Enabling High-Energy/Voltage Lithium-Ion Cells for Transportation Applications:

Part 3 Electrochemistry

Project ID: ES254

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Chemical Sciences and Engineering Division
Argonne National Laboratory

Annual Merit Review
DOE Vehicle Technologies Program
Arlington, VA
8-12 June, 2015

Overview

Timeline

- Start: October 1, 2014
- End: Sept. 30, 2017
- Percent complete: 15%

Budget

- Total project funding
- FY15 - $3000K (total project funding see parts 1 and 2)

Barriers

- Calendar/cycle life of lithium-ion cells being developed for PHEV and EV batteries that meet or exceed DOE/USABC goals

Partners

- Lead PI: Anthony K. Burrell
- Collaborators: ORNL, NREL
- Abraham, Daniel; Balasubramanian, Mahalingam; Bareno Garcia-Ontiveros, Javier; Bloom, Ira D.; Long, Brandon R.; Croy, Jason R.; Dees, Dennis W.; Dogan, Fulya; Gallagher, Kevin G.; Gilbert, James; Iddir, Hakim; Ingram, Brian J.; Johnson, Christopher; Klett, Matilda; Lu, Wenquan; Ren, Yang; Vaughey, John T.; Wu, Huiming; Wu, Rinaldo, Steven G.; Jansen, Andy; Polzin, Bryant; Trask, Steven; Krumdick, Gregory; Shin, YoungHo; Zhang, Zhengcheng; Liao, Chen; Tenent, Robert, Ban, Chunmei; Wood, David; Daniel, Claus; Nanda, Jagjit, Li, Jianlin

Project Objectives - Relevance

Energy fade during calendar-life and cycle-life aging limits the application of lithium-ion cells in transportation applications

- High-performing, high-energy, safe and long-life batteries are needed to reduce petroleum consumption in vehicular applications
- Performance targets of plug-in electric vehicle (PEV) and electric vehicle (EV) batteries can be met by cells containing layered-oxide-based positive electrodes
- To achieve the energy and power density targets, cells with these electrodes must be cycled to voltages that exceed 4.5 V vs. Li/Li^+
- On extended cycling at these voltages, capacity loss, impedance rise and voltage fade reduces the cell’s energy and power output
- Mitigating these performance degradation characteristics is, therefore, critical to increasing longevity, thereby reducing lifetime cost, of these high-energy batteries

Approach - Project

Electrochemical characterization is essential to evaluate and benchmark cell performance characteristics

- Develop standard electrochemical protocols to track, quantify and characterize cell performance and performance degradation characteristics in a reproducible and time-efficient manner
  - Disseminate protocols to partnering institutions and individuals to allow comparison of data generated at multiple laboratories
- Provide continuous feedback to team members for the development of electrolyte additive and coating technologies that minimize cell performance degradation
  - Data from AC Impedance spectroscopy and galvanostatic intermittent titration experiments are used to develop models that explain the reasons for performance degradation
  - Identifying sources of performance degradation is the first step towards designing high-performance, high-energy, long-life cells

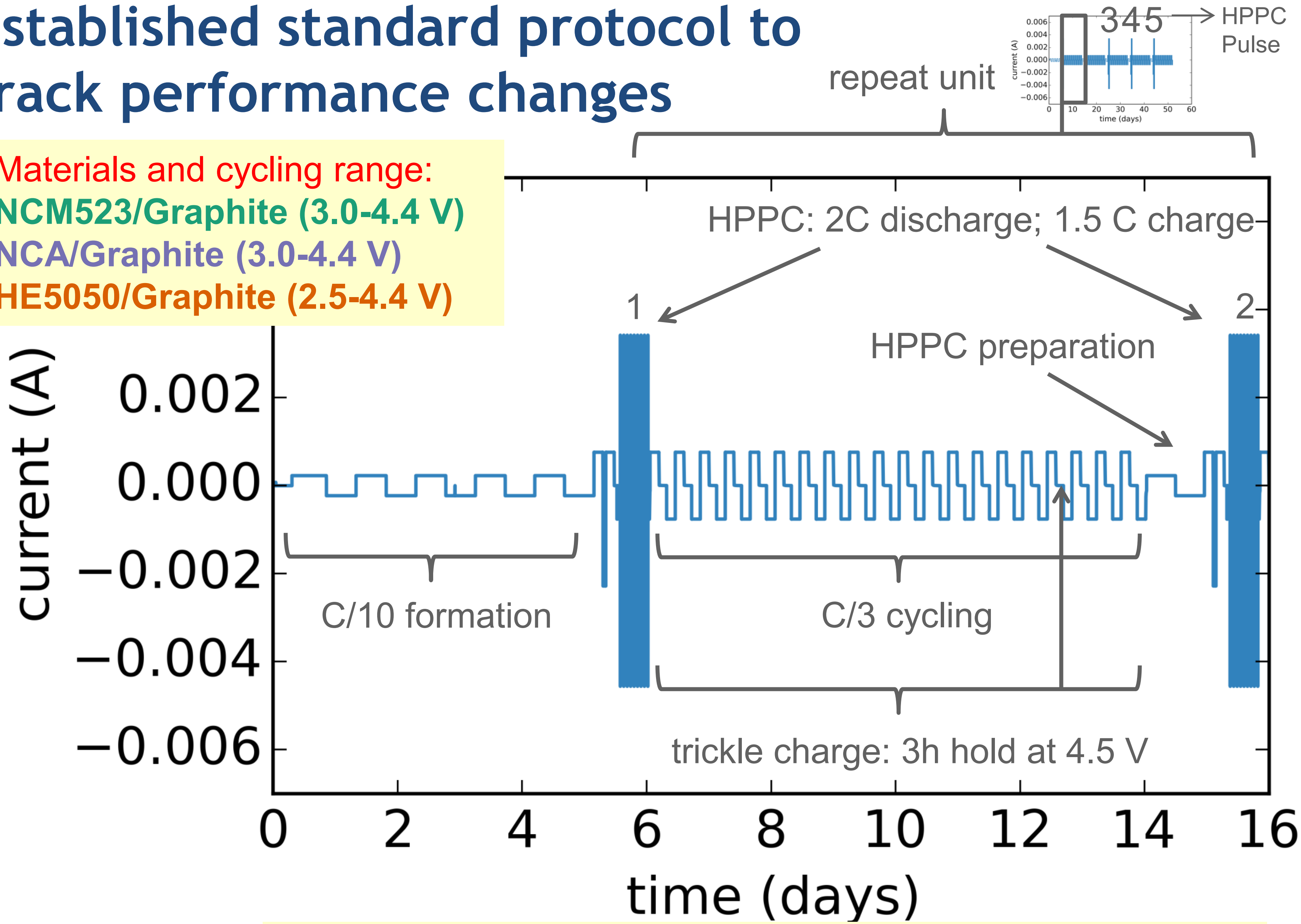
Established standard protocol to track performance changes

Materials and cycling range:

NCM523/Graphite (3.0-4.4 V)

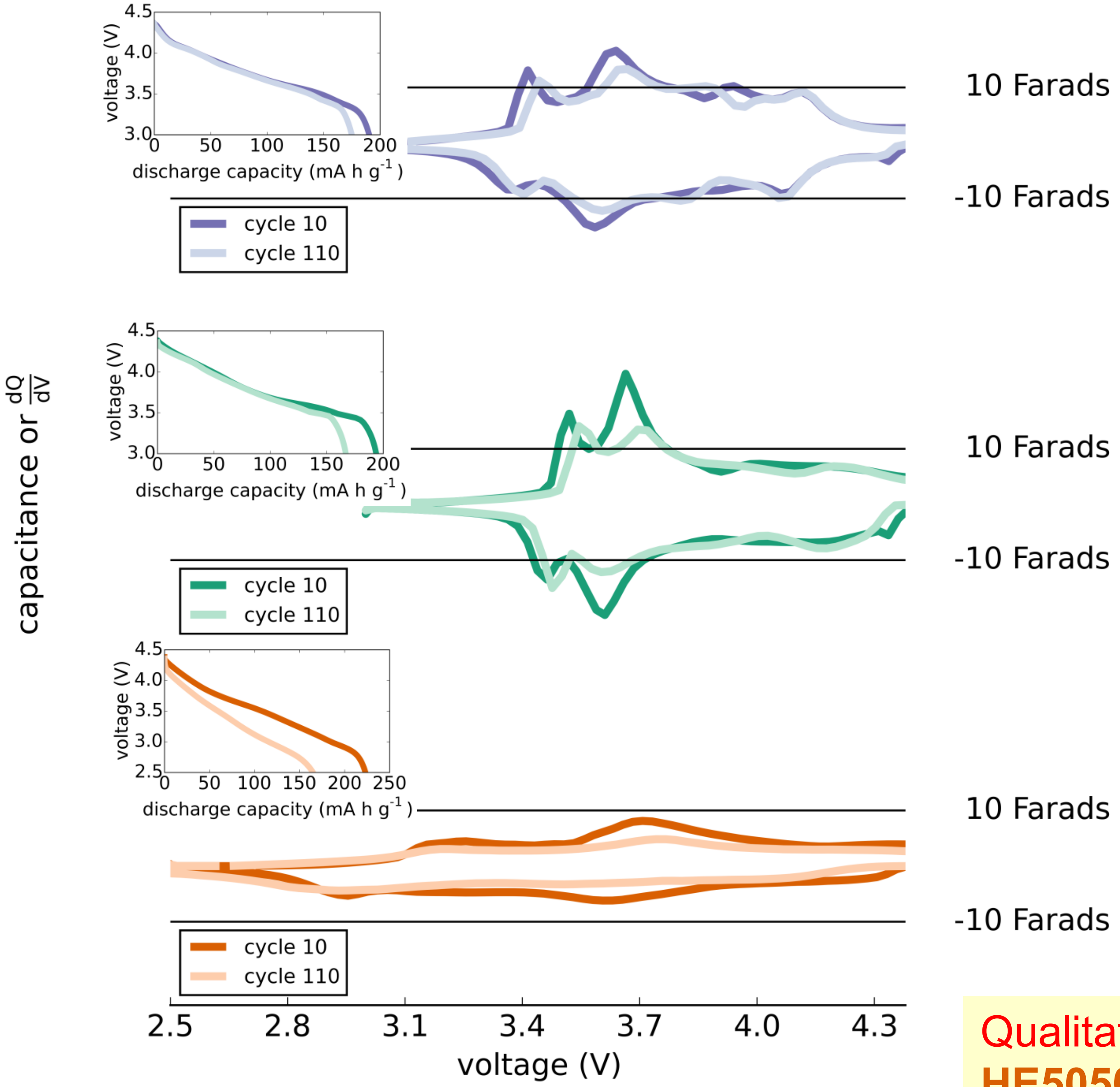
NCA/Graphite (3.0-4.4 V)

HE5050/Graphite (2.5-4.4 V)



Protocol applied to 30 cells for each couple shown above

Profile changes on cycling (a snapshot from “best” cells)



NCA:
cycle 10 ~190 mA h g^{-1}
cycle 110 ~175 mA h g^{-1}

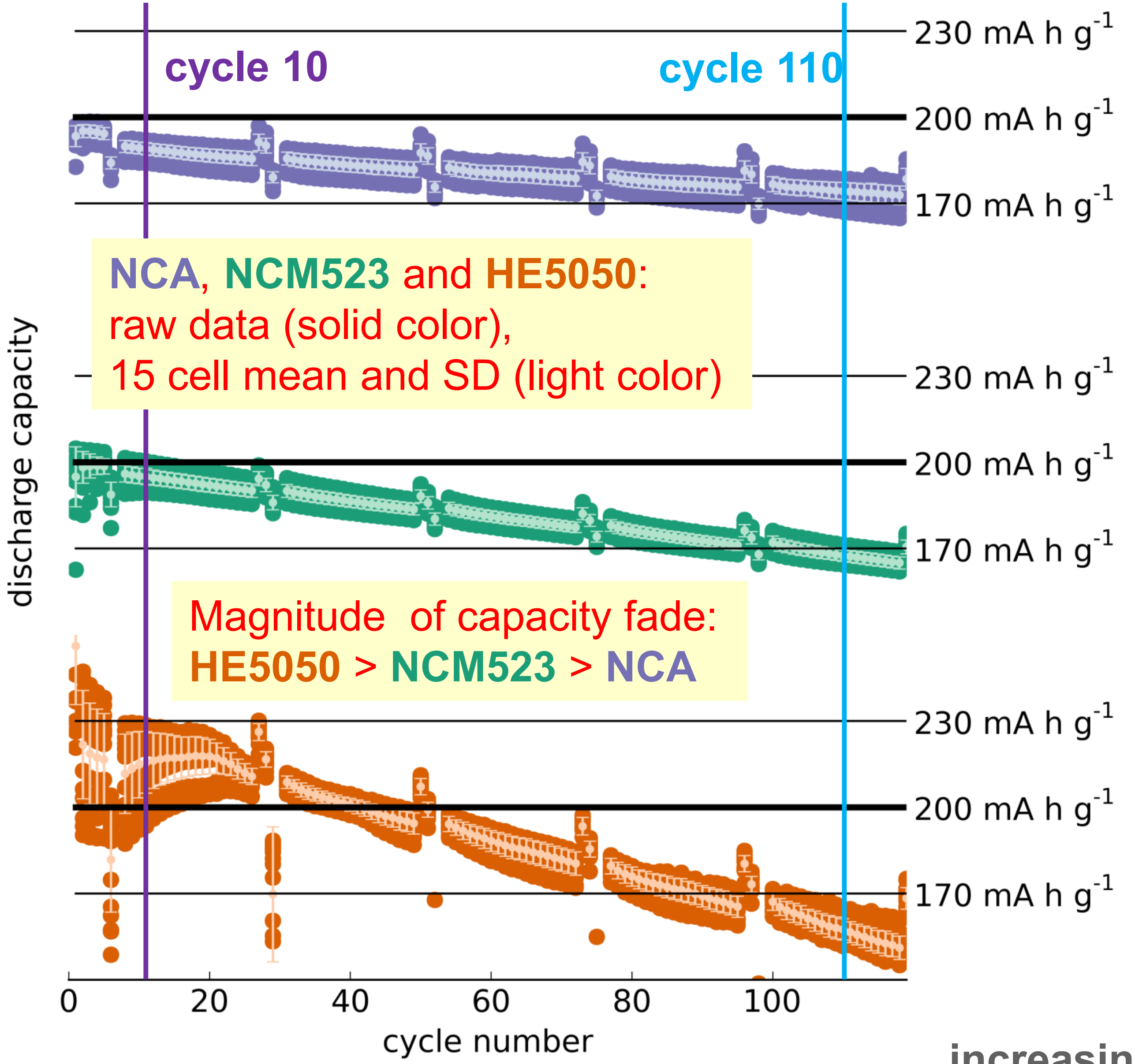
NCM523:
cycle 10 ~194 mA h g^{-1}
cycle 110 ~166 mA h g^{-1}

HE5050:
cycle 10 ~223 mA h g^{-1}
cycle 110 ~165 mA h g^{-1}

Qualitative capacity fade trends
HE5050 > NCM523 > NCA

Capacity Fade vs. cycle number

capacity fade:
100%*((**cycle 10** – **cycle 110**)/(**cycle 10**))



NCA, **NCM523** and **HE5050**:
raw data (solid color),
15 cell mean and SD (light color)

Magnitude of capacity fade:
HE5050 > NCM523 > NCA

NCA capacity fade:
6.7 ± 0.7 %

NCM523 capacity fade:
14 ± 1 %

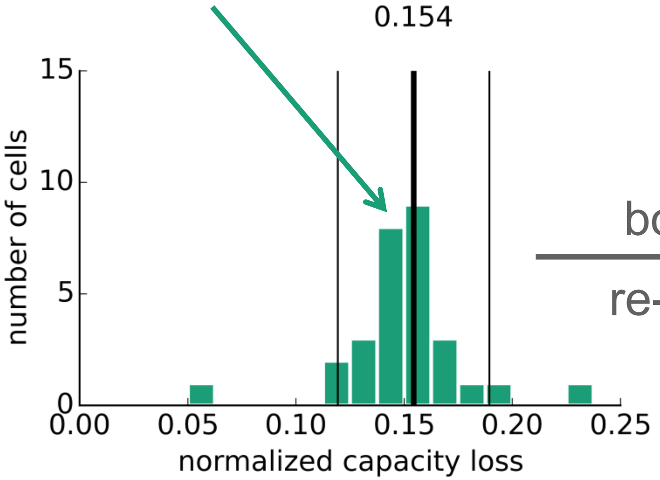
HE5050 capacity fade:
21 ± 5 %

increasing capacity fade

Bootstrap methodology to evaluate modifications to baseline chemistry

Benchmark Map: Capacity Loss

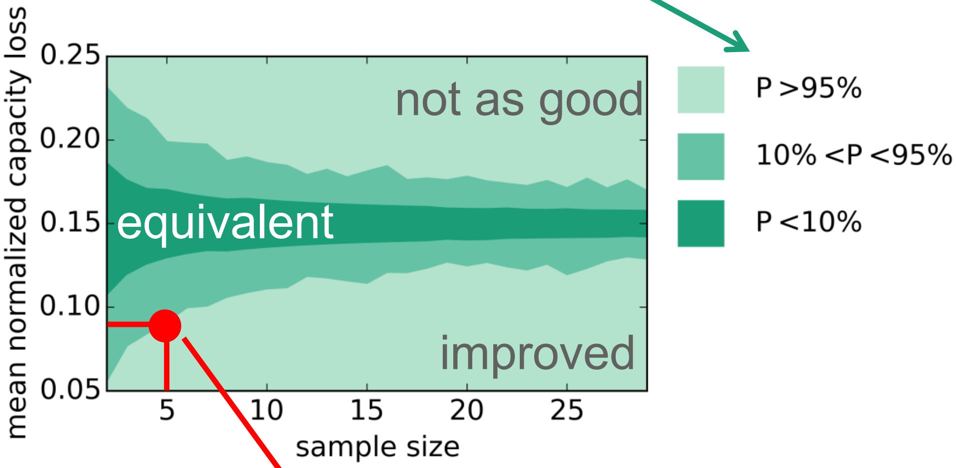
NCM523: number of cells per capacity loss interval from 30 cell distribution.



bootstrap

re-sampling

Probability that the *n*-sample mean differs from the baseline

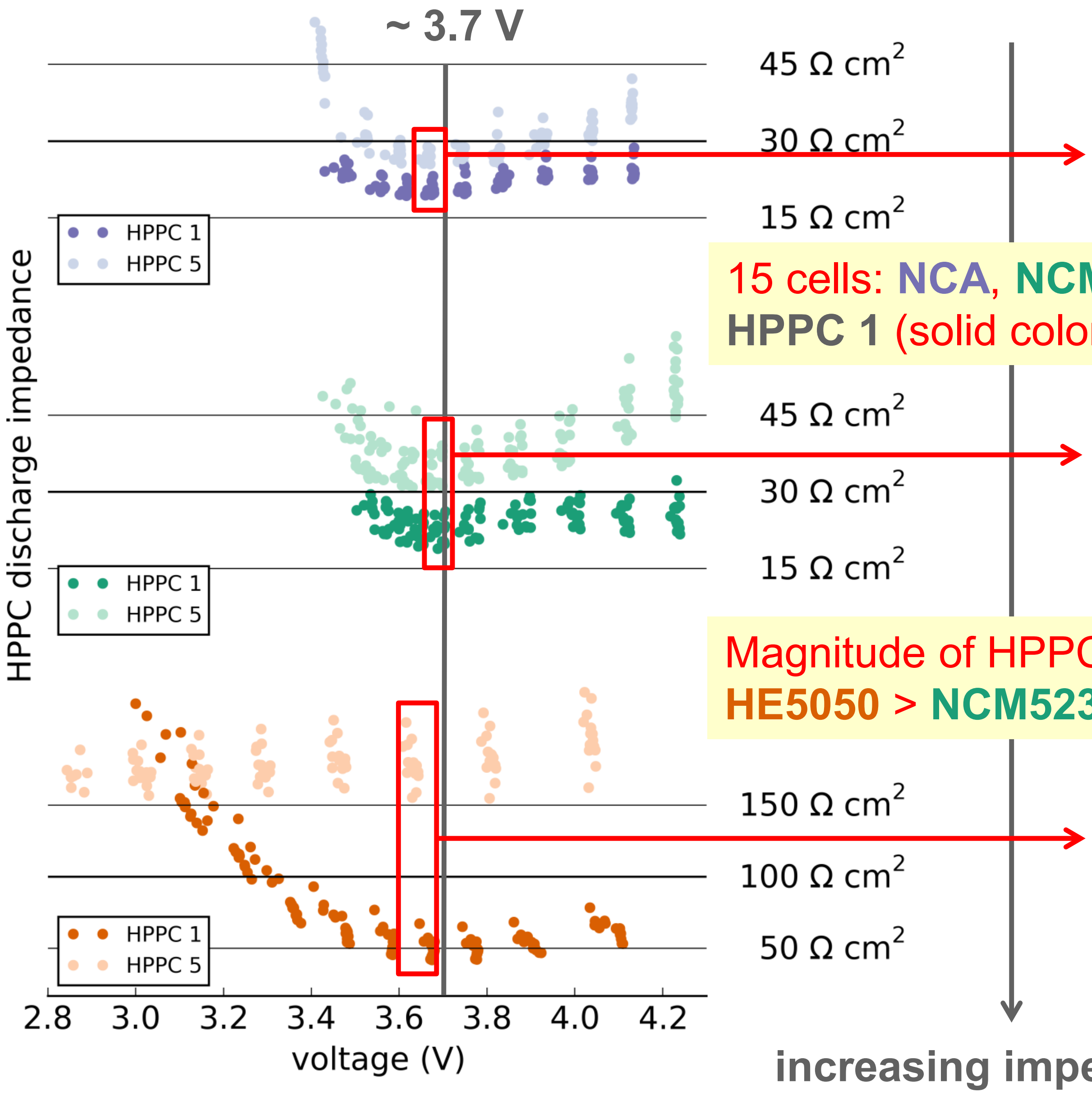


normalized capacity loss:
(**cycle 10** – **cycle 110**)/(**cycle 10**)

For a sample size of *n* = 5 any proposed modification to the **NCM523** baseline chemistry should yield a normalized capacity loss of less than ≈ 0.09 to be considered an improvement.

Impedance Rise on Cycling

impedance rise:
(HPPC 5 – HPPC 1)



NCA impedance rise
At ~3.7V: 3.8 ± 1.6 Ω cm^2

15 cells: **NCA**, **NCM523** and **HE5050**:
HPPC 1 (solid color), **HPPC 5** (light color)

NCM523 impedance rise
At ~3.7V: 8 ± 1 Ω cm^2

Magnitude of HPPC impedance rise:
HE5050 > NCM523 > NCA

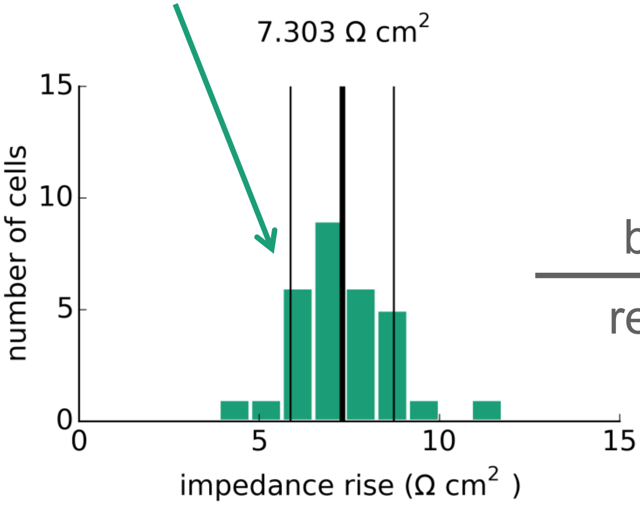
HE5050 impedance rise
At ~3.7V: 100 ± 13 Ω cm^2

increasing impedance rise

Bootstrap methodology to evaluate modifications to baseline chemistry

Benchmark Map: Impedance Rise

NCM523: number of cells per impedance rise interval from 30 cell distribution.

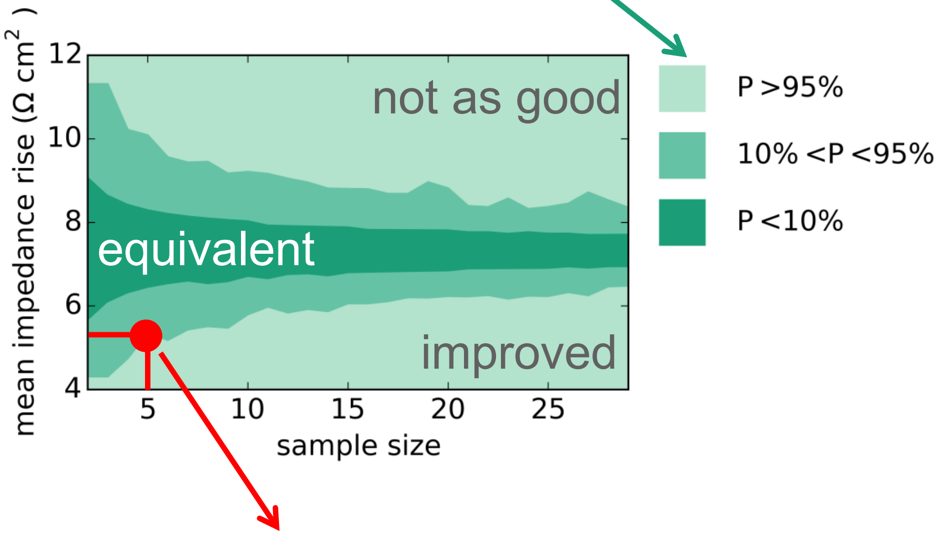


impedance rise:
(**HPPC 5 – HPPC 1**)

bootstrap

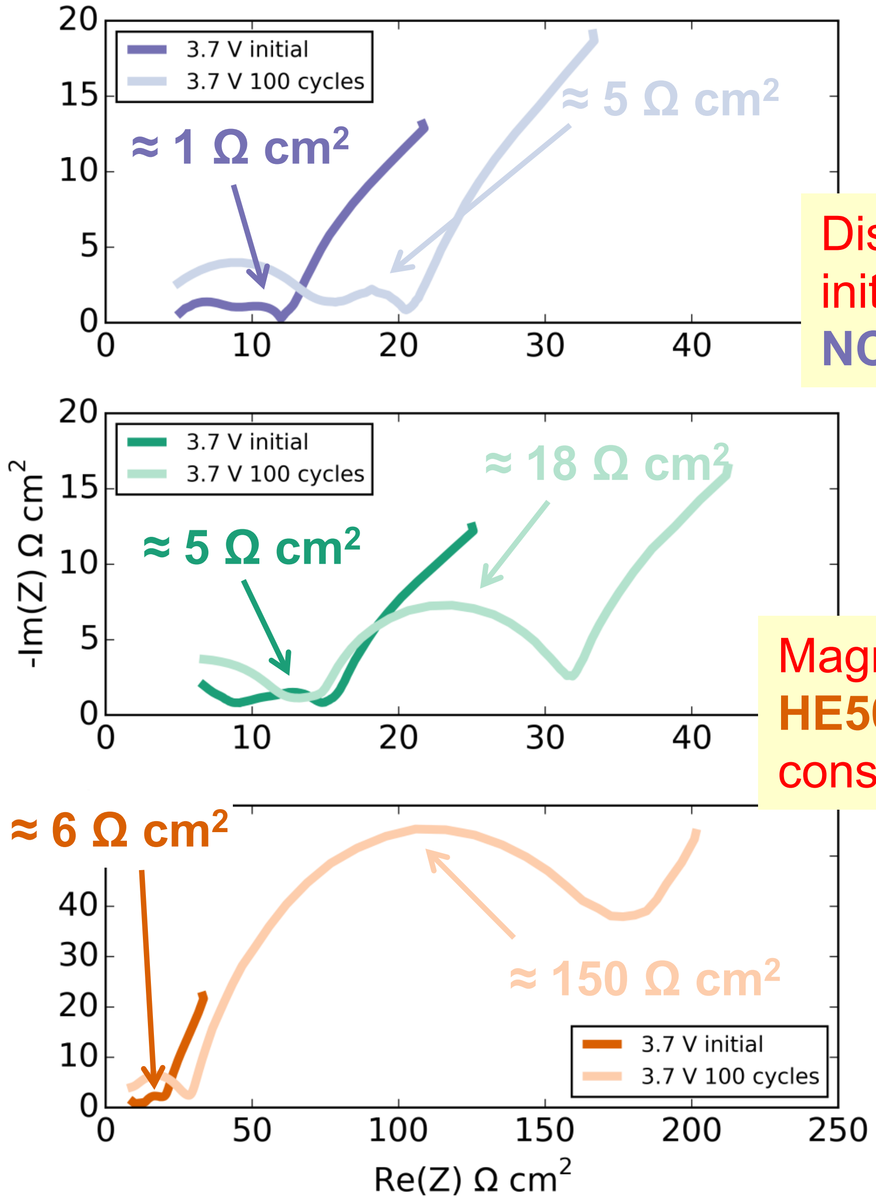
re-sampling

Probability that the *n*-sample mean differs from the baseline



For a sample size of *n* = 5 any modification to the **NCM523** baseline chemistry should yield an impedance rise of less than ≈ 5.2 **Ω cm²** to be considered an improvement.

AC Impedance Spectra changes on Cycling



NCA mid-frequency rise:
100 cycles – initial ≈ 4 Ω cm²

Discharge EIS at 3.7 V:
initial (dark color), 100 cycles (light color)
NCA, **NCM523** and **HE5050**

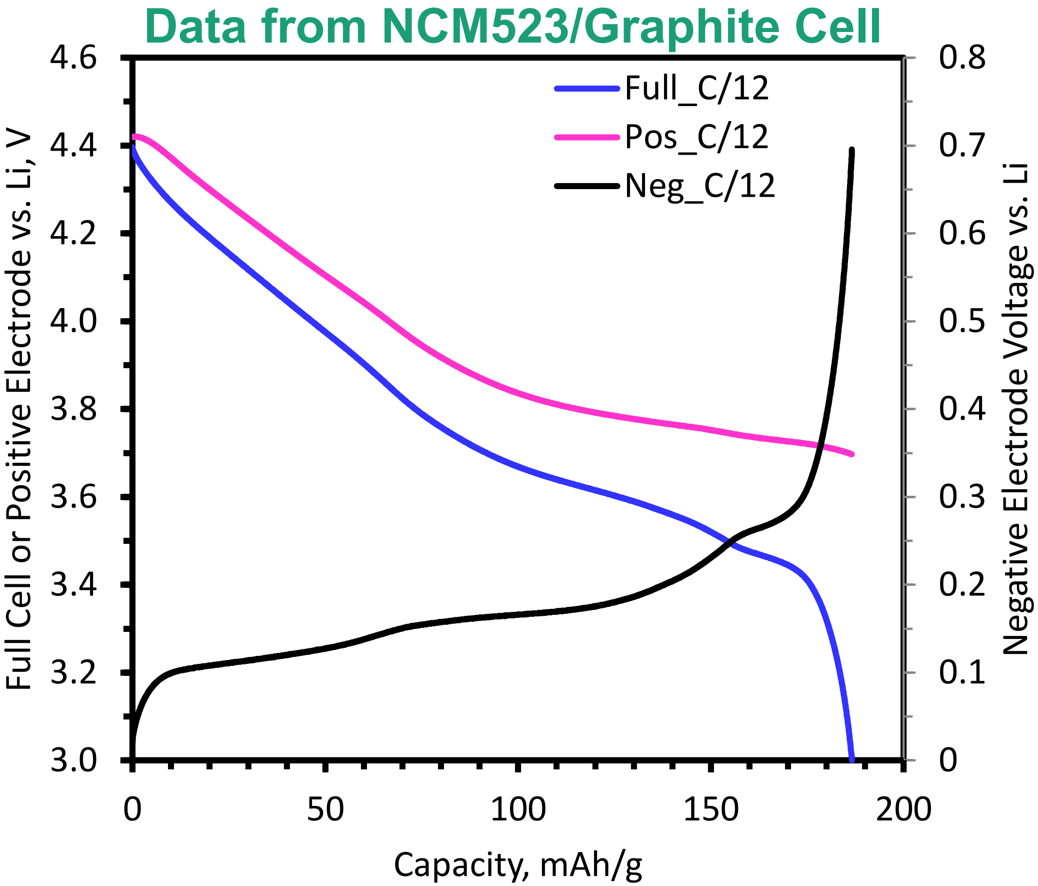
NCM523 mid-frequency rise:
100 cycles – initial ≈ 13 Ω cm²

Magnitude of mid-frequency impedance increase
HE5050 > NCM523 > NCA
consistent with HPPC impedance rise

HE5050 mid-frequency rise:
100 cycles – initial ≈ 144 Ω cm²

The increasing mid-frequency impedance arc is likely associated with the positive electrode (negative electrode same for all cells)

Data from cells with Reference Electrode(s) complement data from coin cells

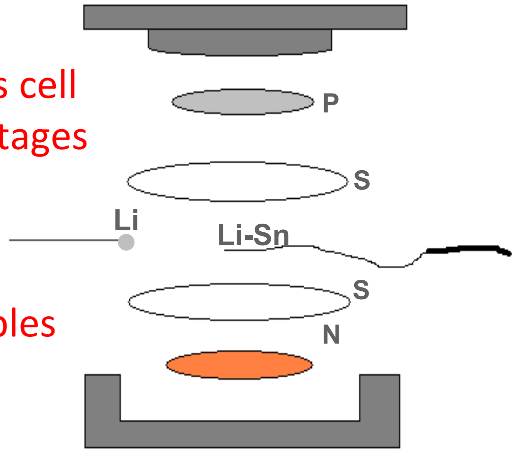


Data from NCM523/Graphite Cell

Full Cell: 4.4 to 3.0 V

Positive Electrode vs. Li: 4.42 to 3.7 V

Negative Electrode vs. Li: 0.02 to 0.7 V



Li RE – monitors cell & electrode voltages

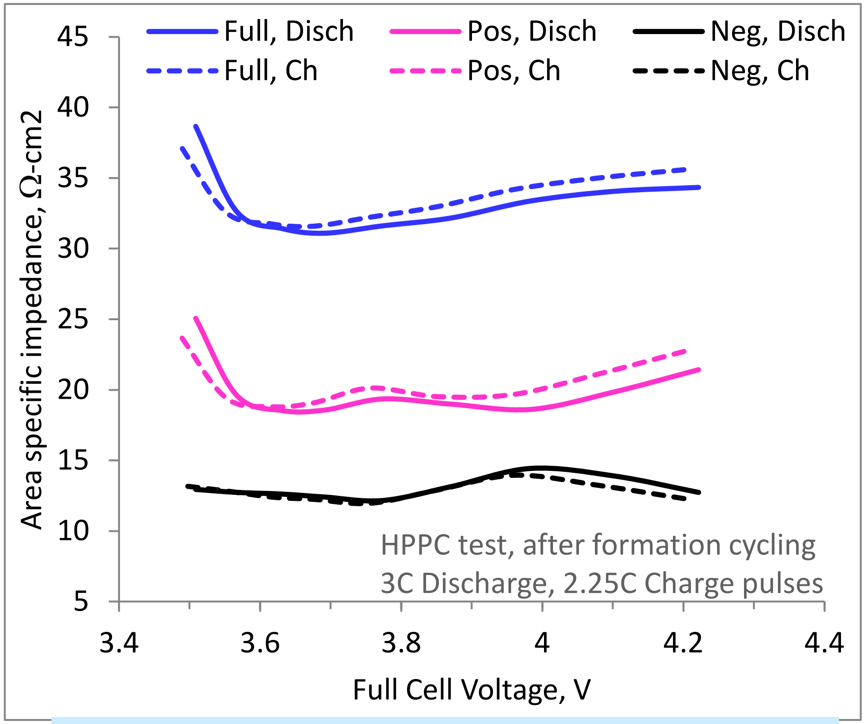
LiSn RE – enables impedance measurement

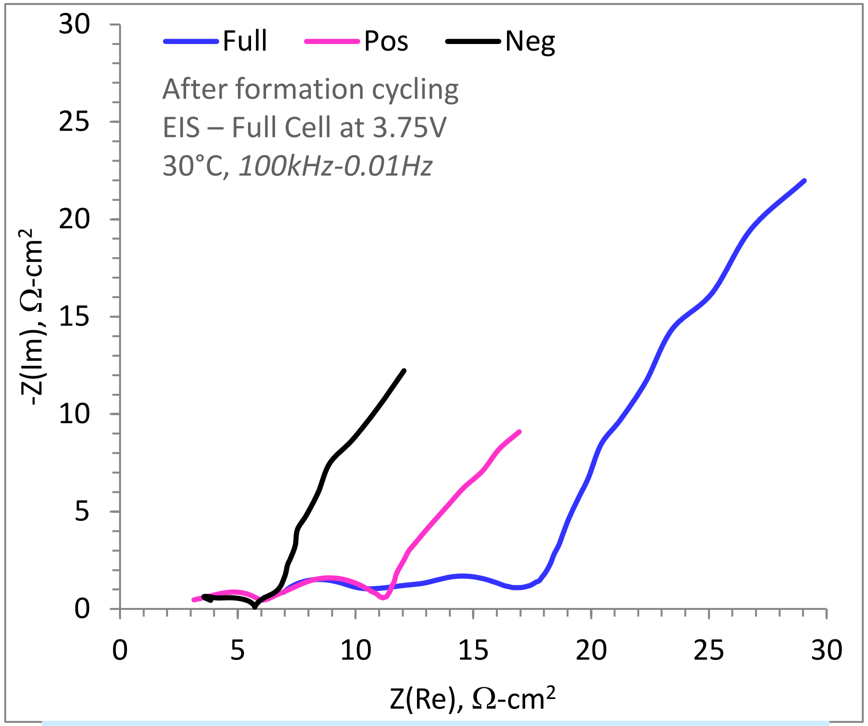
RE cell data are used for

- Electrochemical modeling
- Identifying electrode contributions to cell performance degradation

Data from Reference Electrode cells show electrode contributions to initial cell impedance

NCM523/Graphite Cell





Positive electrode impedance is larger than that of the negative electrode. Impedance values for charge and discharge pulses are similar.

AC impedance data show that positive electrode impedance is higher than that of the negative, consistent with HPPC data.

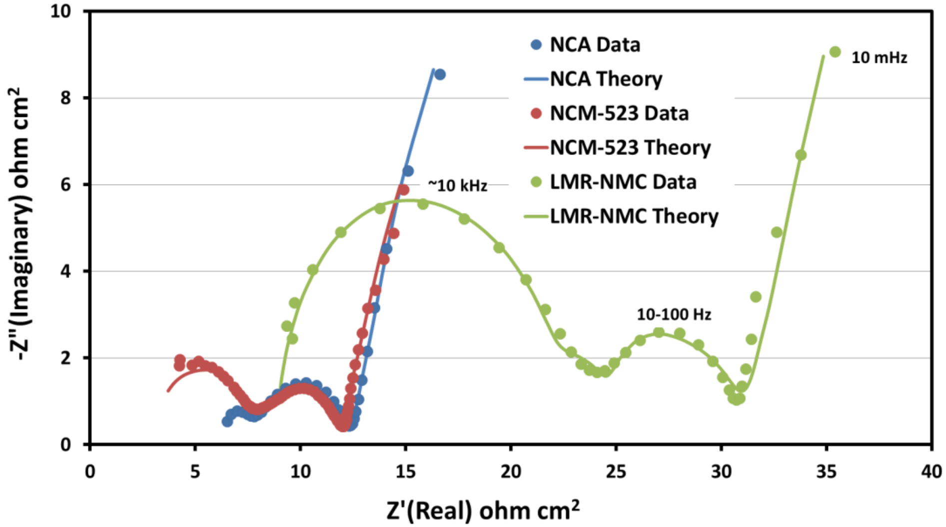
Cycling experiments (in progress) will yield aging-related information

Electrochemical Model for HE/HV Studies Focused on Interfacial Phenomena

- Phenomenological model developed for AC impedance and DC studies using same constituent equations and parameters.
- Differential and algebraic equations describing the transport, thermodynamic, and kinetic phenomena are solved to determine current, potential, and concentration distributions.
- Includes a complex active material / electrolyte interfacial structure.
  - Film on active particles acts as a thin electrolyte layer with restricted diffusion (D_+) and migration (κ_f) of lithium ions with capacitance (C_f).
  - Surface layer of active particle inhibits the diffusion (D_{si}, K_s) of lithium into the bulk active material (D_{sb}).
  - Electrochemical reaction (i_o) and double layer capacitance (C_d) at film/layer interface
  - Particle contact resistance (σ_p) and film capacitance (C_c).
- Volume averaged continuum based transport equations account for the porous multiphase character of lithium ion cells, including multiple active particle fractions.
- Models developed for multi-dimensional, multi-scale, and transient simulations

Electrochemical Modeling Studies on NCM-523 Electrodes: Initial Evaluation and Comparison

Positive Electrode EIS Studies taken with Micro-Reference Electrode Cell



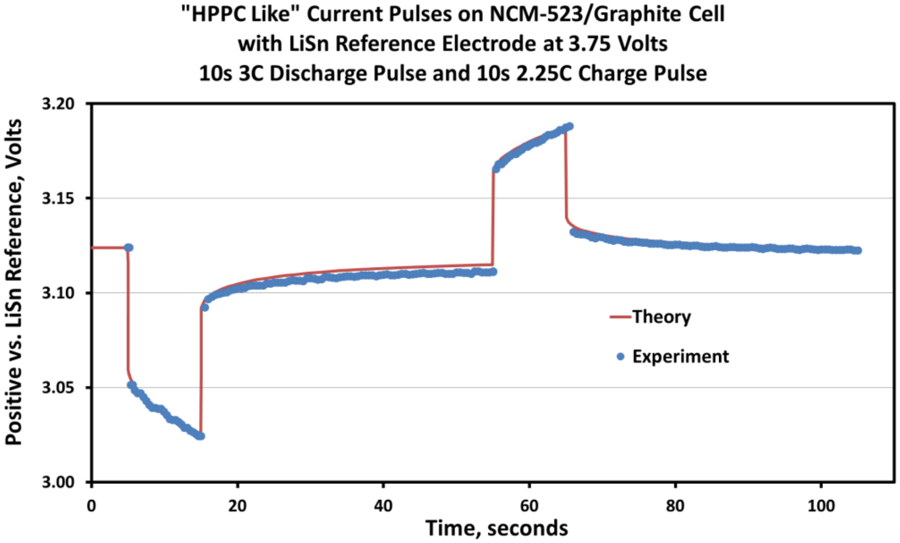
- Generally, NCM-523 electrode performance comparable to NCA.
- Characteristic large high frequency circular arc on NCM materials associated with electronic contact resistance.
- Bulk lithium diffusion coefficient for NCM-523 relatively high (i.e. on the order of 10^{-10} cm^2/s).

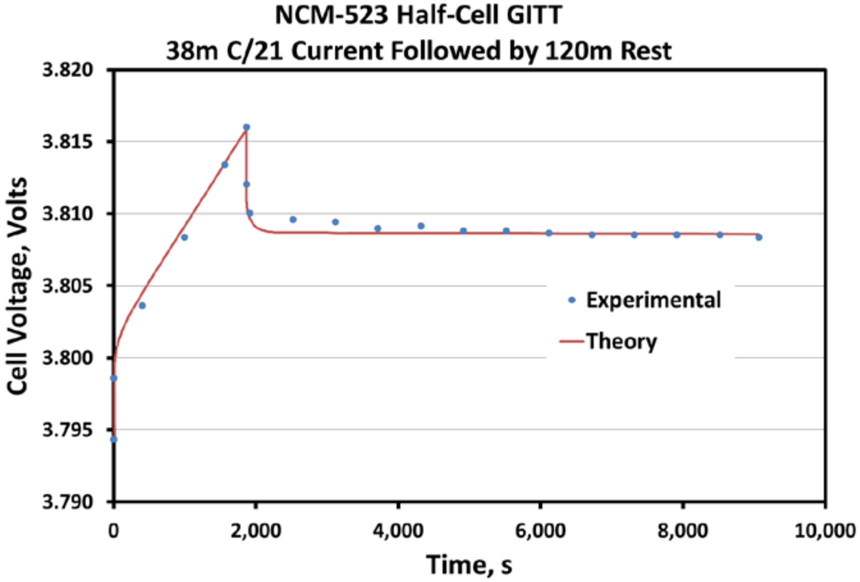
Positive Electrode	Active Material Surface Layer and Bulk				SEI Film on Active Material			Electronic Contact Resistance	Kinetic and Capacitance			
	a	D_{si}	D_{sb}	K_s	D_+	κ_f	c_+	σ_p	i_o	C_c	C_d	C_f
	cm^{-1}	cm^2/s			cm^2/s	$\Omega^{-1}cm^{-1}$	M	Ωcm^2	mA/cm^2	$\mu f/cm^2$		
NCA	8900	5.5×10^{-11}	4.0×10^{-11}	5.0	3.0×10^{-9}	1.0×10^{-7}	7.0×10^{-3}	0	0.49	0	45	0.3
NCM-523	6797	8.0×10^{-12}	3.0×10^{-10}	1.5	5.0×10^{-9}	1.3×10^{-7}	8.0×10^{-3}	70	0.60	0.045	60	0.3
LMR-NMC	48000	2.0×10^{-12}	2.0×10^{-12}	5.5	1.5×10^{-8}	2.3×10^{-8}	4.3×10^{-4}	1800	0.045	0.009	20	0.09

Description of electrochemical model in *Journal of The Electrochemical Society*, **162** (4) A559 (2015)

Electrochemical Modeling Studies on NCM-523 Electrodes: Initial Evaluation of DC Electrochemical Studies

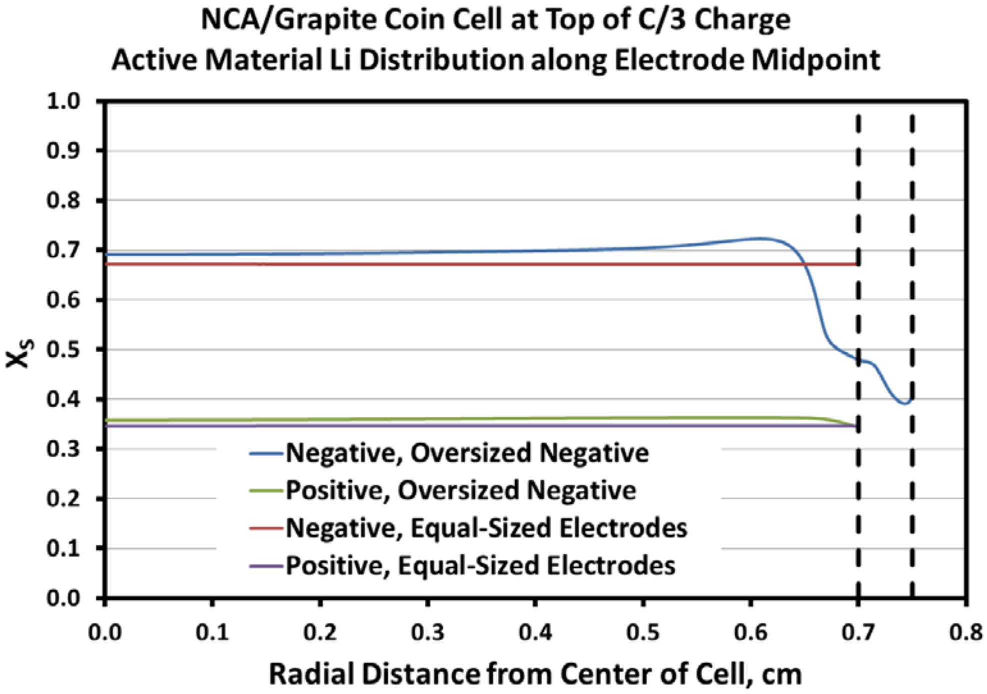
- Model parameters obtained from fitting short current pulse data (e.g. HPPC data at top) are in good agreement with parameters developed from impedance studies.
- Longer time charge/discharge studies (e.g. GITT data at bottom) exhibits a slow relaxation that requires a much lower bulk lithium diffusion coefficient to fit with a standard intercalation active material model.
- Previous studies on LMR-NMC electrodes suggest the slow relaxation may be associated with the Li_2MnO_3 domains in the nanometer scale composite structure of the NCM-523





Electrochemical Modeling was Utilized to Examine Why Oversizing the Negative Electrode in Coin Cell Tests Significantly Enhances Reproducibility

- Model simulations indicate that perfectly aligned equal-sized electrode coin cells should have a much more uniform current distribution than coin cells with oversized negative electrodes as indicated by the lithium distribution in the electrodes.
- However, even aligning the electrodes to within a 0.1 mm tolerance represents a huge challenge on hand assembled coin cells.



- The greater the electrodes are misaligned, the more the current distribution becomes non-uniform, causing greater variation in the cell-to-cell performance.
- Conversely, the oversized negative electrode coin cells essentially have a buffer already built-in to deal with some misalignment. Effectively, the uniformity of the current distribution has been sacrificed for improved reproducibility.

Summary

- Established standard protocol to track performance changes in lithium-ion cells. Protocol has been applied to 30 cells each containing the following chemistries
  - NCM523/Graphite (3.0-4.4 V) ; NCA/Graphite (3.0-4.4 V); HE5050/Graphite (2.5-4.4 V)
- Data obtained from these baseline cells indicate the following:
  - Capacity loss trends: HE5050 > NCM523 > NCA
  - Impedance rise trends: HE5050 > NCM523 > NCA
- A "bootstrap methodology" has been developed to evaluate performance degradation characteristics resulting from modifications to baseline chemistry
  - For a sample size of $n = 5$ any modification to the NCM523 baseline chemistry should yield a normalized capacity loss of less than ≈ 0.09 and an impedance rise of less than $\approx 5.2\ \Omega\ \text{cm}^2$ to be considered an improvement.
- Cycling experiments have been initiated in cells containing reference electrodes to Identify electrode contributions to cell performance degradation
  - For NCM523//Graphite couples, Initial data indicate that impedance of the positive is larger than that of the negative electrode.
- Electrochemical Modeling Studies on NCM-523 Electrodes have been initiated
  - Bulk lithium diffusion coefficient for NCM-523 is on the order of 10^{-10} cm^2/s).
  - Electrode misalignment makes the current distribution more non-uniform, causing greater variation in cell-to-cell performance

Future Work

- Complete electrochemical evaluation of baseline cell couples
- Develop performance metrics from the baseline cell data to evaluate modifications to cell chemistry, which may include the use of electrode coatings and electrolyte additives
- Develop electrochemical models that highlight causes of cell performance degradation and recommend solutions to improve cell performance and life
- Disseminate standard protocols to partnering institutions and individuals
- Document data in reports and peer-reviewed articles