Electrochemistry Cell Model

Presented by Dennis Dees
Electrochemical Energy Storage
Chemical Sciences and Engineering Division

May 18th-22nd, 2009

Vehicle Technologies Annual Merit Review and Peer Evaluation
Washington, D.C.

Project ID:
esp_01_dees

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

Vehicle Technologies Program

Overview

Timeline

- Start: October 2008
- Finish: September 2014
- <8% Complete
- Ongoing project from HEV Program now emphasizing PHEV applications

Budget

- Total project funding
- 100% DOE
- FY2009: $350K

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
- Sun-Ho Kang, Argonne
- Andrew Jansen, Argonne
- Wenquan Lu, 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 studies
  - Identify performance limitations and aging mechanisms
- Milestones for this year:
  - Develop an efficient parameter fitting technique for model (partially completed)
  - Initiate electrochemical modeling studies on PHEV lithium-ion battery technologies (completed)
  - Develop improved electrochemical model for two-phase active materials (mostly completed)
- Approach for electrochemical modeling activities is to build on earlier successful HEV characterization and modeling studies in extending efforts to PHEV technologies
  - Expand and improve data base and modeling capabilities

Major Accomplishments and Technical Progress

- Equivalent circuit interfacial model developed for streamlining electrode parameter determination
  - Parameter estimation remains primary challenge for examining new intercalation active material electrodes
- Initiated examination of changes in general battery characteristics and testing protocols going from HEV to PHEV battery studies (e.g. thicker electrodes, different operating currents, wider state-of-charge swings, controlled power testing, etc.)
  - Conducted electrode thickness cell performance simulations
- Developed new phase-transition reaction-diffusion lithium transport model for two-phase electrode active materials (e.g. LiC_6, $LiFePO_4$, $LiMn_2O_4$, $Li_4Ti_5O_{12}$)
  - Integrated new two-phase active material model into electrochemical cell model and examined graphite negative electrode as test case
  - Compared new model to earlier shell-core two-phase model

Description of Electrochemical Model

- Phenomenological model developed for AC impedance and DC studies using same constituent equations and parameters
- Combines thermodynamic 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 in active particles and multiple particle fractions
- The system of partial differential equations are solved numerically

Electrochemical Modeling Effort uses AC Impedance Model to Estimate Interfacial and Active Material Parameters

Lithium-Ion Electrochemical Model

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

$$i_2 = -\frac{\kappa\varepsilon}{\tau}\frac{\partial \Phi_2}{\partial x} - \nu RT \frac{\kappa\varepsilon}{F\tau}\left(\frac{s_+}{n\nu_+} + \frac{t_+^o}{z_+\nu_+} \right)\left(1 + \frac{\partial \ln f_\pm}{\partial \ln c} \right)\frac{1}{c}\frac{\partial c}{\partial x}$$
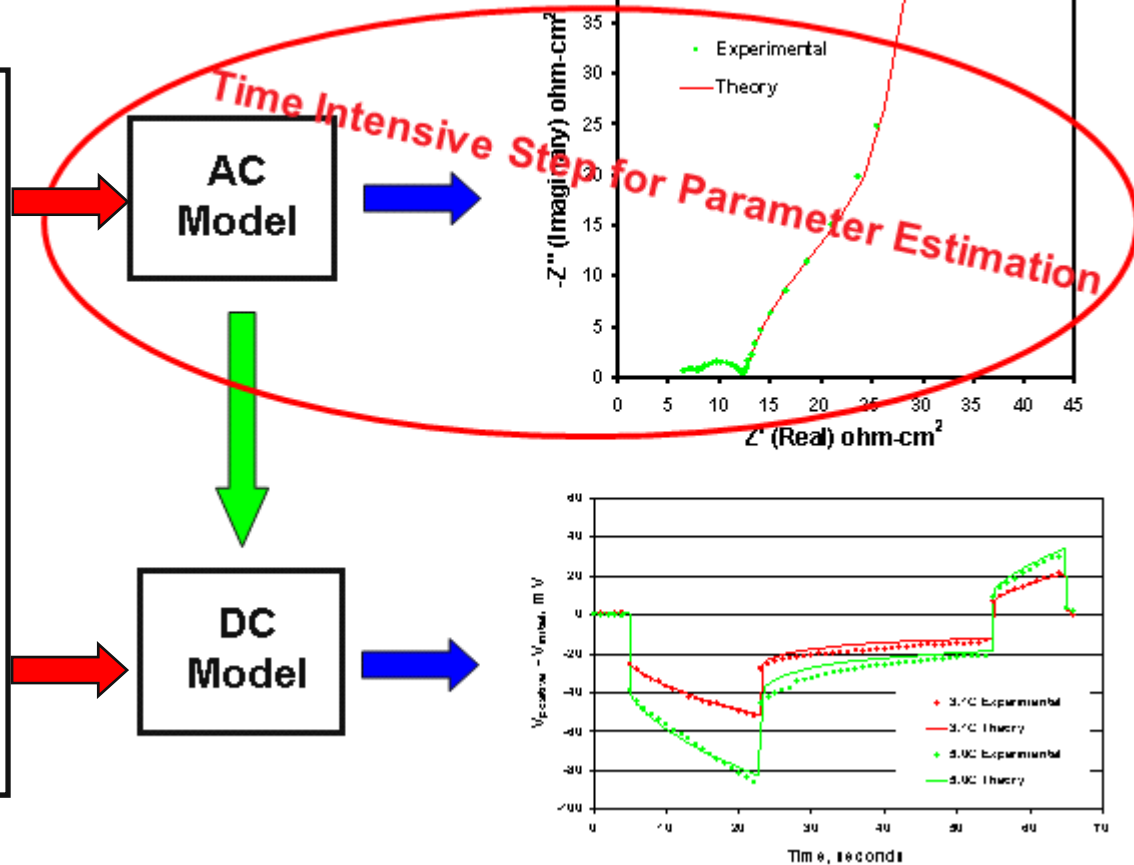
$$\frac{\partial i_2}{\partial x} = F z_+ \sum_k a_k j_{kn} \qquad I = i_1 + i_2 \qquad i_1 = -\sigma_{eff}\frac{\partial \Phi_1}{\partial x}$$

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

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

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

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

AC Model

DC Model

Time Intensive Step for Parameter Estimation

- Experimental
- Theory

Z'' (Imaginary) ohm-cm² vs Z' (Real) ohm-cm²

3.7C Experimental / 3.7C Theory / 5.0C Experimental / 5.0C Theory

V_{Cell Pt} − V_{Initial}, mV vs Time, seconds

■ Electrolyte parameters provided by Kevin Gering at INL utilizing his Advanced Electrolyte Model

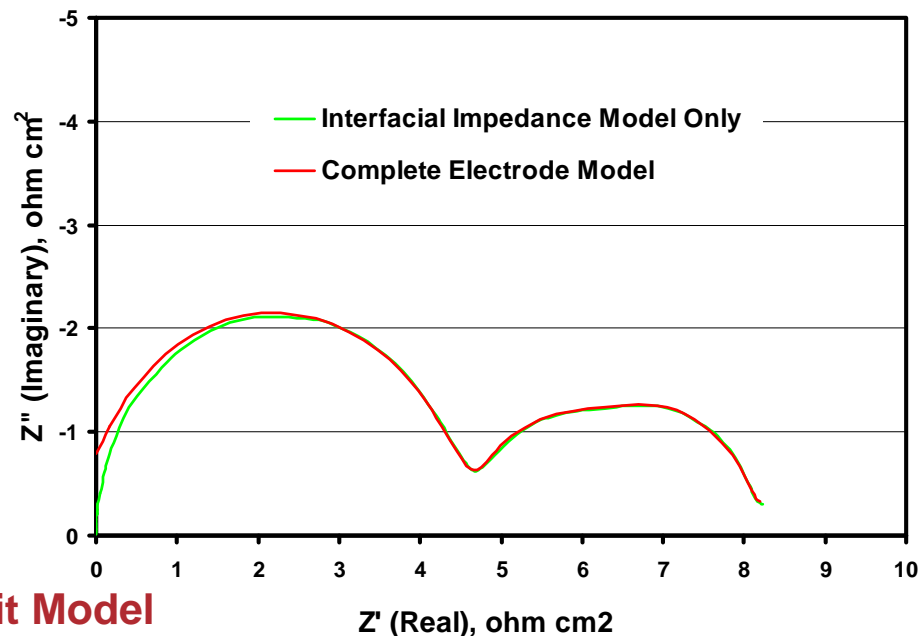# *Equivalent Circuit Model Developed For Streamlining Electrode Interfacial Parameter Determination*

- Interfacial portion of impedance model is similar to full electrode model
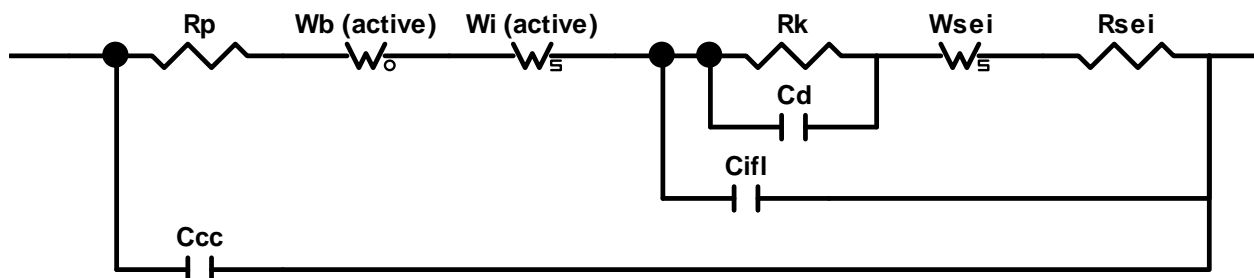 - Relatively uniform current distribution in electrode
- Suggests interfacial parameters can be fit separately without using full impedance model
- Therefore with an equivalent circuit model, existing fitting programs can be utilized to determine interfacial parameters
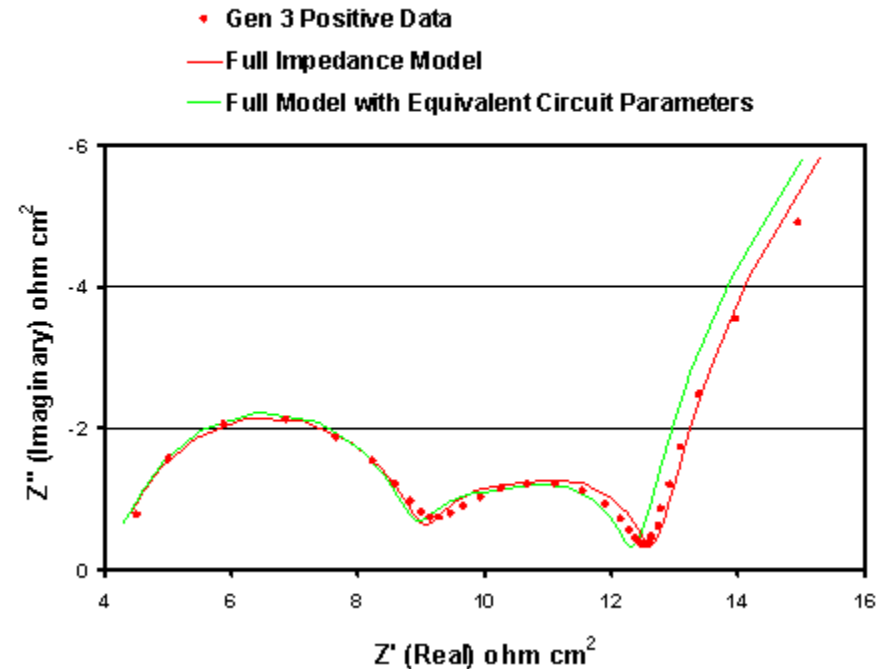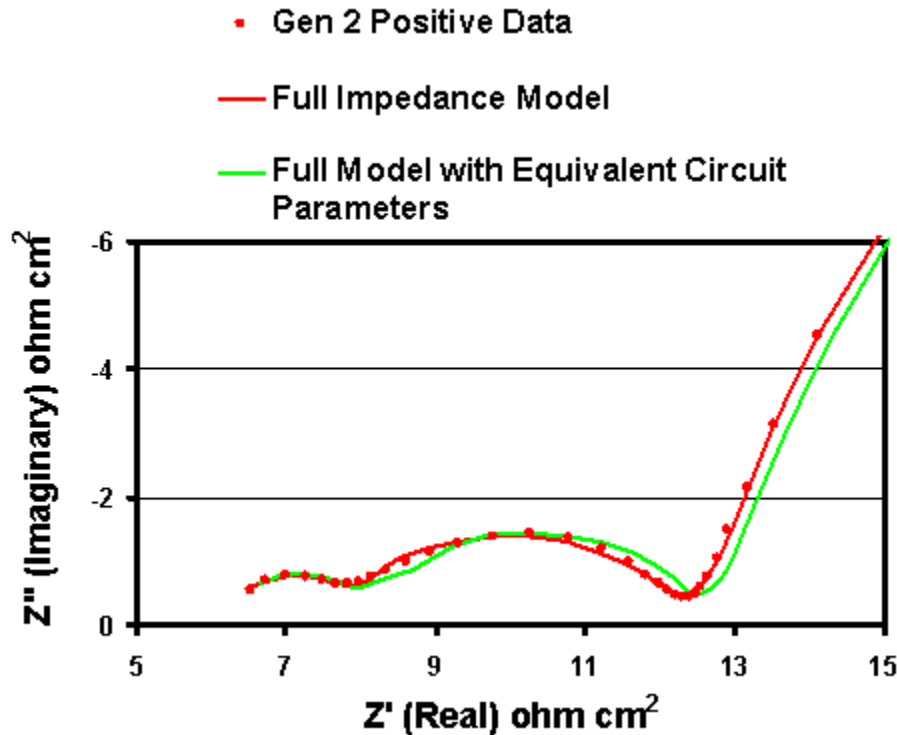
Simulation of Interfacial Impedance for Gen 3 NMC Positive Electrode

Legend: Interfacial Impedance Model Only (green); Complete Electrode Model (red)

Y-axis: Z'' (Imaginary), ohm cm^2

X-axis: Z' (Real), ohm cm2

Equivalent Circuit Model

Circuit elements: Rp, Wb (active), Wi (active), Rk, Wsei, Rsei, Cd, Cifl, Ccc

Equivalent Circuit Model Utilized to Determine Electrode Interfacial Parameters

- Good agreement to full model determined interfacial parameters for Gen2 NCA and Gen3 NMC positive electrodes

- A full impedance model optimization program is needed to efficiently fit the active material parameters associated with the low frequency impedance
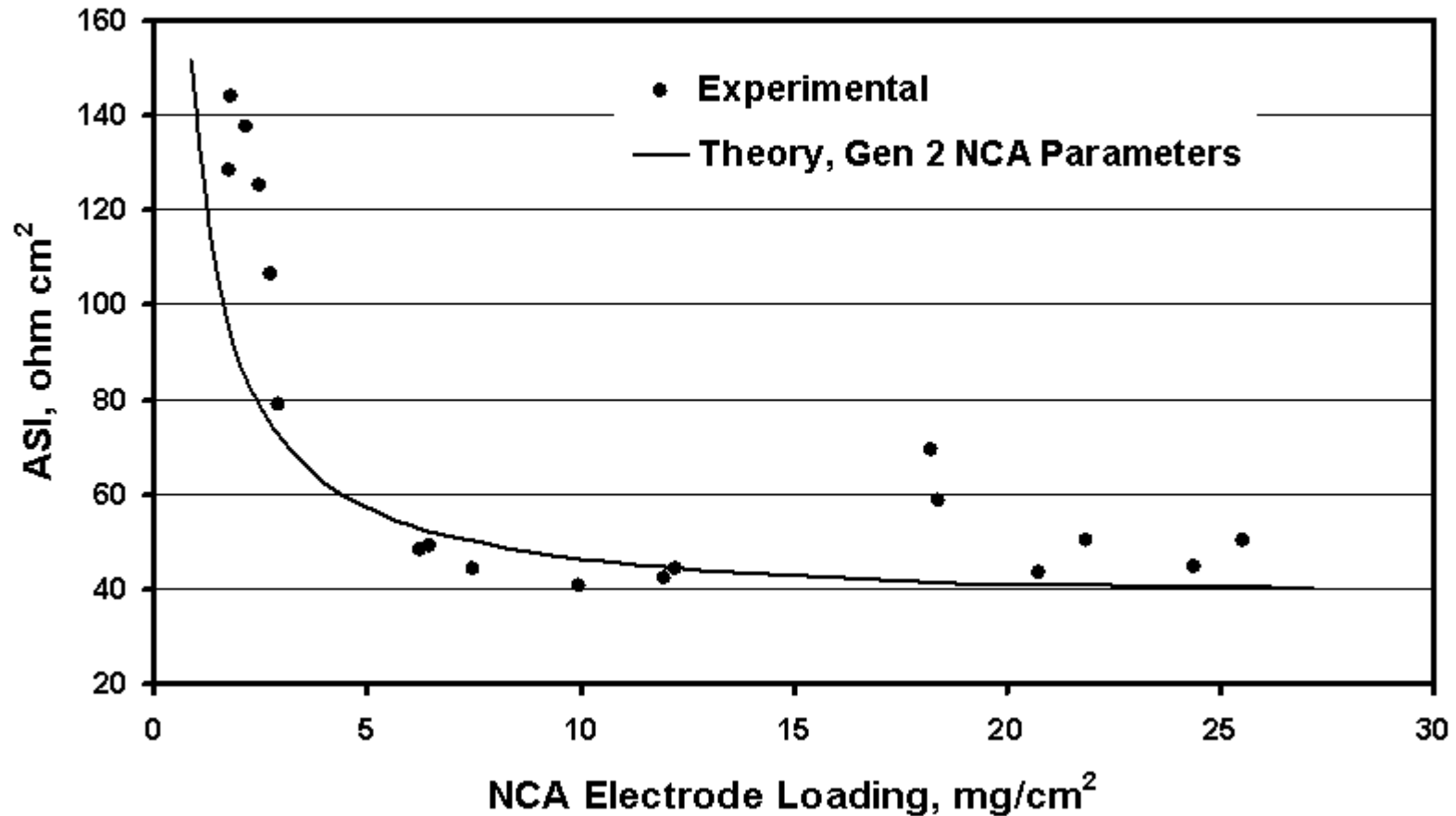
Transition from Modeling HEV to PHEV Battery Technology Studies

- Generally, two levels of model changes
  - Straight forward modifications (e.g. thicker electrodes, wider state-of-charge swings, new testing protocols, etc.)
  - More extensive modifications that involve fundamental changes in the active material and/or interfacial portion of the electrochemical model (e.g. coated active materials, two phase reaction active materials, new degradation mechanisms, etc.)
- PHEV studies initiated with electrode thickness cell performance simulations on a series of NCA positive electrodes using previously established Gen 2 parameters
  - Experimental confirmation of rapid increase in electrode impedance as thickness and active area approach zero
  - Consistently high experimental values at low electrode loadings attributed to partial breakdown of volume averaging assumption
  - Spread in experimental results at high electrode loadings attributed to stability of lithium counter electrode
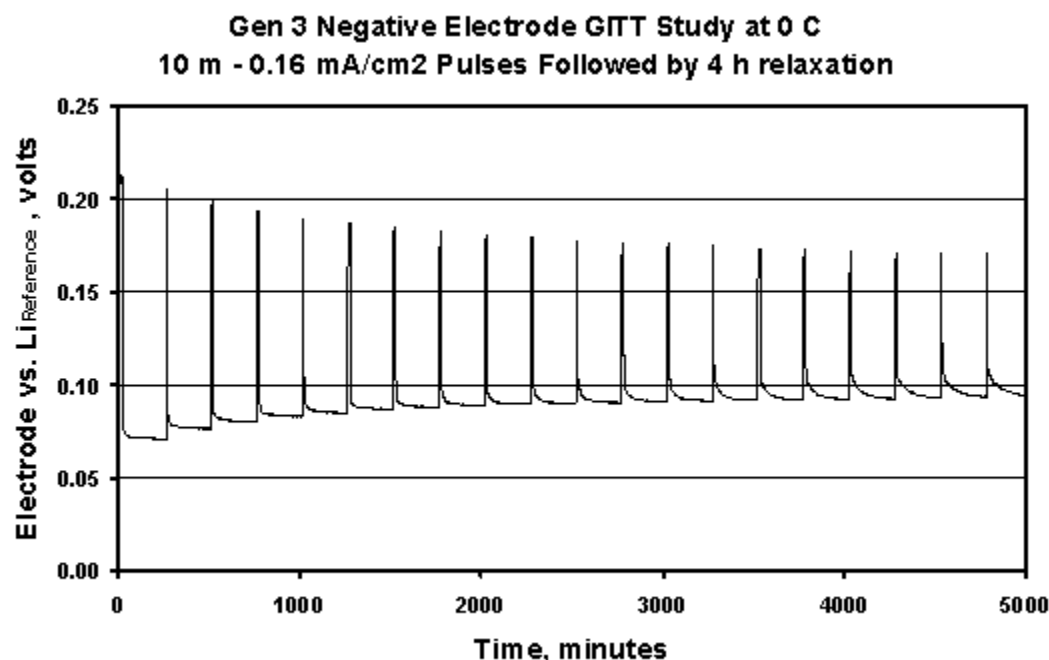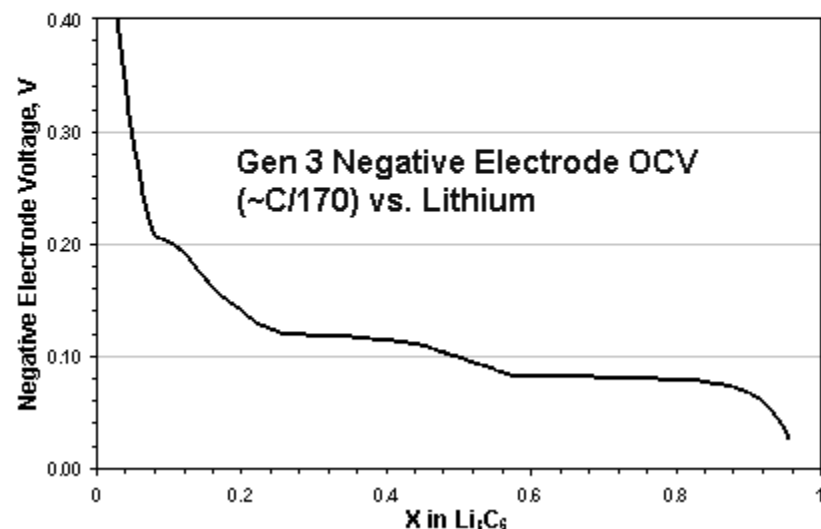
NCA Positive Electrode Loading Study: Half-Cell Experimental Impedance Compares Favorably to Electrochemical Model with Gen 2 Electrode Parameters

Discharge 1.8C HPPC ASI for NCA/Li Cell at 50% DOD
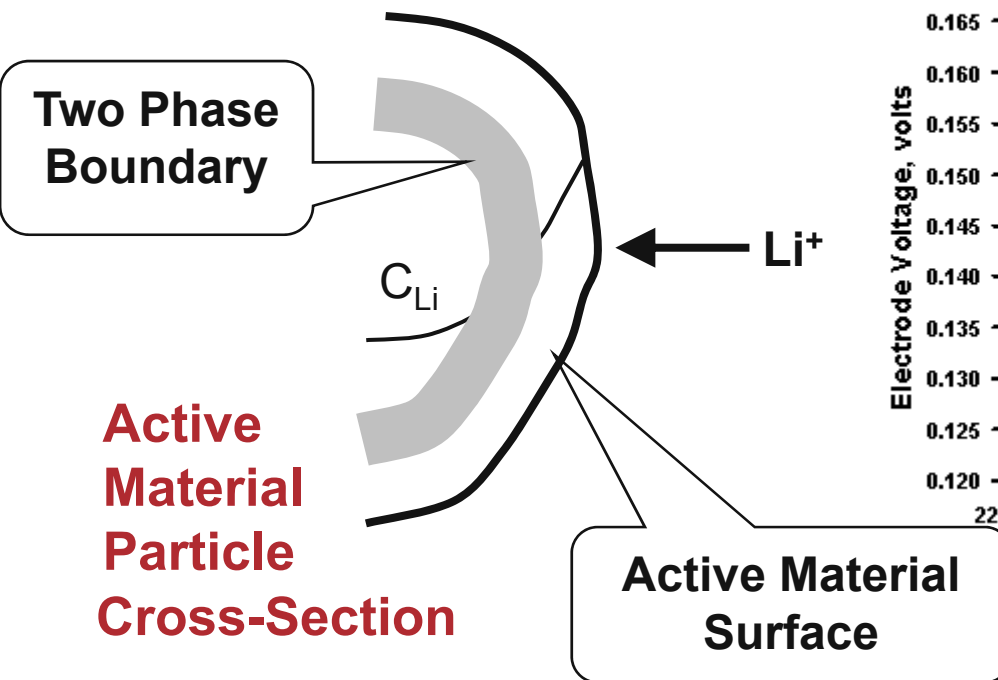
Graphite Negative Electrode Used as a Test Case for New Phase-Transition Reaction-Diffusion Lithium Transport Model for Two Phase Electrode Active Materials
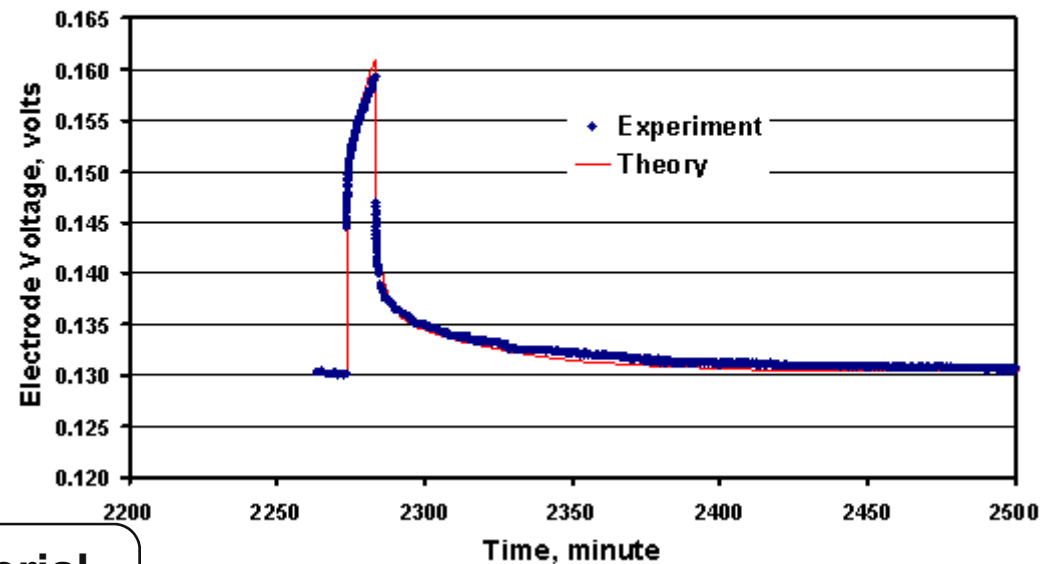
- Staged lithium intercalation into graphite well established in literature with open circuit voltage curve showing regions of single and two phase reactions

- Galvanic Intermittent Titration Technique (GITT) studies used to compare new two phase active material model to earlier shell-core two phase model

Gen 3 Negative Electrode OCV (~C/170) vs. Lithium

Gen 3 Negative Electrode GITT Study at 0 C
10 m - 0.16 mA/cm2 Pulses Followed by 4 h relaxation

Earlier Development of Modified Shell-Core Two Phase Active Material Model

LiC$_{12}$ / LiC$_{32}$ Two Phase Region Room Temperature GITT Experiment (0.2 mA/cm^2 for 10 min)

Two Phase Boundary

C_{Li}

Li$^+$

Active Material Particle Cross-Section

Active Material Surface

- Standard shell-core model modified by including lithium diffusion in both phases and a lithium concentration dependent finite phase transition rate

- Finite phase transition rate needed to account for the slow GITT relaxation data

- The slow phase transition rate suggests that the two phase boundary may occur over a region rather than at an interface

- Analytical diagnostic studies generally indicate the shell-core model is incorrect

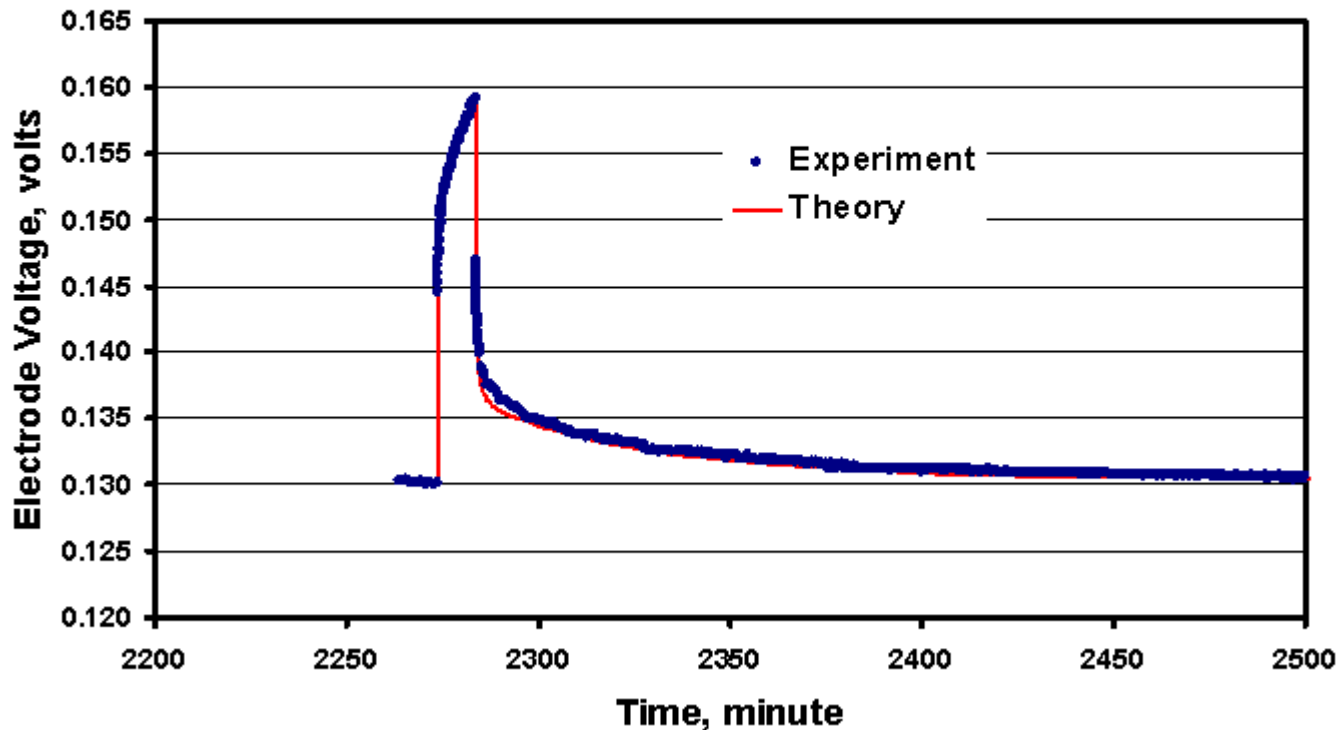# New Phase-Transition Reaction-Diffusion Lithium Transport Model for Two Phase Electrode Active Materials

Active Material Surface

C_{Li}

Li⁺

Second Phase Growth Following Avrami Equation

$$\varepsilon_{S2} = 1 - e^{\left(-kt^n\right)}$$

Active Material Particle Cross-Section Showing Two Phase Reaction Mechanism

- Lithium diffusion in both phases of active material and equilibrium at interfaces
  - Volume averaged transport equations
- Well known Avrami phase growth equation with a lithium concentration dependent rate constant is used to describe the phase transition
- Avrami, equilibrium, and diffusion equations integrated into full electrochemical cell model to simulate graphitic negative electrode GITT studies

New Phase-Transition Reaction-Diffusion Lithium Transport Model Able to Accurately Simulate Graphite Electrode GITT Data

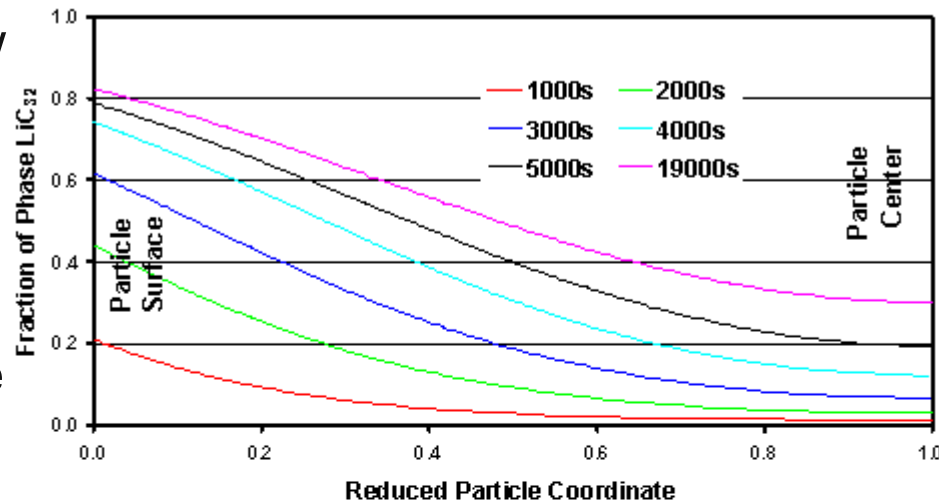LiC_{12} / LiC_{32} Two Phase Region Room Temperature GITT Experiment (0.2 mA/cm^2 for 10 min)

- New two phase model adds only one variable to electrochemical model and is easily able to track changes in size and direction of cell current
- Should be able to follow transport of lithium in single phase regions

Argonne
NATIONAL LABORATORY
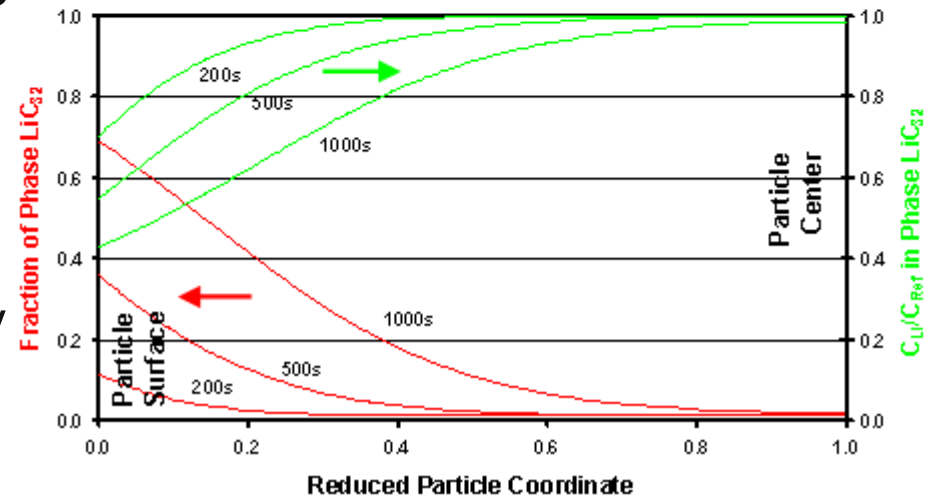
Vehicle Technologies Program

Graphite Particle Li Concentration and Phase Distribution with Observed Slow Transition Rate

- As current is passed, there is a slow change in the phase distribution throughout the particle that agrees with analytical diagnostic studies

- The phase distribution continues to change after current is halted as the lithium concentration gradients in the cell relax

- At higher currents the phase change occurs faster and closer to the surface

- The phase distribution mirrors the Li concentration distribution because the phase transition rate is driven by Li concentration gradients in the particle

Phase Distribution in Graphite Particle in LiC_{12} / LiC_{32} Two Phase Region during and after a 4000 s 0.2 mA/cm^2 Discharge
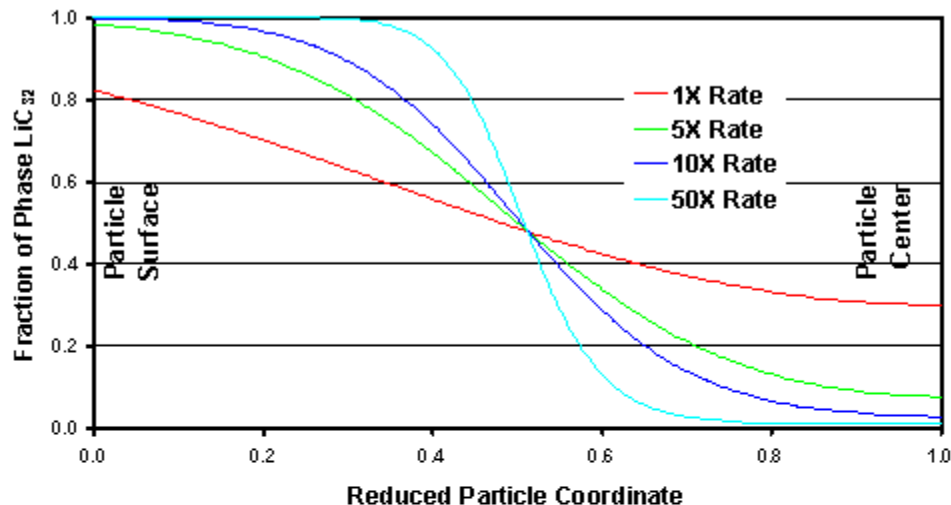

Phase Distribution in Graphite Particle in LiC_{12} / LiC_{32} Two Phase Region during and a 1000 s 1.0 mA/cm^2 Discharge

Artificially Increasing the Phase Growth Rate Dramatically Changes the Phase Distribution in the Active Particles
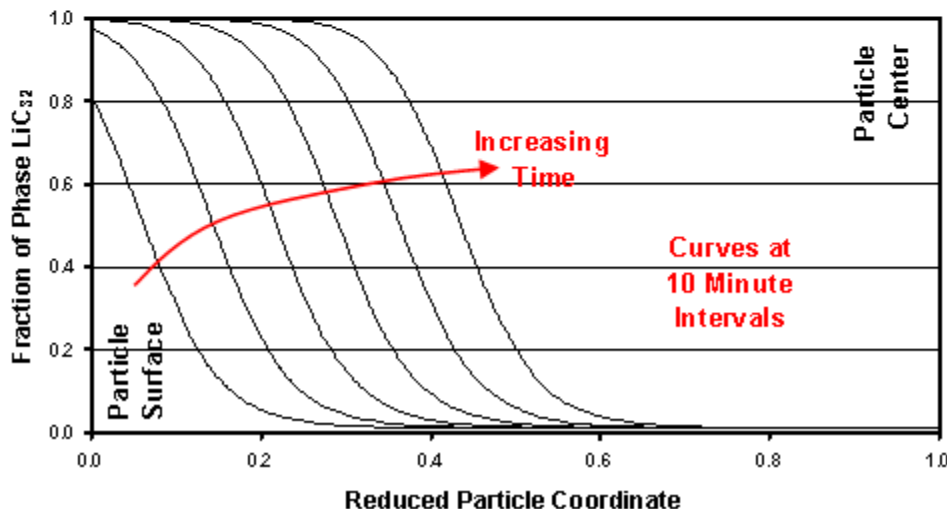

Transition Rate Effect on Phase Distribution in Graphite Particle at Midpoint in LiC_{12} / LiC_{32} Two Phase Region

- Increasing the phase growth rate narrows the phase change region in the particle

- During current passage in active materials with a fast phase growth rate the change in the phase distribution approaches that of the shell-core model

Phase Distribution in Graphite Particle in LiC_{12} / LiC_{32} Two Phase Region at 50X Transition Rate with 0.2 mA/cm^2 Discharge Current
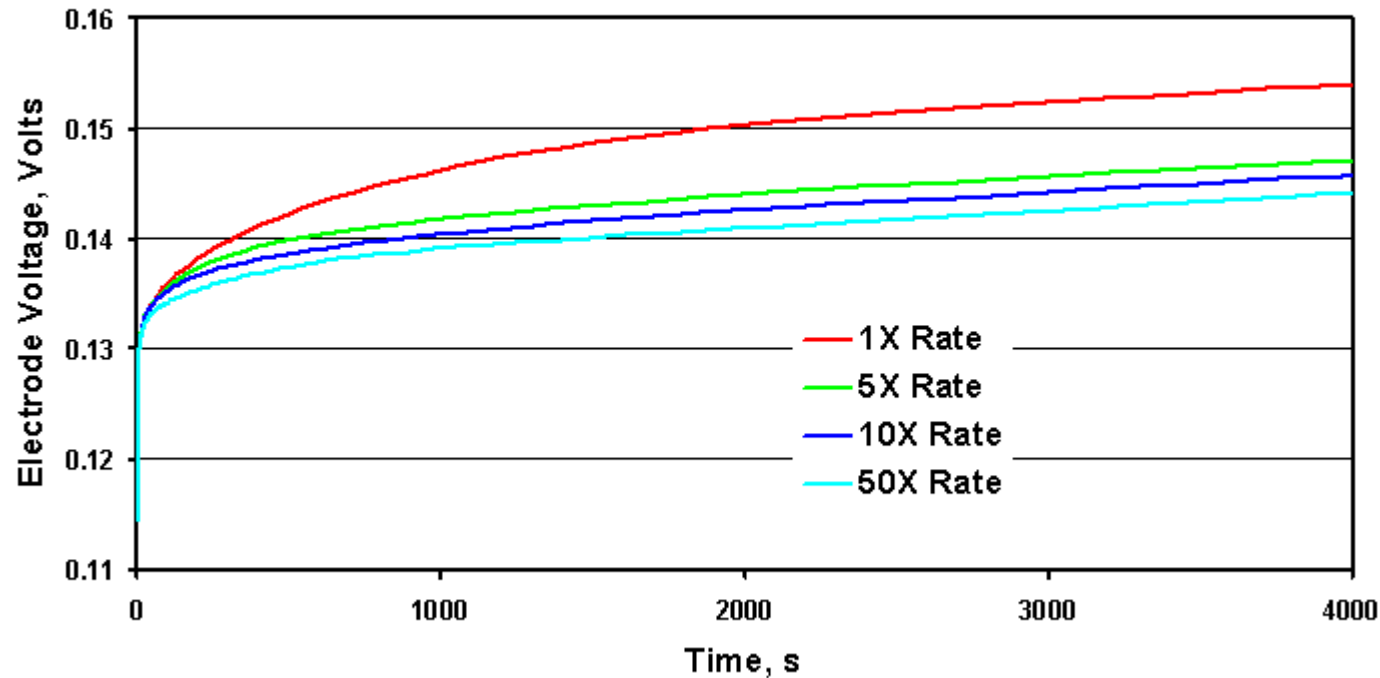
Artificially Increasing the Phase Growth Rate Reduces the Electrode Voltage Rise and Impedance During Discharge

Transition Rate Effect on Graphite Electrode Voltage in LiC_{12} / LiC_{32}
Two Phase Region during a 0.2 mA/cm2 Discharge

- At low currents the slow voltage rise of the electrode follows the inverse of the lithium concentration at the surface of the active material

- Increasing the phase growth rate reduces lithium concentration gradients at the surface of the active material, because of the increasing rate that lithium is being released by the phase change

Argonne NATIONAL LABORATORY

Vehicle Technologies Program

Future Plans

- Further improve electrochemical model parameter fitting methods
  - Establish a systematic parameter estimation framework for full AC impedance lithium-ion electrochemical model
- Continue development of PHEV focused electrochemical models
  - Alternative materials, additives, testing protocols
  - Capacity loss degradation mechanisms
- Complete development of electrochemical model for two-phase active materials and extend to other electrodes
- Improve DC electrochemical model to match AC model capabilities
  - Include non steady-state interfacial effects
  - Add capability for multiple active material particle fractions
- Milestones for next year
  - Complete development of parameter fitting method
  - Complete development of two phase active material model
  - Initiate development of capacity loss 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 HEV characterization and modeling studies in extending efforts to PHEV technologies

- Technical Accomplishments

  - Equivalent circuit interfacial model developed for streamlining electrode parameter estimation

  - Conducted electrode thickness cell performance simulations

  - Developed new phase-transition reaction-diffusion lithium transport model for two phase electrode active materials

- Future plans include completion of parameter fitting methods and two phase active material model development, as well as continued development of PHEV focused models

Acknowledgment

Support for this work from DOE-EERE, Office of Vehicle Technologies is gratefully acknowledged
      - David Howell

Vehicle Technologies Program