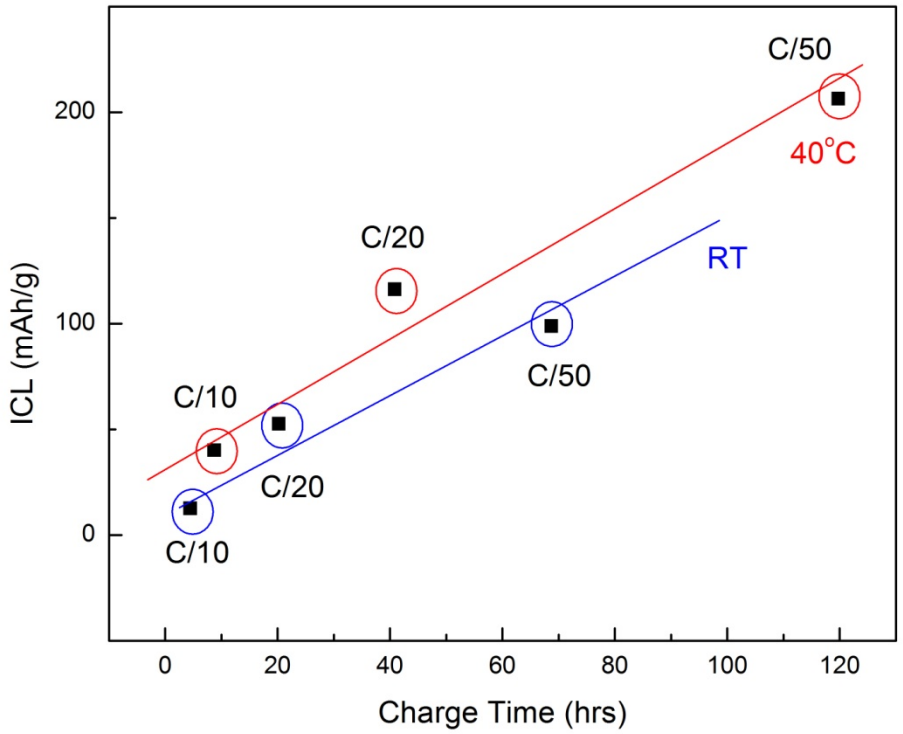
- $2^{nd}$_chg: the $2^{nd}$ charge capacity, etc. The $1^{st}$ is the 2-4.8V activation cycle.
- The capacities were plotted versus to charge capacity of activation cycle.




However, $Li_2MnO_3$ activated at 40°C with C/50 shows lower capacity then one at 40°C with C/20 and one at RT with C/50

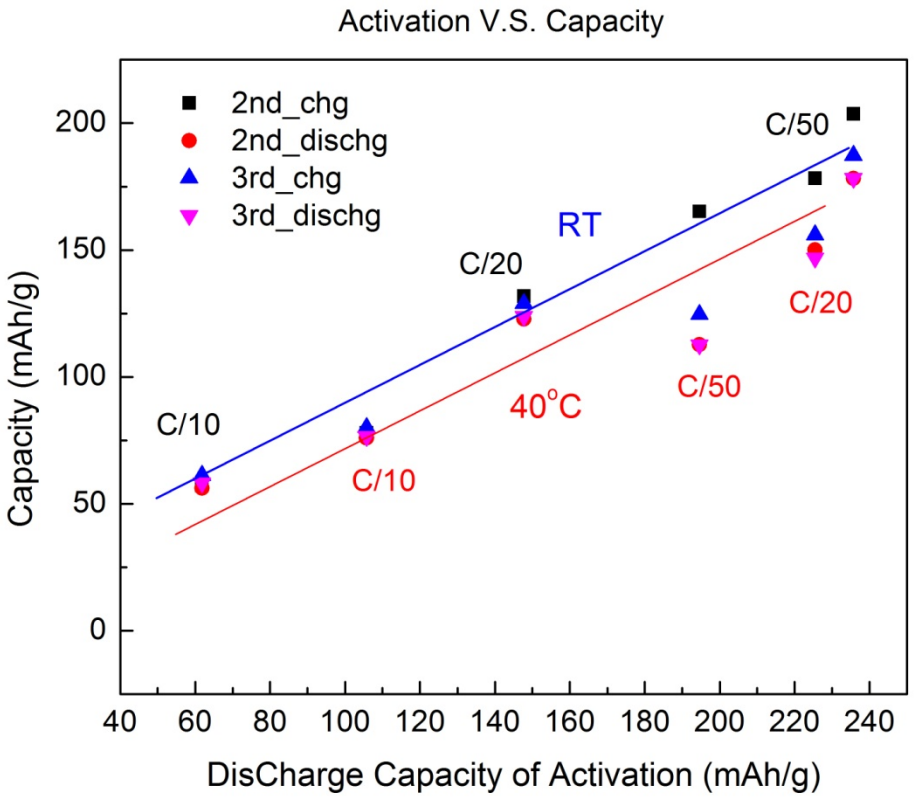
- ~ 400 mAh/g energy density was taken with 3 mA/g (C/50) charge current.
- The process is kinetically controlled, speeded up by raised temperature.
- The coulombic capacity of $Li_2MnO_3$ in the following cycles mainly depends on the capacity of the charging in the activation process.

# Irreversible Capacity Loss Increases With Charging Time



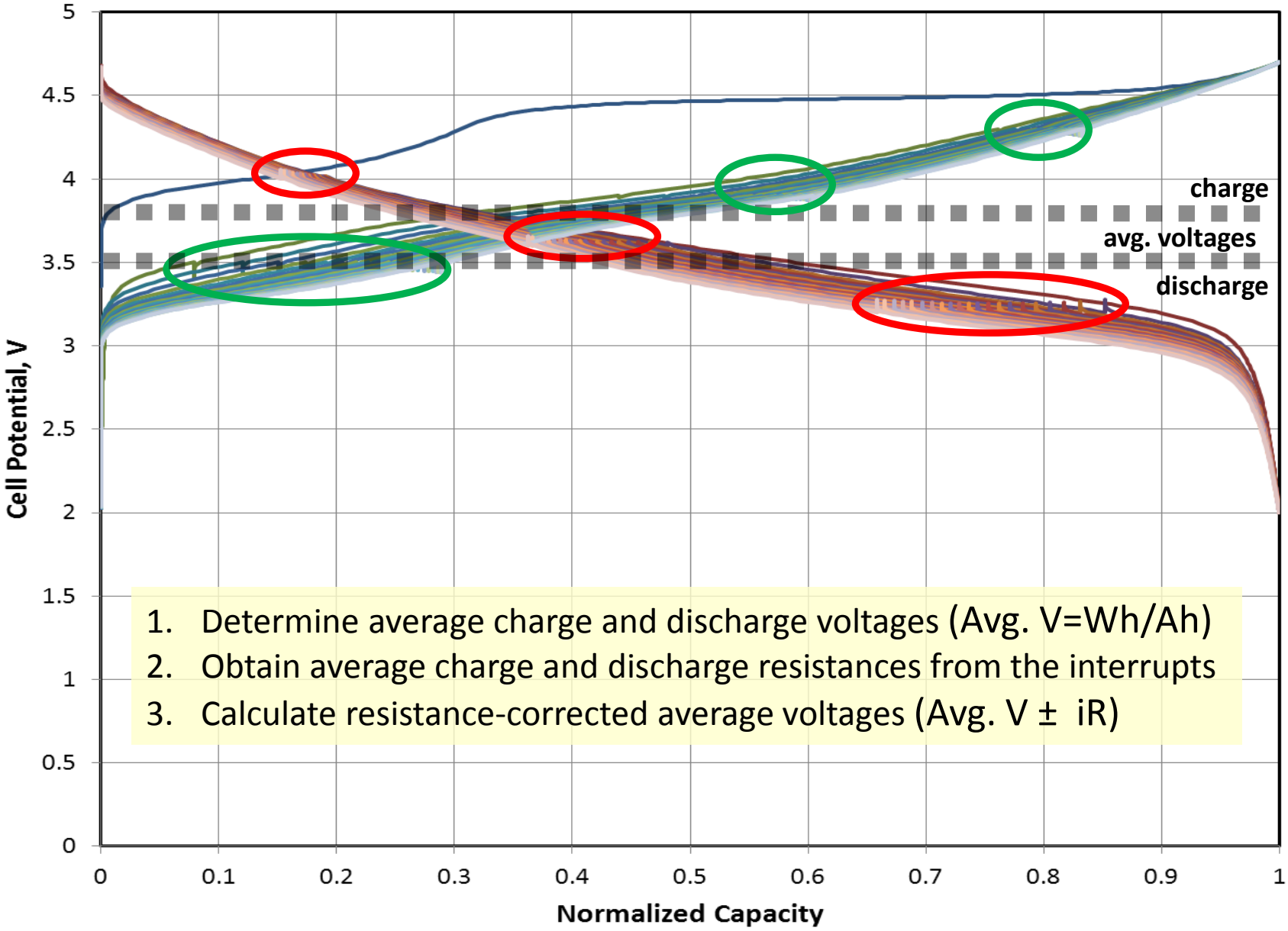

- Higher capacity can be reached with slower charging rate. However, the charging times increase irreversible capacity loss (ICL)
- ~200 mAh/g ICL at 40°C with C/50 decreases capacity in the following cycles

# Capacity of $Li_2MnO_3$ Increases With Degree of Activation



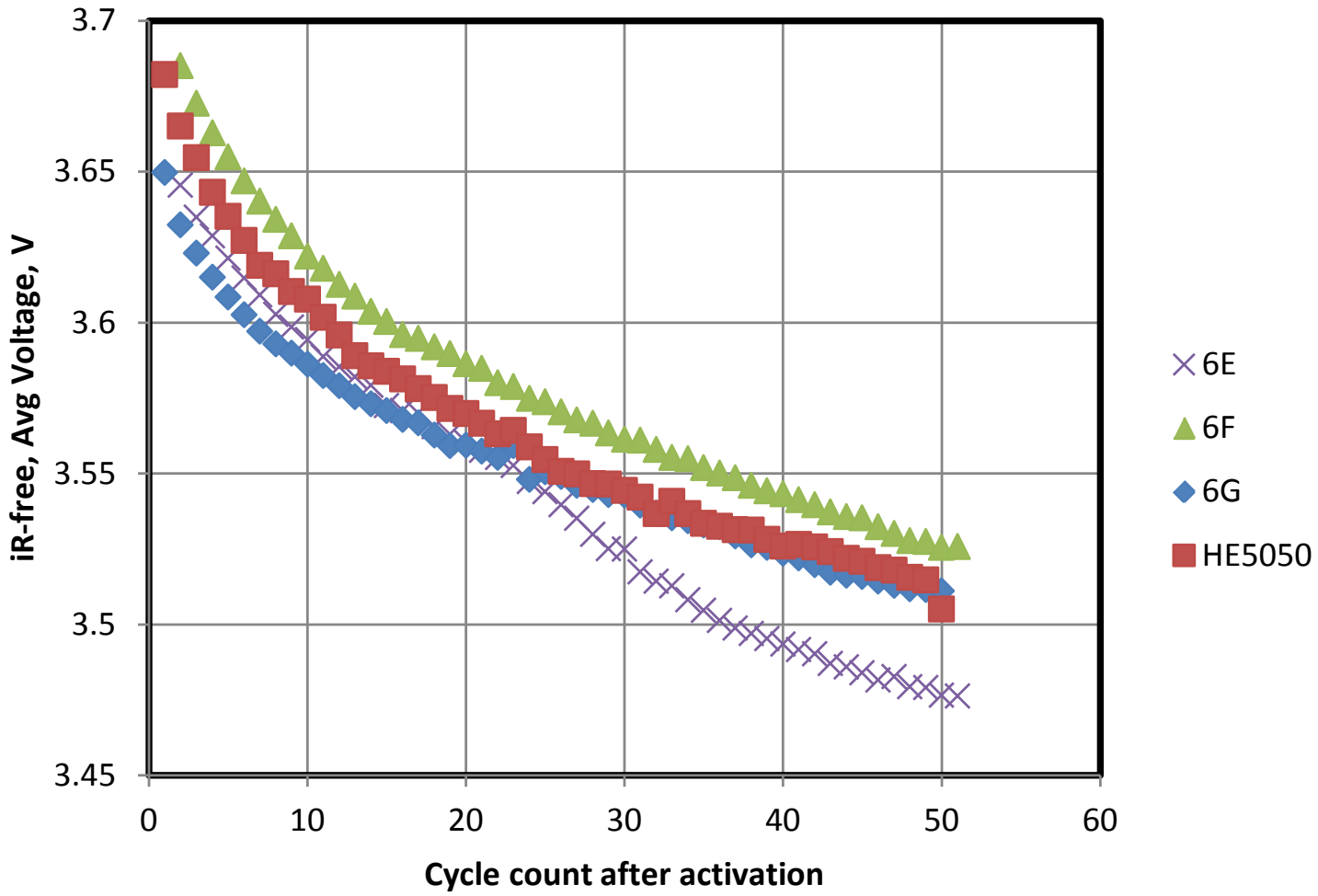

- Considering the various ICL in different activation process, it is better to plot the capacity of $Li_2MnO_3$ to the capacity of the discharging in the activation process
- The columbic capacity of Li2MnO3 in the following cycles shows linear relationship to the capacity of the discharging in the activation process

# iR-Corrected Average Voltage is Used To Track Voltage Fade




1. Determine average charge and discharge voltages (Avg. V=Wh/Ah)
2. Obtain average charge and discharge resistances from the interrupts
3. Calculate resistance-corrected average voltages (Avg. V ± iR)

# Composition Affects Voltage Fade



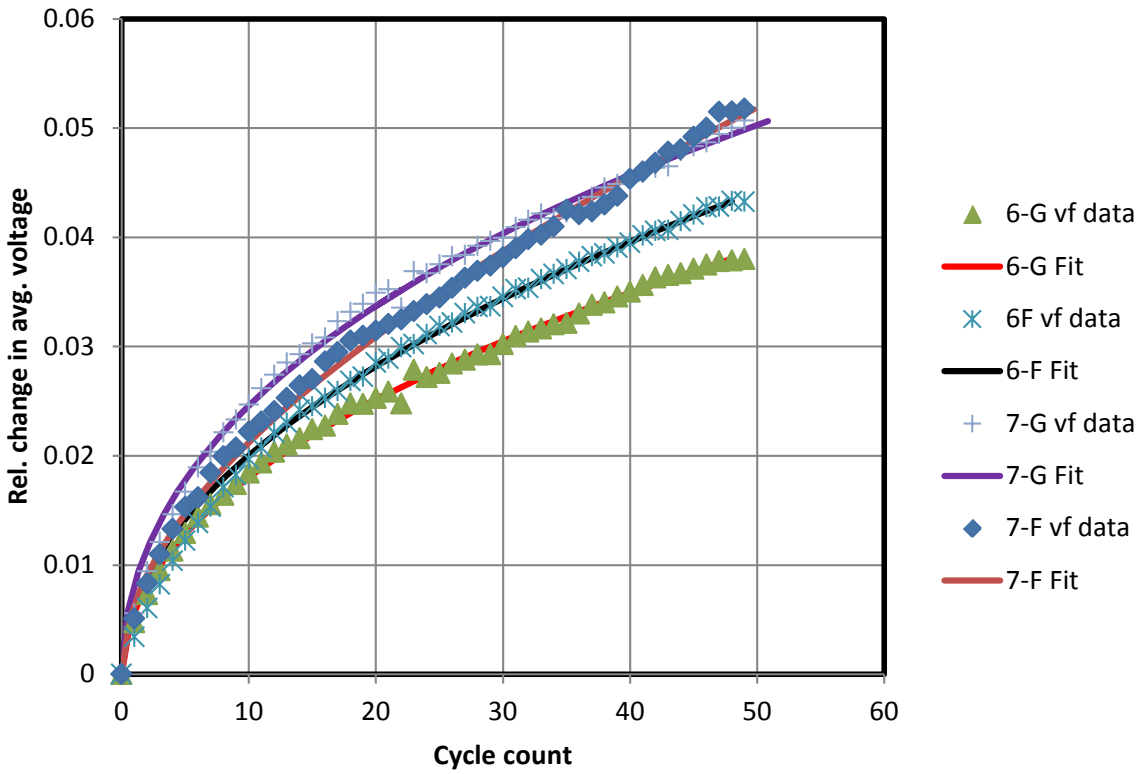
# Kinetics of Average Voltage Fade

- The decline in average voltage data were fit to a paralinear kinetic rate law[1]

$$x = \frac{K_p}{K_l} ln \frac{K_p}{K_p - K_l(x\text{-}K_l t)}$$

where $x$ is the change in relative average voltage, $K_p$ and $K_l$ are the parabolic and linear rate constants, respectively, and $t$ is time

- In general, the regression coefficients, $r^2$, were high, > 0.99




[1]E. W. Haycock, J. Electrochem. Soc., 106 (1959) 771–775

# Use Methods of Scheffé To Model Dependence of Kinetic Parameters On Composition

- Limit modeling to those compositions that crystalize in the R-3m space group (layered-layered materials)
- $K_p$ and $K_l$ data were treated by multiple linear regression analysis using the cubic simplex equation for four-component mixtures, based on the work of Scheffé[2,3]

$$Y=a_1x_1 + a_2x_2 + a_3x_3 + a_4x_4 + a_{12}x_1x_2 + a_{13}x_1x_3 + a_{14}x_1x_4 + a_{23}x_2x_3 + a_{24}x_2x_4 + a_{34}x_3x_4 + a_{123}x_1x_2x_3 + a_{124}x_1x_2x_4 + a_{134}x_1x_3x_4 + a_{234}x_2x_3x_4 + b_{12}(x_1 - x_2) + b_{13}(x_1 - x_3) + b_{14}(x_1 - x_4) + b_{23}(x_2 - x_3) + b_{24}(x_2 - x_4) + b_{34}(x_3 - x_4)$$, where $x_j$ is the mole fraction of the $j^{th}$ component

- The candidate fits must contain the $x_1$, $x_2$, $x_3$ and $x_4$ terms and were limited to 11 terms because dataset contained 20 entries
- For each kinetic parameter, examined 26,333 combinations of terms seeking an equation which
  - Used the fewest number of terms
  - Had high value of $r^2$, typically > 0.98
  - Had lowest RMS error

[2]H. Scheffé, J. Royal Statistical Soc. (B) 20 (1958) 344.

[3]H. Scheffé, J. Royal Statistical Soc. (B) 25 (1963) 235.

# Results From Simplex Modeling Produced Good Fits

- 11-term equations were obtained for $K_p$ and $K_I$ which met the selection criteria

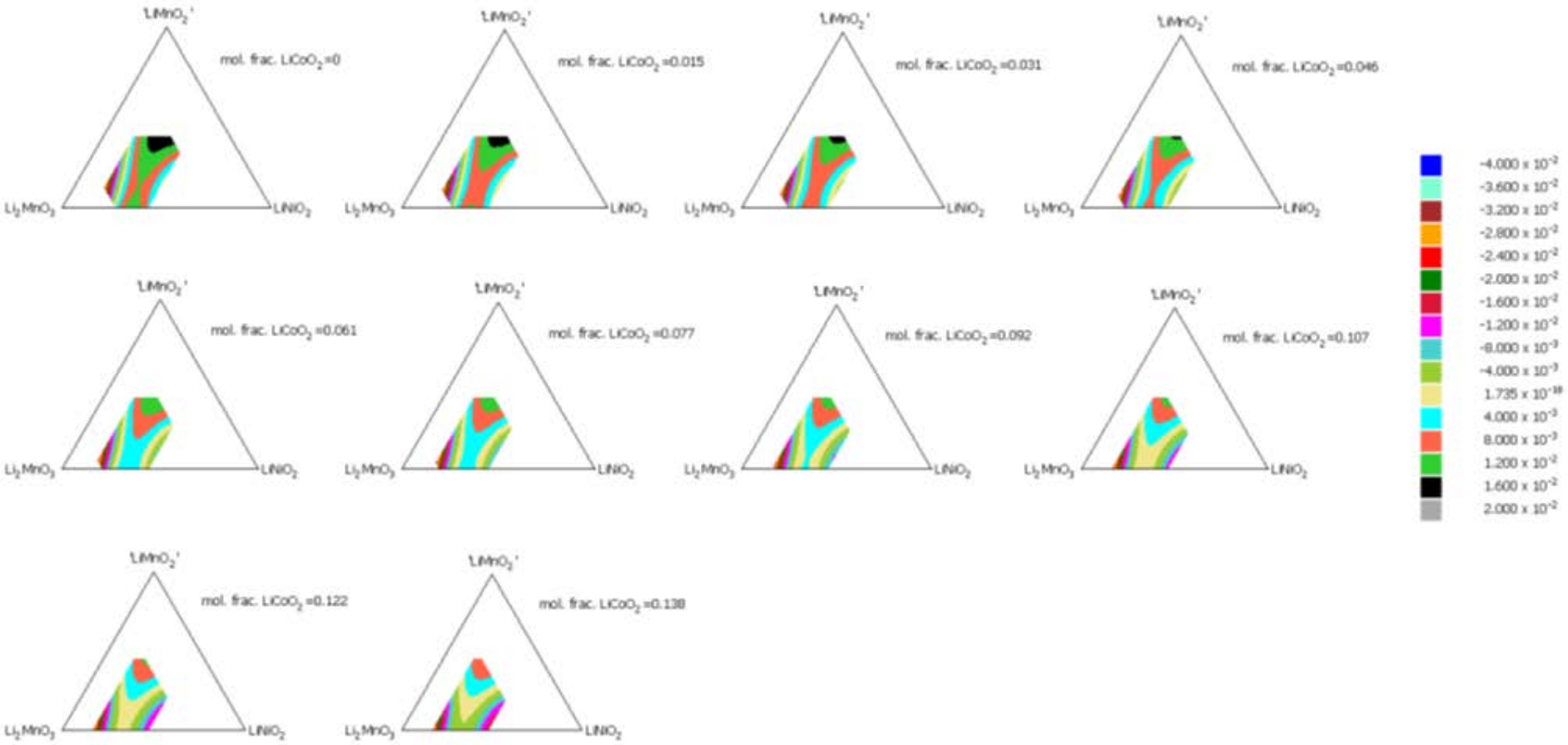
$K_p = a_1x_1 + a_2x_2 + a_3x_3 + a_4x_4 + a_{14}x_1x_4 + a_{24}x_2x_4 + a_{124}x_1x_2x_4 + a_{134}x_1x_3x_4 + b_{12}(x_1 - x_2) + b_{14}(x_1 - x_4) + b_{34}(x_3 - x_4)$; $r^2$ =0.99; RMS error=3.9%

$K_I = a_1x_1 + a_2x_2 + a_3x_3 + a_4x_4 + a_{12}x_1x_2 + a_{13}x_1x_3 + a_{23}x_2x_3 + a_{134}x_1x_3x_4 + b_{12}(x_1 - x_2) + b_{14}(x_1 - x_4) + b_{23}(x_2 - x_3)$; $r^2$ =0.99; RMS error=5.4%

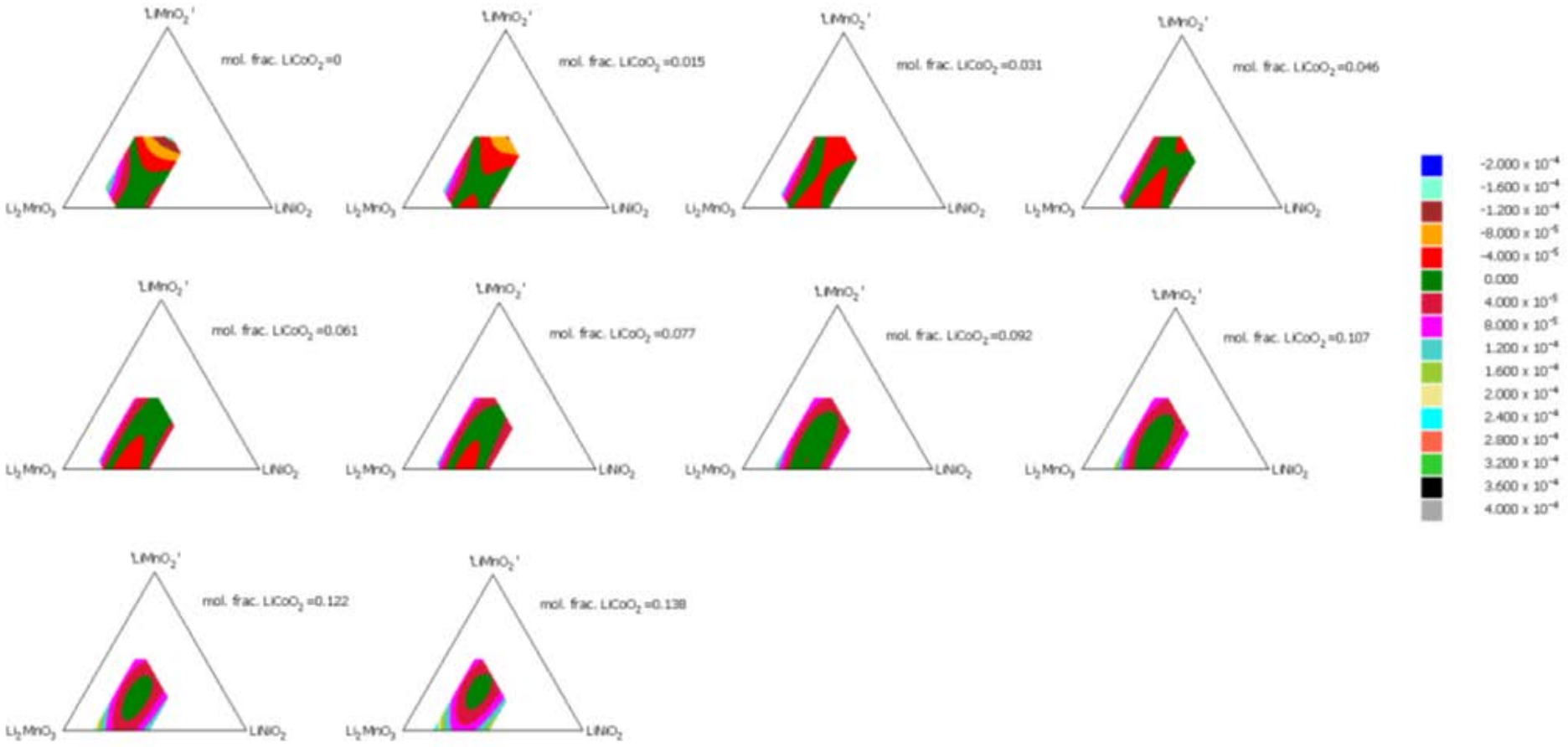
- Use model to guide selection of compositions to make and to characterize

# There Are Indications of Compositional Regions For Low Values of the Kinetic Parameters --$K_l$

- Low values of the kinetic constants are desired to slow the voltage fade process



# There Are Indications of Compositional Regions For Low Values of the Kinetic Parameters -- $K_P$



# Work in Progress/Future Work

- Continue to characterize compositions in region of interest
- Characterize compositions that the models suggest would possess low values of the kinetic parameters
- Use these results to fine-tune the models

# Summary

**LMR-NMC phase system, in general,**

- .. has complex phase relationships
- .. shows that the amount of Co on the transition metal site affects $Li_2MnO_3$ activation
- .. displays nonlinear kinetics for the voltage fade process
- .. is amenable to modeling of the kinetics of voltage fade

Acknowledgment
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