Electrochemistry Cell Model

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Project ID# ES031

Overview

Timeline

- Start: October 2008
- Finish: September 2012
- Future: Will continue to support ABR programs
  - Voltage fade
  - Electrochemical couples
  - ABR facilities

Budget

- Total project funding
  - 100% DOE
- FY2011: $400K
- FY2012: $400K

Barriers

- Development of a safe cost-effective PHEV battery with a 40 mile all electric range that meets or exceeds all performance goals
  - Interpreting complex cell electrochemical phenomena
  - Identification of cell degradation mechanisms

Partners (Collaborators)

- Daniel Abraham, Argonne
- Wenquan Lu, Argonne
- Andrew Jansen, Argonne
- Kevin Gering, INL

Objectives, Milestones, and Approach

- The objective of this work is to correlate analytical diagnostic results with the electrochemical performance of advanced lithium-ion battery technologies for PHEV applications
  - Link experimental efforts through electrochemical modeling
  - Identify performance limitations and aging mechanisms
- Milestones for this year:
  - Complete conversion of existing models into gPROMS (Complete)
  - Initiate parameter estimation of LMR-NMC cathodes (Complete)
  - Complete SEI growth model (Delayed due to focus on cathode)
- Approach for electrochemical modeling activities is to build on earlier successful characterization and modeling studies in extending efforts to new PHEV technologies
  - Expand and improve database and modeling capabilities

Major Accomplishments and Technical Progress

- Initiated model development and parameter refinement of LMR-NMC cathode materials, $xLi_2MnO_3(1\text{-}x)LiMO_2$
- Initial fits of Toda HE5050 Cathode AC Impedance
- Simulation of most likely sources of impedance growth
- Measurement and early model development of
  - Hysteresis and path dependence in open-circuit voltage curve
  - Slow relaxation process observed in GITT studies
- Completed conversion of models to more advanced differential equation solver software (PSE gPROMS)

Description of 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
- Lithium diffusion and possible phase change in active particles included, along with multiple particle fractions
- The system of coupled differential equations are solved numerically
- Model parameters determined independently (e.g. electrolyte parameters are supplied by Kevin Gering’s Advanced Electrolyte Model)

Electrochemical Model Effectively Used to Examine Interfacial and Diffusional Phenomena in Intercalation Positive Electrode Active Materials

Lithium-Ion Electrochemical Model

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

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

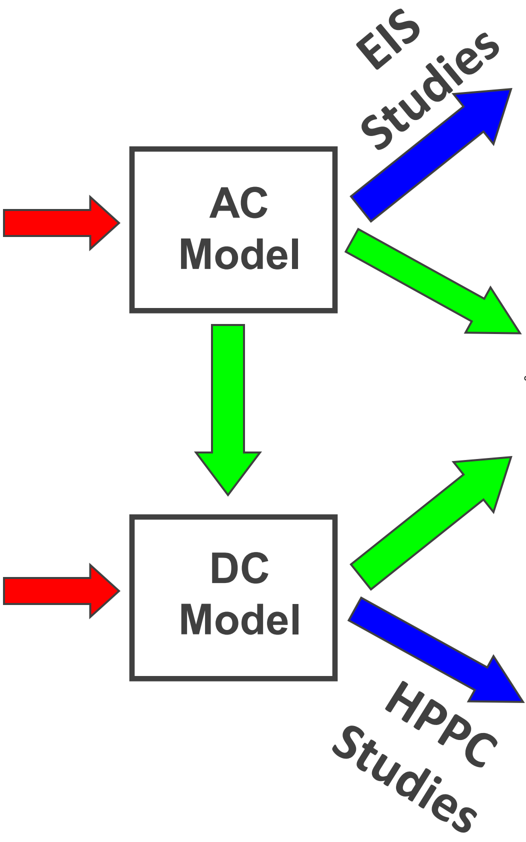
$$\frac{\partial i_2}{\partial x} = Fz_+\sum_k a_k j_{kn} \qquad I = i_1 + i_2 \qquad i_1 = -\sigma_{eff}\frac{\partial\Phi_1}{\partial x}$$

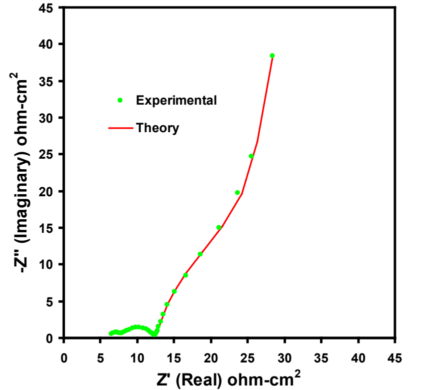
$$\frac{\partial c_+}{\partial t} = D_+\left(\frac{\partial^2 c_+}{\partial y^2}\right) \qquad \eta_f = \frac{i_n\delta_f}{\kappa_f} + \frac{RTs_+}{nF}\ln\frac{c_+|_{electrolyte}}{c_+|_{active\ material}}$$

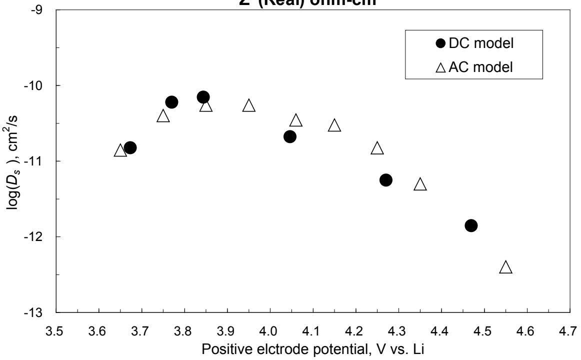
$$\frac{\partial c_{Si}}{\partial t} = D_{Si}\left(\frac{\partial^2 c_{Si}}{\partial y^2}\right) \qquad \frac{\partial c_{Sb}}{\partial t} = \frac{\partial}{\partial z}\left(D_{Sb}\frac{\partial c_{Sb}}{\partial z}\right)$$

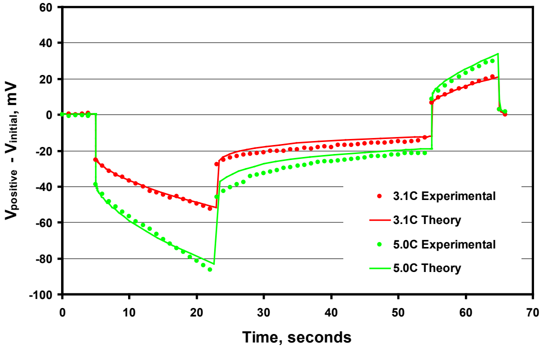
$$i_n = i_0\left(\frac{c_+}{c_{+,ref}}\right)^{\alpha_A}\left(\frac{c_{Ti}-c_{Si}}{c_{Ti}-c_{Si,ref}}\right)^{\alpha_A}\left(\frac{c_{Si}}{c_{Si,ref}}\right)^{\alpha_C}\left\{e^{\left[\frac{\alpha_A F\eta_K}{RT}\right]} - e^{\left[-\frac{\alpha_C F\eta_K}{RT}\right]}\right\}$$

$$\eta_R = \sigma_P z_+ F j_n$$









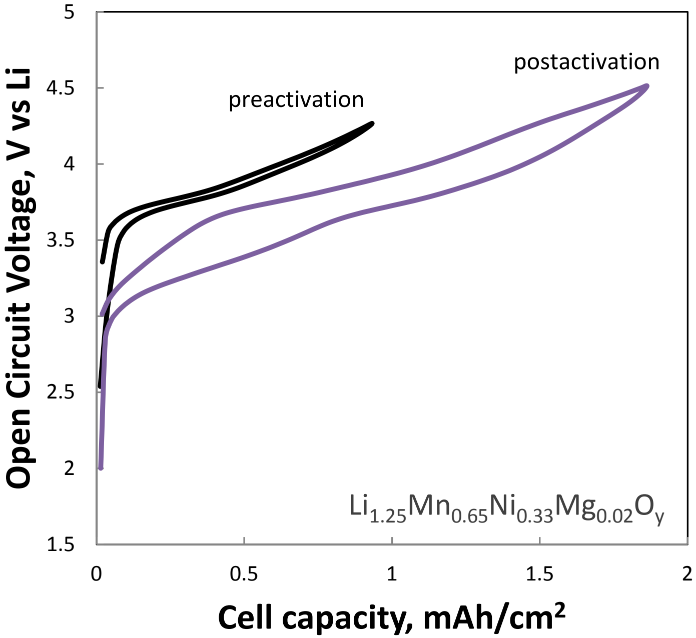
- Diffusion coefficient obtained from GITT studies using DC model shows strong correlation with AC modeling studies

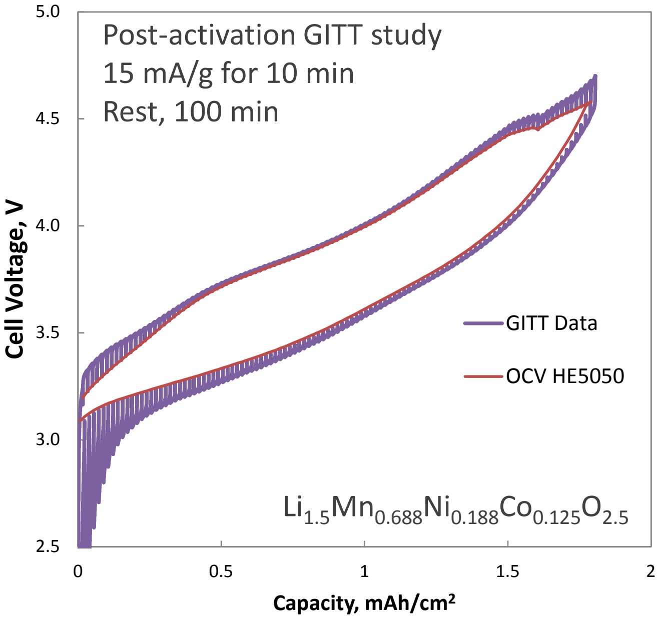
Focus of current work: Positive Electrode

- Electrochemical couples ABR-1 and ABR-2 use graphite and LMR-NMC, $x\mathrm{Li_2MnO_3}(1-x)\mathrm{LiMO_2}$
- LMR-NMC is currently the least understood of the couple
- Initial diagnostic effort has singled out LMR-NMC cathode
  - Largest source of impedance rise leading to capacity loss at relevant current densities
  - Voltage fade: change in open-circuit voltage (OCV) with aging
  - Instability of the electrolyte at the oxidizing potentials
- Path forward
  - Understand OCV function after activation
  - Fit parameters with GITT and EIS (DC and AC models)
  - Inform aging studies by exercising model

Measurement of Open-Circuit Voltage Function

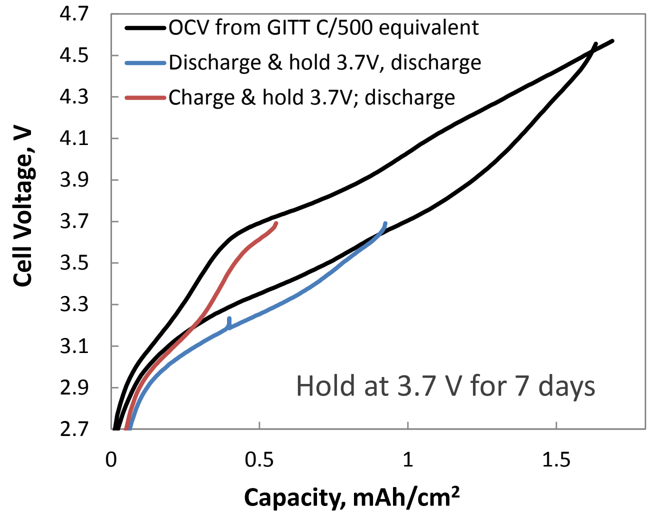
- Use slow cycling or GITT study to determine open-circuit voltage as function of lithium concentration
- Large hysteresis observed in LMR-NMC cathodes after activation Li_2MnO_3 domains in $xLi_2MnO_3(1\text{-}x)LiMO_2$
- Standard layered oxides (e.g. NCA) do not show this behavior

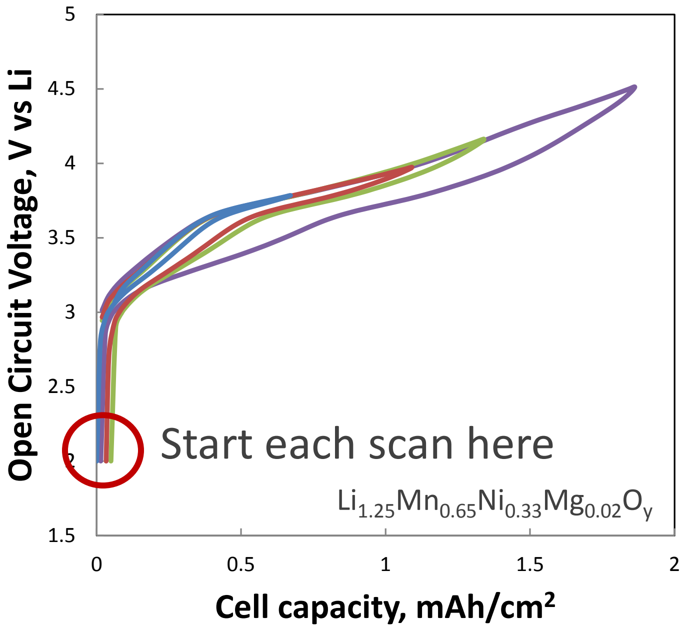


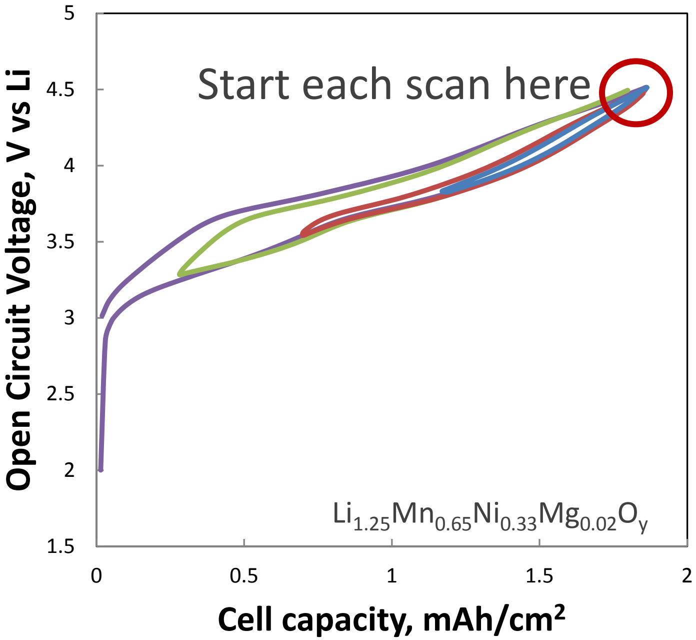


Hysteresis and Path-Dependence in OCV Curve

- Unknown physical process leading to stable hysteresis
- Scanning curves show shift from one boundary to other depends on voltage
- Current hypotheses: two set of vacancies (sites) or reversible structural change

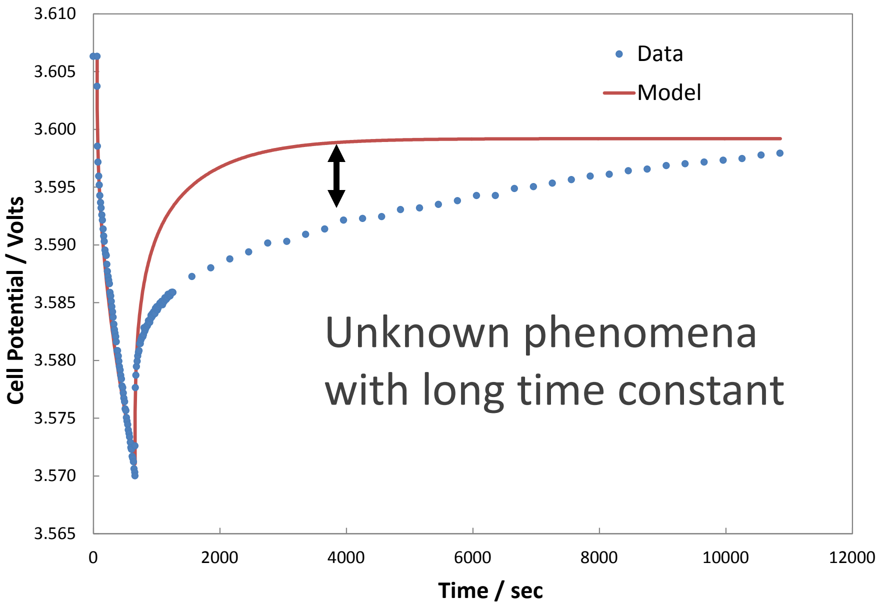






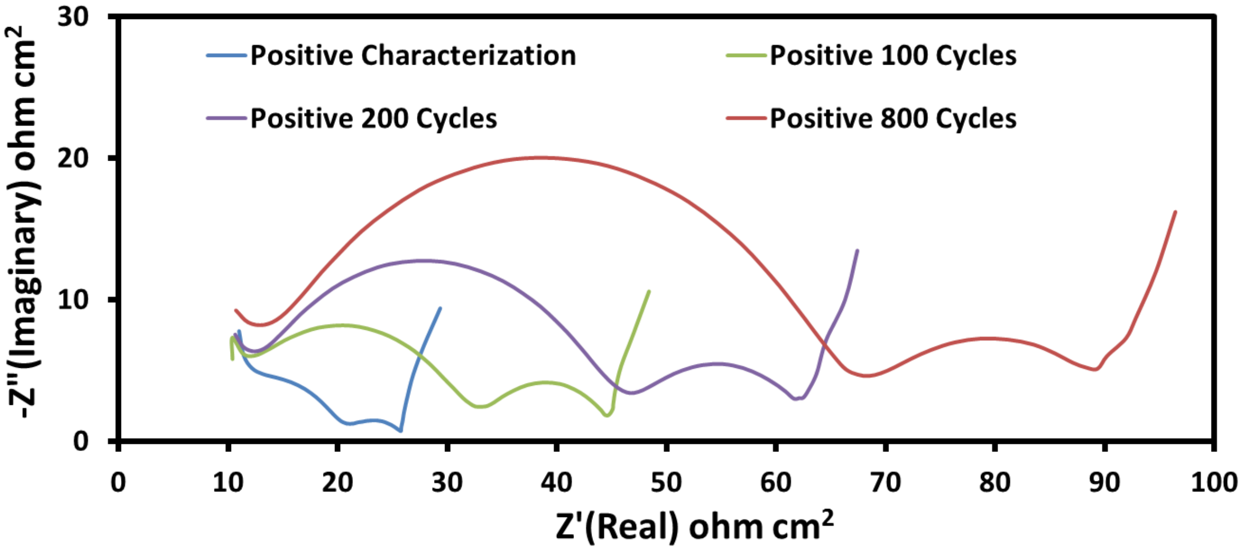
DC Model: GITT Analysis

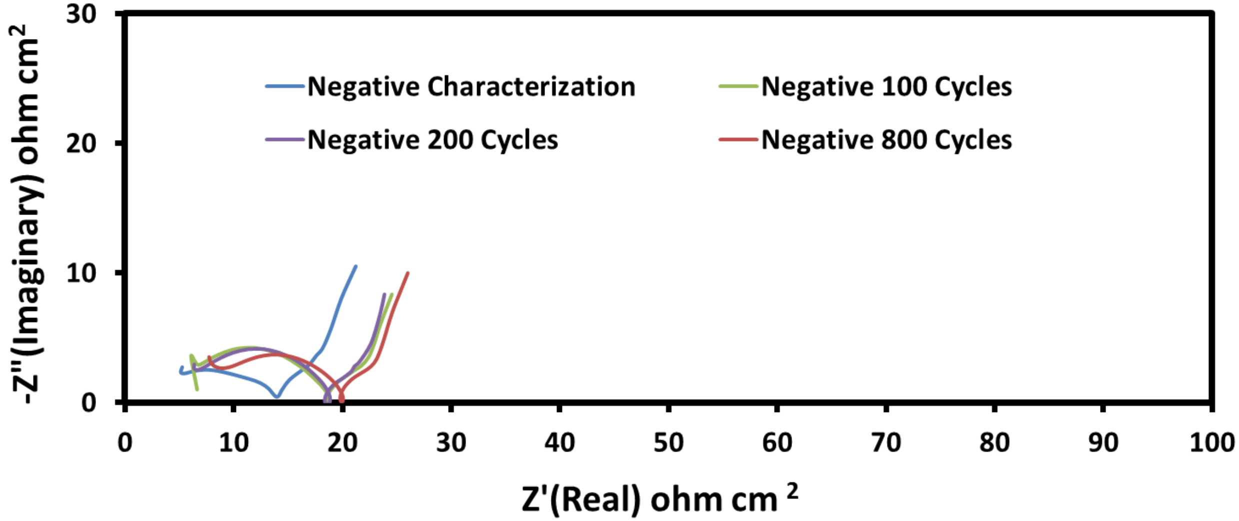
- Unknown slow relaxation process not accounted for with current physical model of standard intercalation material
- Fitted diffusion coefficient << smaller than NCA and NCM
  - 10^{-14} as compared to 10^{-10}-10^{-11} cm^2/s
  - Must capture physics generating slow time constant in DC model
- Evaluate interfacial behavior with AC Model

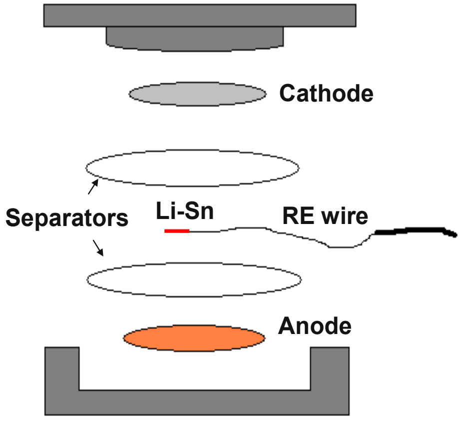


Unknown phenomena with long time constant

Major Source of Impedance Rise in LMR-NMC/Graphite Cells is Interfacial Impedance at the Positive Electrode

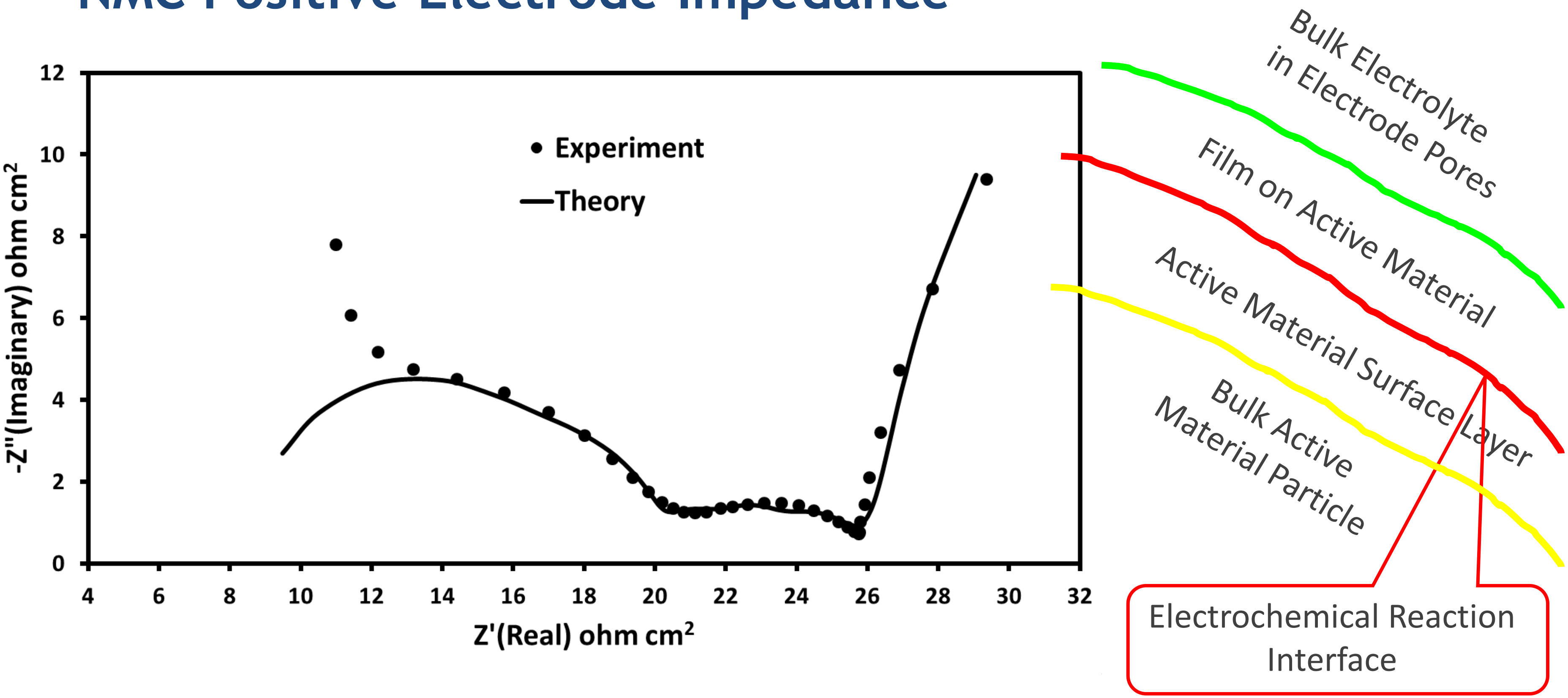






- Diagnostic aging studies taken on LMR-NMC positive and graphite negative reference electrode cell (no electrolyte additives).
- Impedance data (100 kHz-10 mHz) taken at 3.75 volts and 30°C.
- Focus of modeling efforts on positive electrode.

AC Model: Electrochemical Model Simulation of LMR-NMC Positive Electrode Impedance



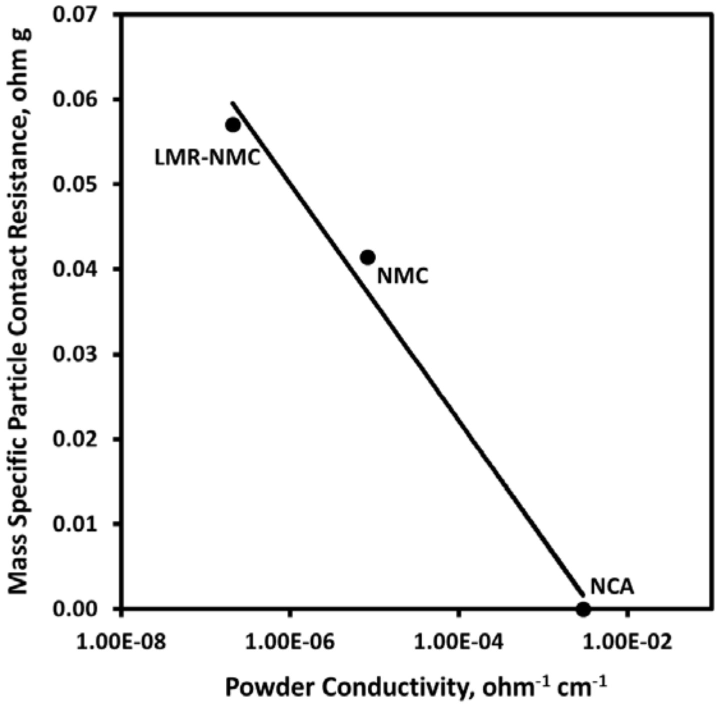
- Impedance dominated by high frequency interfacial arc associated with electronic contact resistance between oxide active material and conducting carbon additive.
- Multiple particle fractions of oxide active material used to improve fit of low frequency Warburg diffusional impedance.

Comparison of Positive Electrode Interfacial and Oxide Active Material Parameters

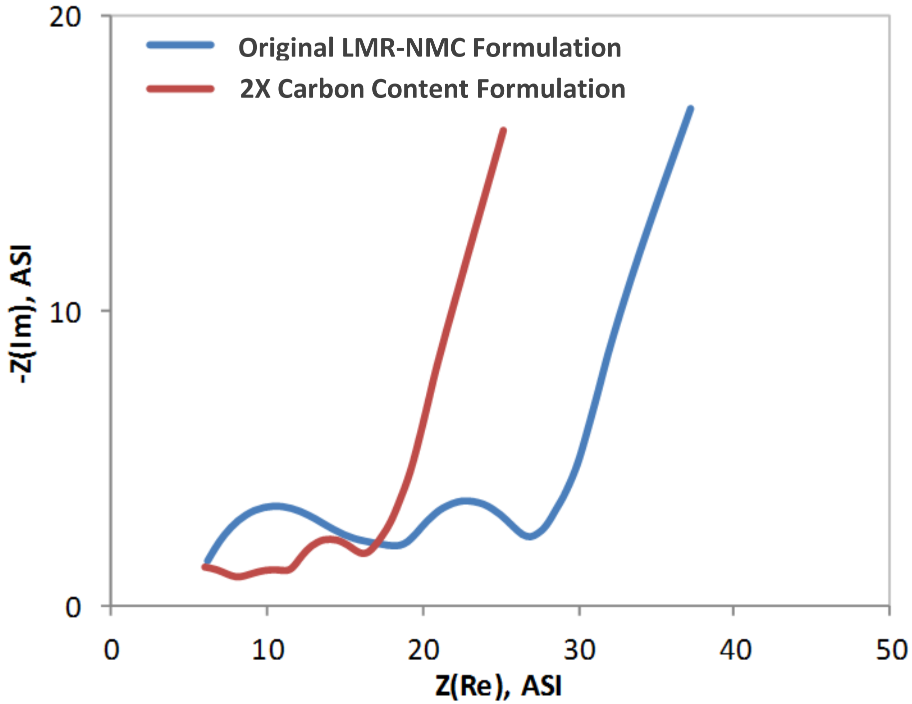
	Active Material Surface Layer				**SEI Film on Active Material**			**Electronic Contact Resistance**	**Kinetic and Capacitance**			
Parameter	a	D_{si}	D_{sb}	K_s	D_+	κ_f	c_+	σ_p	i_o	C_c	C_d	C_f
	cm^{-1}	cm^2/s			cm^2/s	$\Omega^{-1}cm^{-1}$	M	Ωcm^2	mA/cm^2	$\mu f/cm^2$		
NCA	8900	10^{-10}	10^{-10}	5	10^{-9}	10^{-7}	10^{-2}	0	1	0	40	0.3
NMC	7700	10^{-11}	10^{-11}	1	10^{-9}	10^{-7}	10^{-2}	170	0.1	0.06	100	0.5
LMR-NMC	48000	10^{-12}	10^{-12}	6	10^{-8}	10^{-8}	10^{-3}	1500	0.1	0.005	20	0.1

- LMR-NMC assumed to have thicker SEI film thickness (100 vs. 40 nm) and thinner oxide surface layer thickness (5 vs. 10 nm) than NCA
- The LMR-NMC positive electrode has a high electronic contact resistance.
- The lithium diffusion coefficient in LMR-NMC bulk is an order-of-magnitude lower than that of conventional NMC material; although, much closer than DC prediction
- **The LMR-NMC positive electrode's general interfacial characteristics are somewhat worse than the other oxides, but are offset by the higher surface area (~ 6X).**

The Lower Electronic Conductivity of NMC Electrode Active Materials Make Them More Challenging

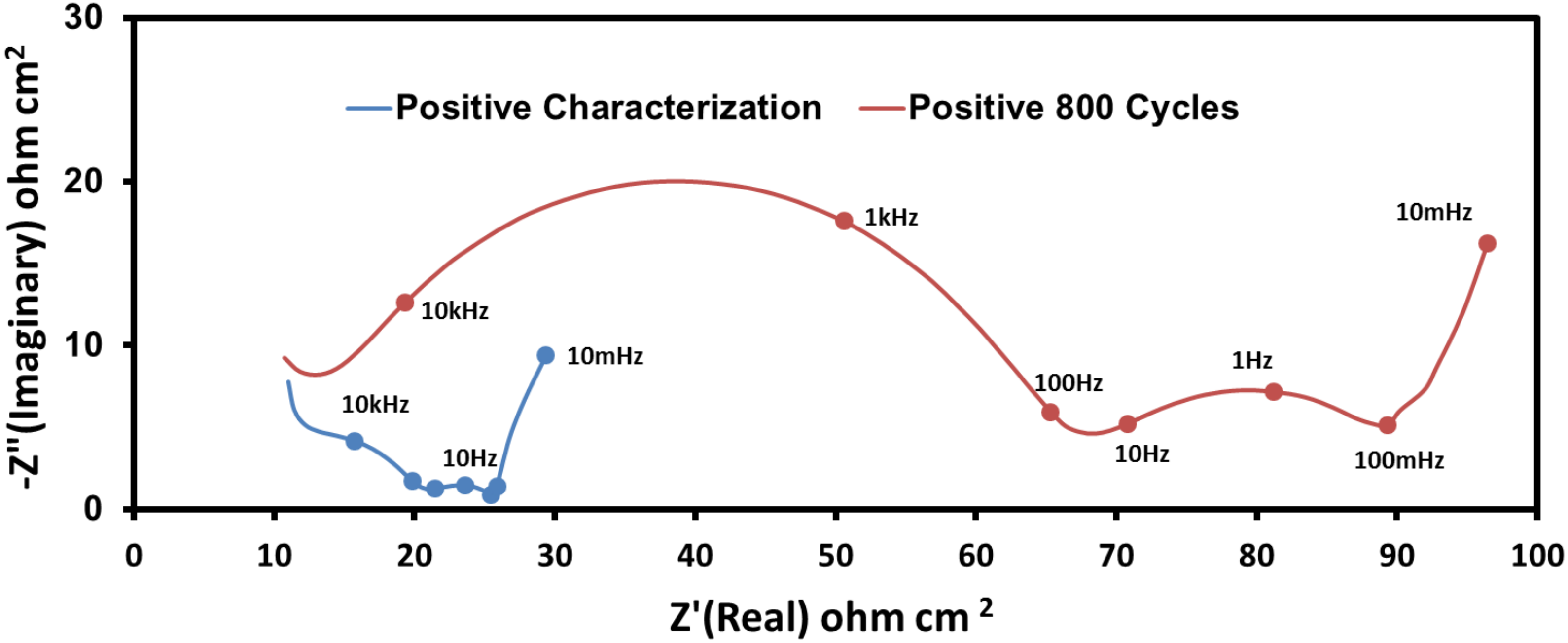


LMR-NMC/Graphite Full Cell EIS Data



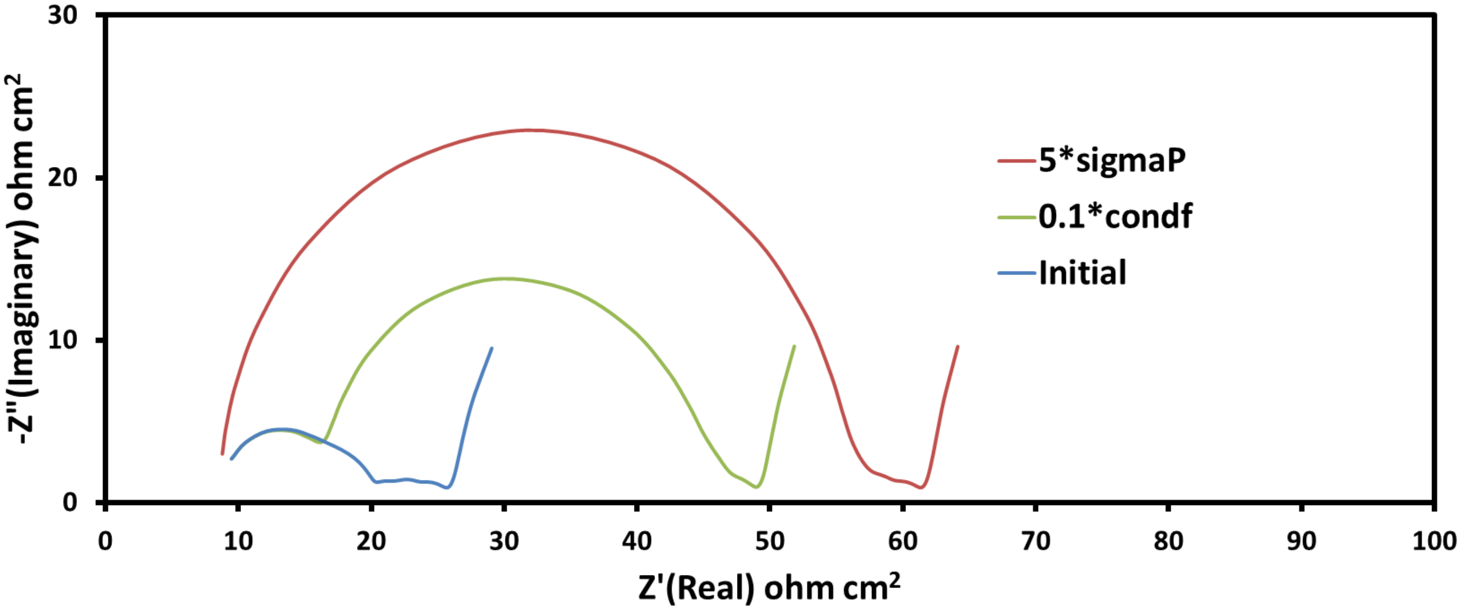
- Modeling studies indicate a correlation between the powder electronic conductivity of active materials and their particle contact resistance in the cell
- Limited electrode formulation optimization studies suggest that it is possible to significantly reduce the contact resistance associated with NMC materials

EIS Aging Study on the LMR-NMC Positive Electrode



- The positive electrode impedance growth with aging is dominated by the high frequency interfacial arc, but the mid frequency interfacial arc and the low frequency Warburg impedance also increases.
- The interfacial impedance shifts to lower frequencies as the cell ages. This is generally the case for parallel RC circuits or Warburg diffusive phenomena where there is a significant increase in impedance.

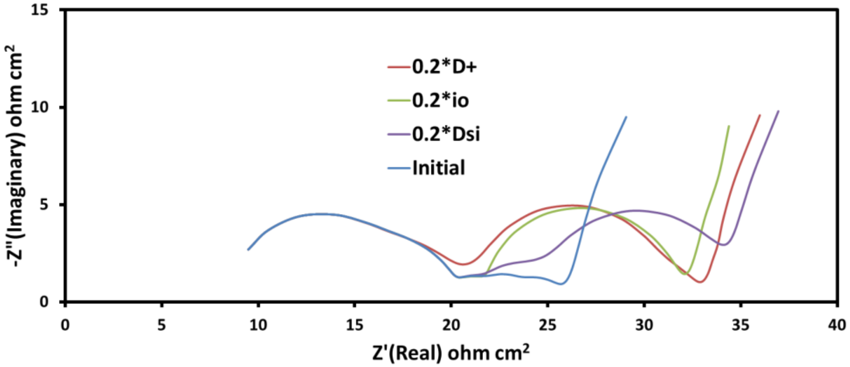
Aging of LMR-NMC Positive Electrodes: Increasing size of the high frequency interfacial arc

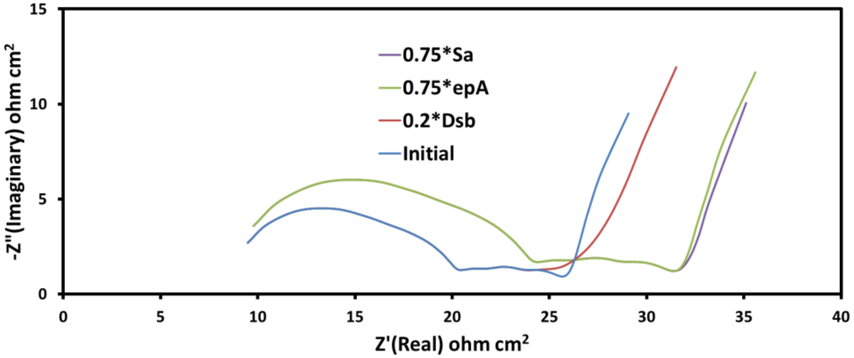


- Based on the initial assumption that the majority of the high frequency arc impedance is associated with the electronic contact resistance between the oxide and the conductive carbon (σ_p), it is also the likely source of the increasing impedance.
- The only other possible source in the electrochemical model with the present parameter set is the SEI resistance (κ_f).
- Because of the high characteristic frequency (~10 kHz) of the arc it is possible that an electronic contact resistance at the electrode/current collector interface is responsible, at least partially, for the increase in impedance.

Aging of LMR-NMC Positive Electrodes : Increasing impedance in lower frequencies

- Three physical processes affecting mid-frequency interfacial arc
  - Butler Volmer kinetics (i_o)
  - Diffusion through the SEI (D_+)
  - Diffusion in oxide surface layer (D_{si}).
- Experimental observations and model sensitivities point to growth of SEI layer & slowing B-V kinetics
- Changes in Warburg impedance could derive from possible changes in the bulk oxide material
- Alternatively, a loss of 25% of active materials (0.75epA) or surface area (0.75Sa) would increase impedance in both mid and low frequency response





Future Work

- Transitioning project to new ABR format
  - Supporting Voltage Fade project
  - Supporting development of Electrochemical Couples
  - Supporting ABR facilities (CFF, MERF, Post-Test)
- Develop understanding of slower time constant phenomena in LMR-NMC cathode materials
  - Faster time constant behavior fits in current modeling approach
- Refine negative electrode SEI growth model
- Milestones for next year
  - Understand slow relaxation in GITT study
  - Understand hysteresis and path dependence in OCV curve
  - Initiate voltage fade model

Summary

- The objective of this work is to correlate analytical diagnostic results with the electrochemical performance of advanced lithium-ion battery technologies for PHEV applications
- Approach for electrochemical modeling activities is to build on earlier successful characterization and modeling studies in extending efforts to new PHEV technologies
- Technical Accomplishments
  - Simulated AC impedance of LMR-NMC cathodes
  - Propose most likely sources of impedance rise for ABR-1 cathode
  - Analyzed hysteresis and path-dependence in OCV curve
  - Identified presence of slow relaxation process of currently unknown physical origin.
- Future plans include the continued development of PHEV focused electrochemical models, further development of models examining impedance growth and capacity fade phenomena, and support of other ABR projects

Acknowledgements & Collaborators

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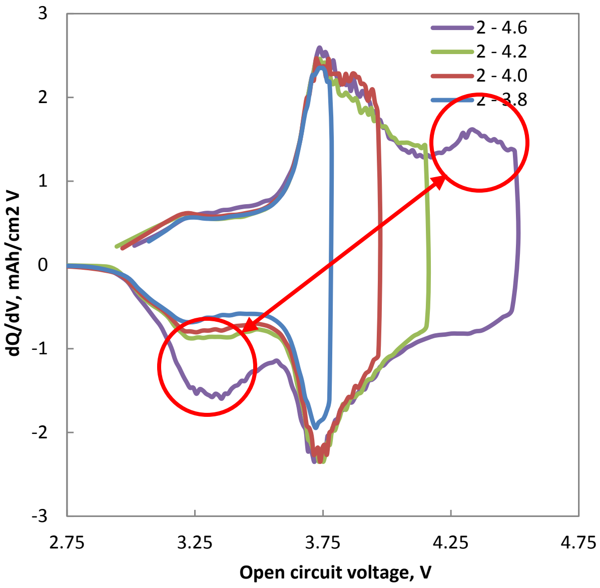
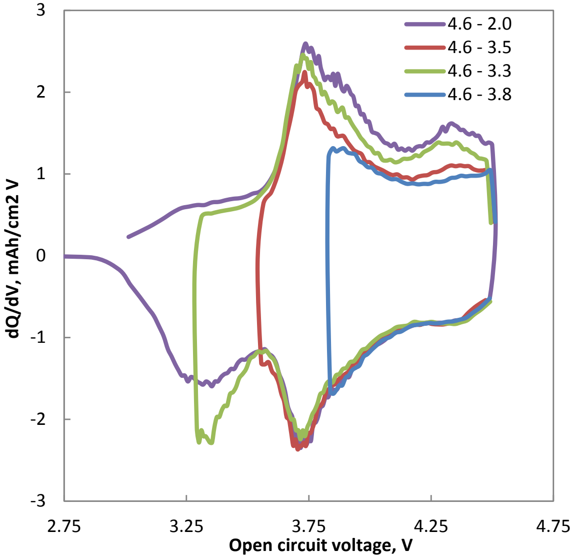
Collaborators:

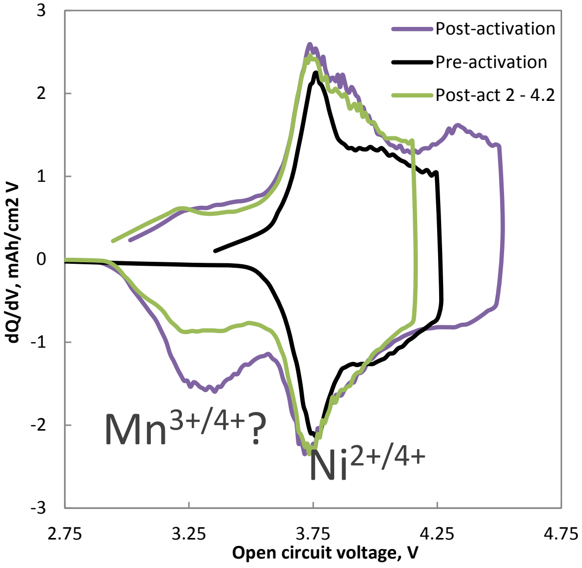
- Argonne National Laboratory
  - Daniel Abraham, Y. Li, M. Bettge
  - Wenquan Lu, Q. Wu, M. Miguel, K. Yassin Lakhsassi
  - Sun-Ho Kang, D. Kim, J. Croy, M.M. Thackeray
  - Andrew Jansen, Chris Johnson, Javier Bareno, Jack Vaughey
  - Huiming Wu, K. Amine
- Idaho National Laboratory
  - Kevin Gering

Technical Back-Up Slides

Examining hysteresis in LMR-NMC cathodes

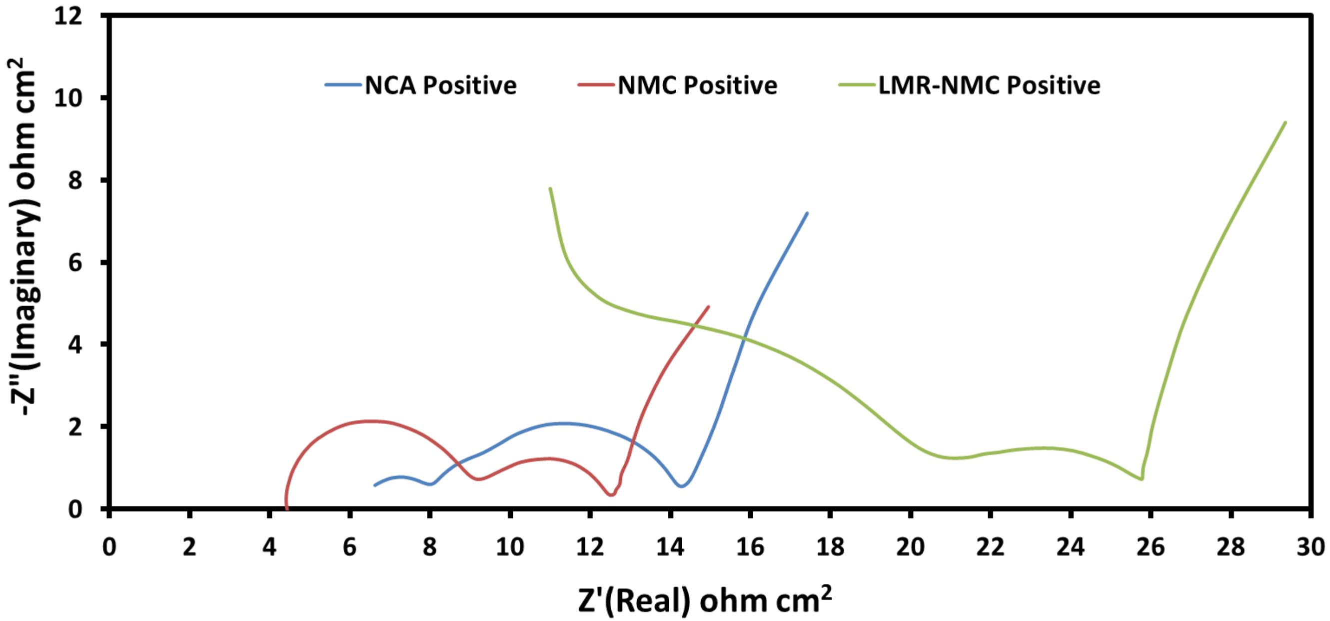






- Analysis of post-activated dQ/dV suggests lithium removed from activated Li_2MnO_3 component above 4.3 V but does not fill these sites until 3.25 V on discharge

Comparison of LMR-NMC Positive Electrode Impedance to Earlier Positive Electrode Studies



- Electrodes have similar formulations and oxide particle size (secondary 9-12 µm average diameter), but vary in active material and loading:
  - NCA: Active Loading 8 mg/cm^2, BET 0.39 m^2/g, Electrode Thickness 35 µm
  - NMC: Active Loading 10.4 mg/cm^2, BET 0.41 m^2/g, Electrode Thickness 55 µm
  - LMR-NMC: Active Loading 6.4 mg/cm^2, BET 2.63 m^2/g, Electrode Thickness 35 µm
- **The LMR-NMC positive electrode's general interfacial characteristics are somewhat worse than the other oxides, but are offset by the higher surface area (~ 6X).**