Electrochemistry Cell Model

Presented by Dennis Dees
Chemical Sciences and Engineering Division

June 7-11, 2010

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

Project ID:
ES031

Overview

Timeline

- Start: October 2008
- Finish: September 2014
- ~25% Complete

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

Budget

- Total project funding
  - 100% DOE
- FY2009: $400K
- FY2010: $400K

Partners (Collaborators)

- Kevin Gallagher, Argonne
- 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:
  - Complete development of two phase active material model (completed)
  - Initiate development of capacity loss model (completed)
  - Complete development of an efficient parameter fitting method (mostly completed)
- 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 data base and modeling capabilities

Major Accomplishments and Technical Progress

- Further development and evaluation of phase transition lithium diffusion transport model for two phase electrode active materials (e.g. LiC_6, $LiFePO_4$, $LiMn_2O_4$, $Li_4Ti_5O_{12}$)
  - Model simulations indicate the coexistence of three phases (i.e. Stage 1, Stage 2, and Stage 3) in graphitic negative electrode (MCMB, Gen 3) during normal cell operation
  - Model was modified to account for coexistence of three phases and changes were integrated into full cell model
  - Initiated study of second graphite negative electrode (Mag 10, PHEV baseline)
- Initiated development of capacity loss degradation model
  - Conducted literature review and considered possible phenomena
  - SEI model developed to examine growth mechanisms
- Supported other development efforts in program
  - Integrated improved electrode impedance and limiting current estimates into Paul Nelson's Battery Design Model
  - Developed spherical geometry four probe conductivity model for single particle conductivity measurements
  - Initiated modeling studies on binder-carbon-free electrodes to examine primary-secondary active particle microstructure and interactions

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 in active particles and multiple particle fractions
- The system of partial 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

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

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

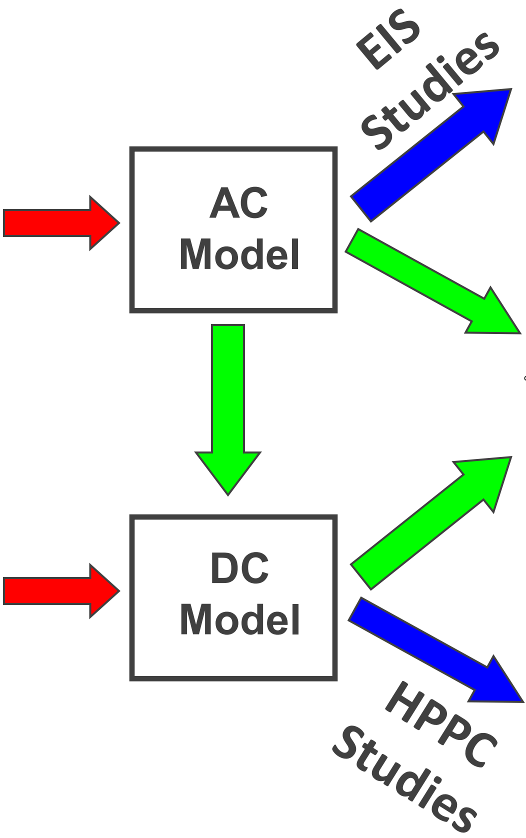
$$\frac{\partial i_2}{\partial x}=Fz_+\sum_k a_k j_{kn}\qquad I=i_1+i_2\qquad i_1=-\sigma_{eff}\frac{\partial\Phi_1}{\partial x}$$

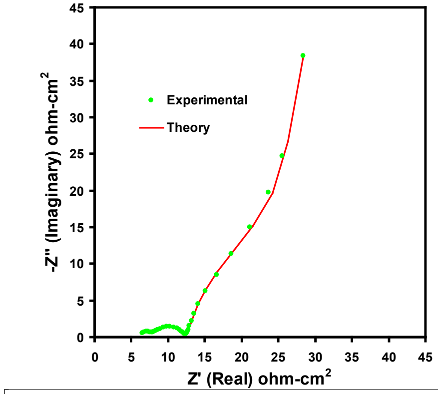
$$\frac{\partial c_+}{\partial t}=D_+\left(\frac{\partial^2c_+}{\partial y^2}\right)\qquad \eta_f=\frac{i_n\delta_f}{\kappa_f}+\frac{RTs_+}{nF}\ln\frac{c_+\big|_{electrolyte}}{c_+\big|_{active\ material}}$$

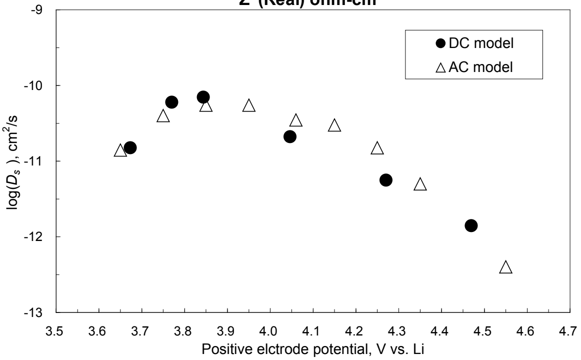
$$\frac{\partial c_{Si}}{\partial t}=D_{Si}\left(\frac{\partial^2c_{Si}}{\partial y^2}\right)\qquad \frac{\partial c_{Sb}}{\partial t}=\frac{\partial}{\partial z}\left(D_{Sb}\frac{\partial c_{Sb}}{\partial z}\right)$$

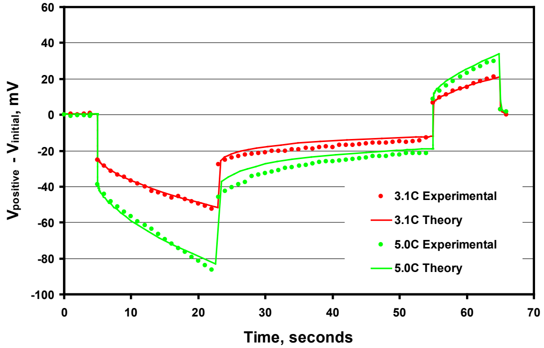
$$i_n=i_0\left(\frac{c_+}{c_{+,ref}}\right)^{\alpha_A}\left(\frac{c_{Ti}-c_{Si}}{c_{Ti}-c_{Si,ref}}\right)^{\alpha_A}\left(\frac{c_{Si}}{c_{Si,ref}}\right)^{\alpha_C}\left\{e^{\left[\frac{\alpha_AF\eta_K}{RT}\right]}-e^{\left[-\frac{\alpha_CF\eta_K}{RT}\right]}\right\}$$

$$\eta_R=\sigma_Pz_+Fj_n$$



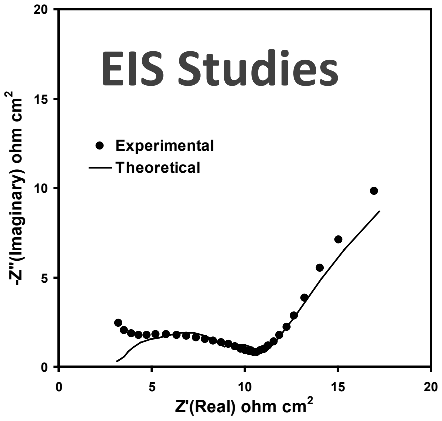






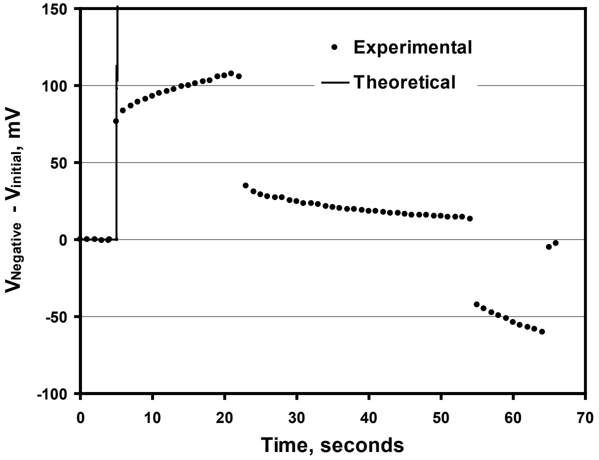
- Diffusion coefficient obtained from GITT studies using DC model shows strong correlation with AC modeling studies

Parallel Development for Graphitic Negative Electrode was not Near as Productive



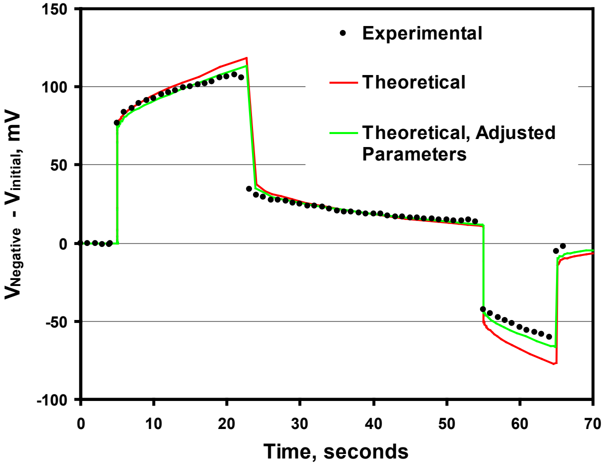
- Initially, no correlation was obtained between AC and DC models using established electrochemical intercalation electrode model.

HPPC Studies



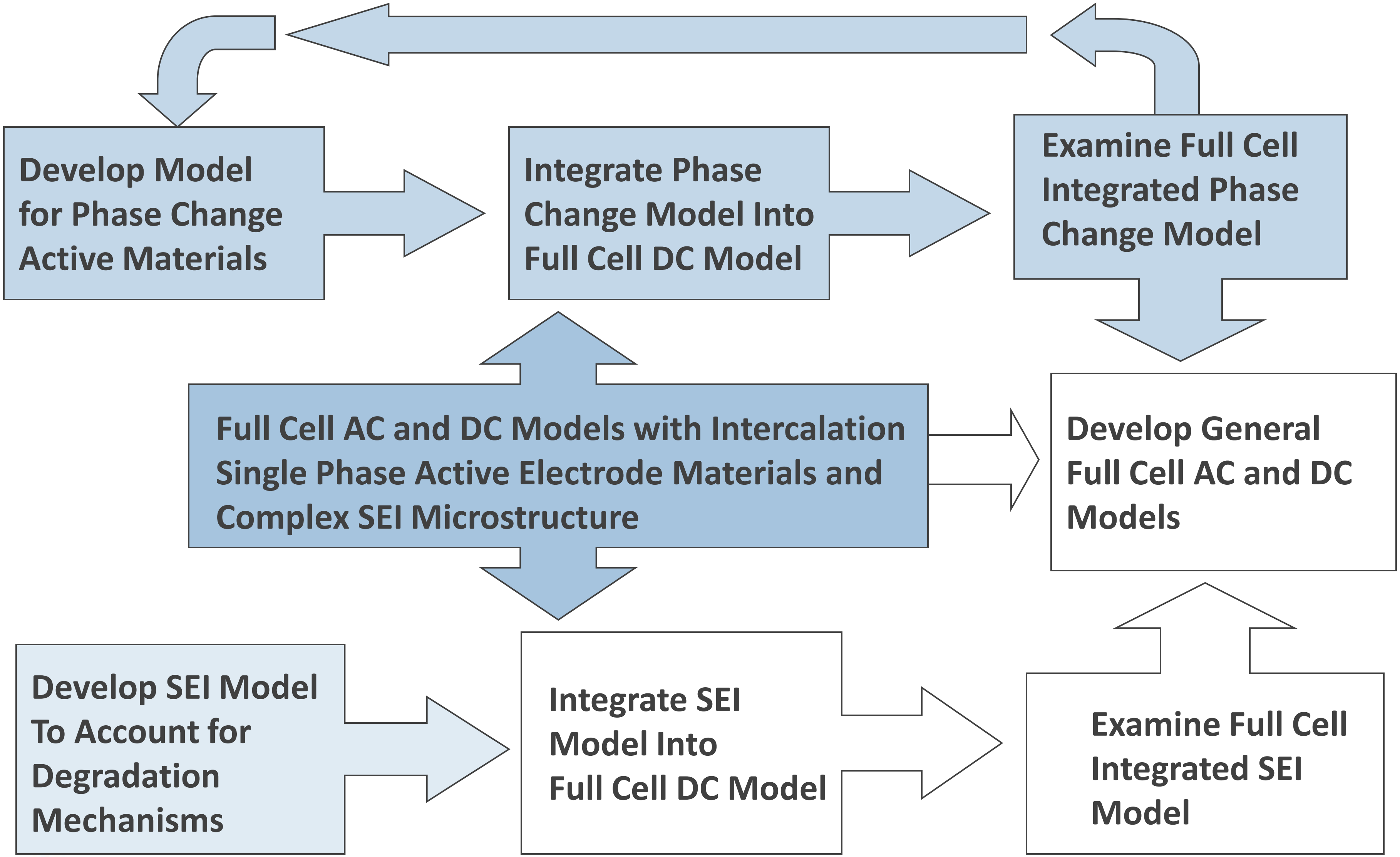
- Correlation between AC and DC models obtained through empirically based model and parameter modifications
- Analysis indicated that potential effects associated with diffusion of lithium in the graphite was not being accurately described (i.e. treating the lithium diffusion in graphite as a single phase process was not adequate)

HPPC Studies



Electrochemical Model Development

Darker Blue Shade Indicates More Mature Effort



Develop Model for Phase Change Active Materials

Integrate Phase Change Model Into Full Cell DC Model

Examine Full Cell Integrated Phase Change Model

Full Cell AC and DC Models with Intercalation Single Phase Active Electrode Materials and Complex SEI Microstructure

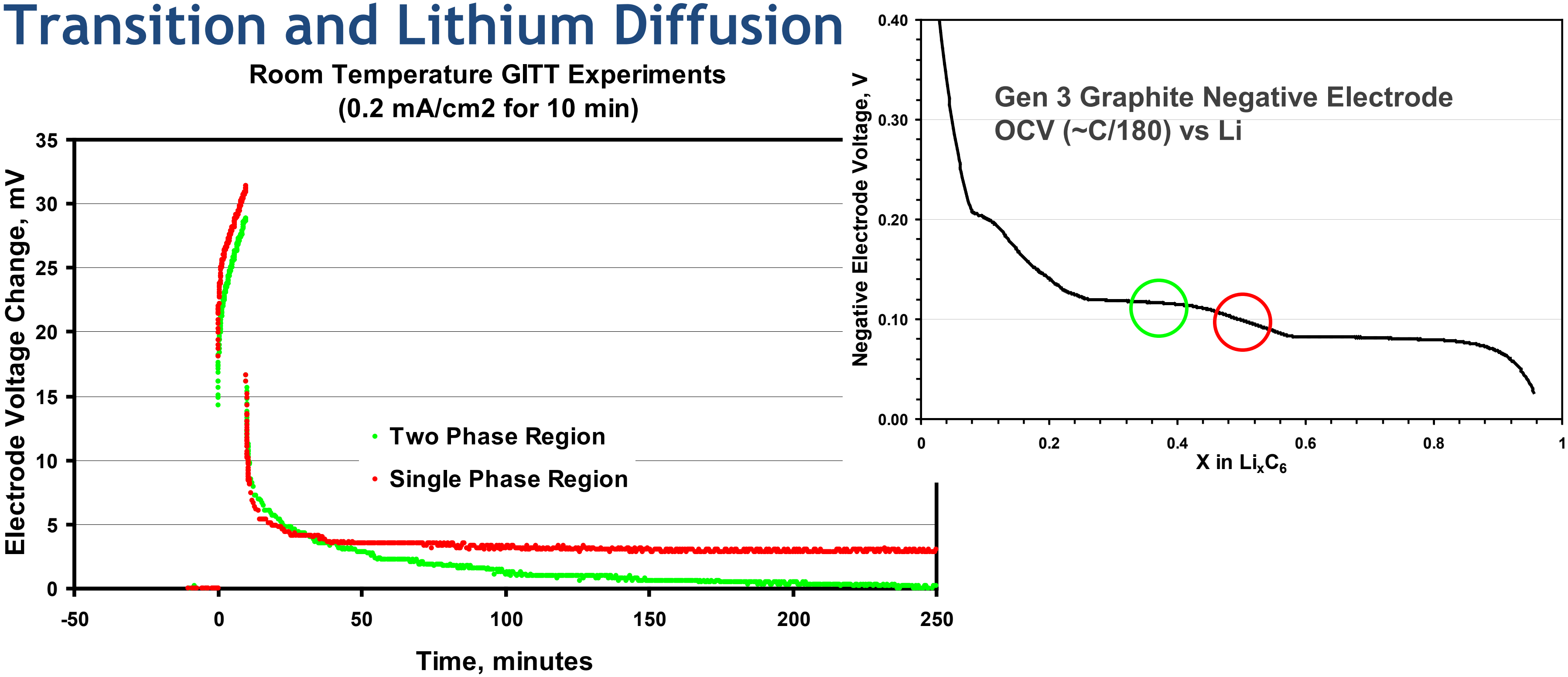
Develop General Full Cell AC and DC Models

Develop SEI Model To Account for Degradation Mechanisms

Integrate SEI Model Into Full Cell DC Model

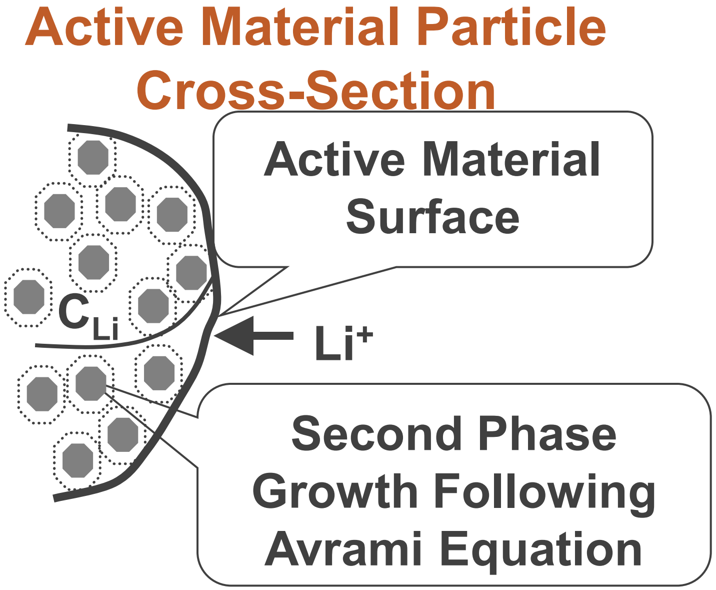
Examine Full Cell Integrated SEI Model

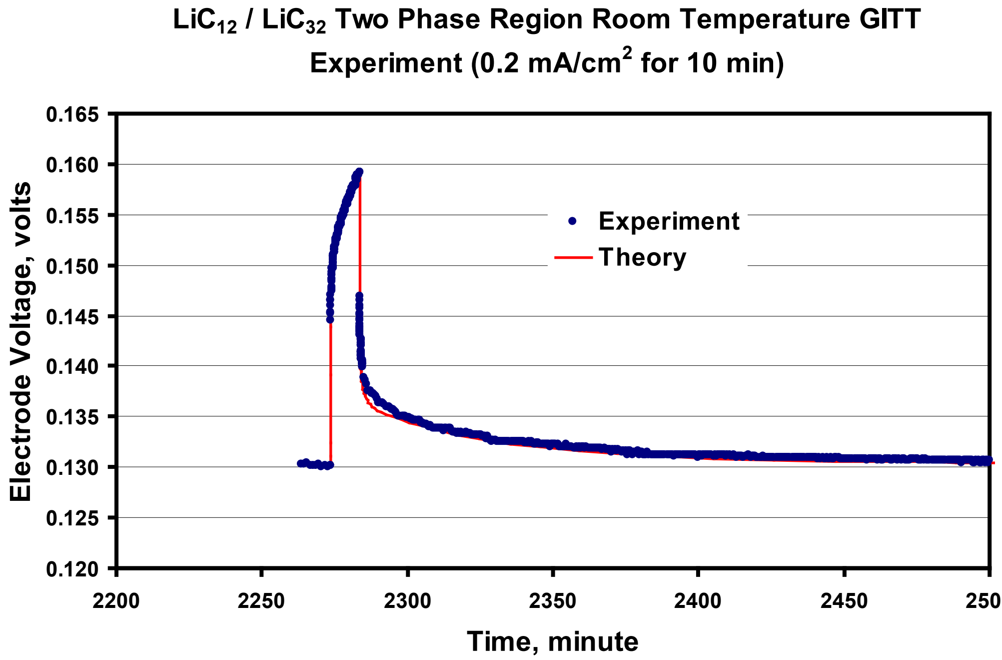
Galvanic Intermittent Titration Technique (GITT) Studies on Graphite Negative Electrode Used to Examine Phase Transition and Lithium Diffusion



- Staged lithium intercalation into graphite well established in literature with open circuit voltage (OCV) curve showing single and two phase regions
- Polarization diffusional potential rise similar in both single and two phase regions despite significant differences in slope of OCV curve
- Very slow relaxation of potential apparent in two phase region

Phase Growth Model Based on Avrami Equation Adopted after Alternative Phase Transition Models Examined

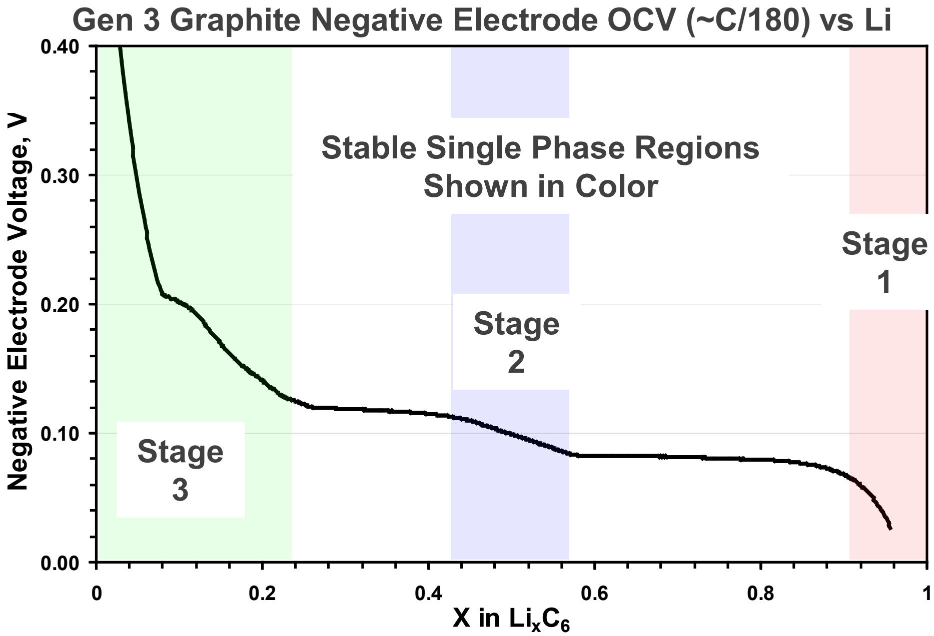


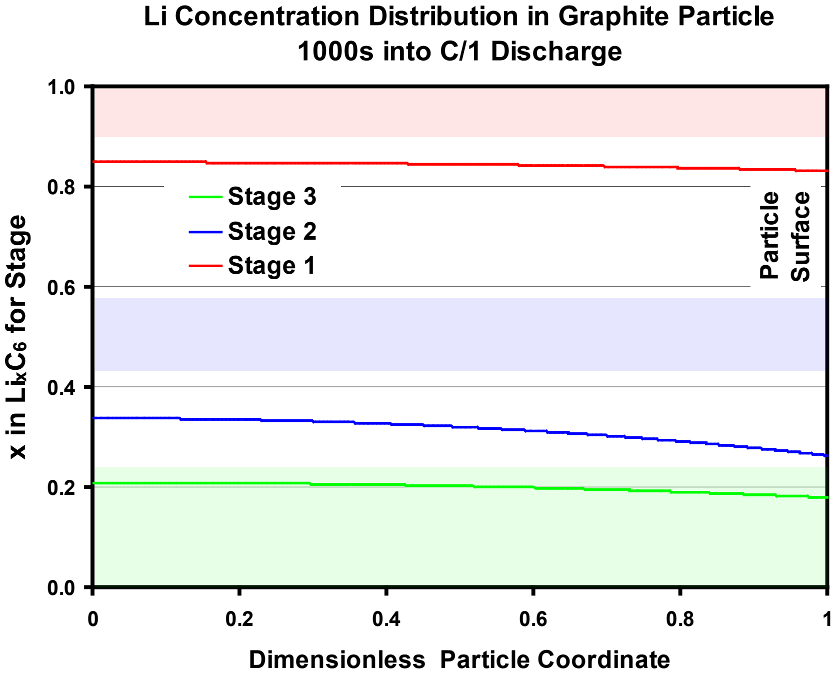


$$\varepsilon_{S2} = 1 - e^{-(kt)^n}$$

- 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

Phase Growth Model Modified to Allow for Coexistence of Three Phases and Changes Integrated into Full Cell Electrochemical Model

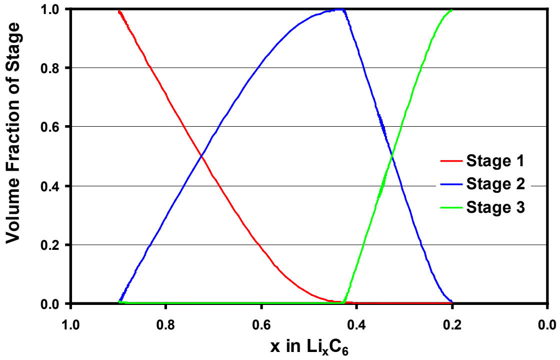




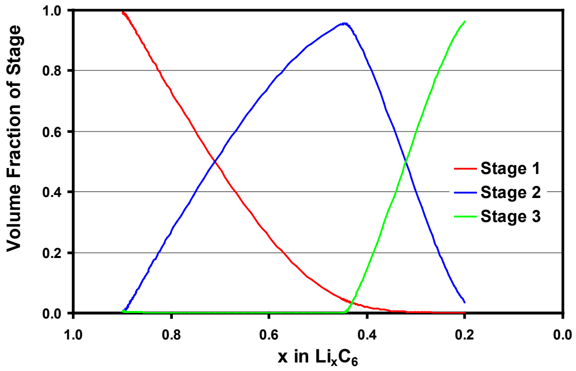
- OCV curve used to establish stable single phase regions. For simplicity, Stages greater than Stage 2 treated as Stage 3.
- As the cell is discharged, the lithium concentration in each phase drops
- When the lithium concentrations in each phase falls below its stability limit the lower concentration phase begins to form following the Avrami equation
- Early modeling studies with two phase model on the graphite negative electrode indicated that the lithium concentration in both phases could drop below their stability limit

Impact of Slow Phase Transition Rate Constant on Stage Formation During Discharge: Simulation of Graphite Negative Active Material

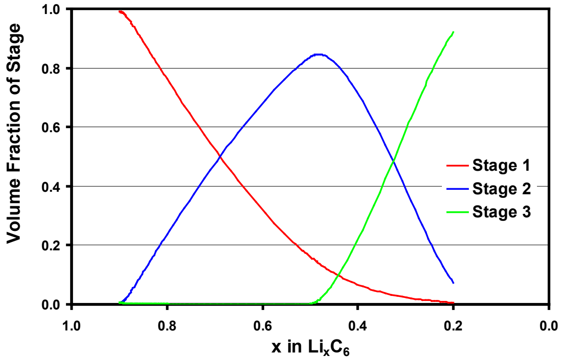
Graphite Particle during C/50 Discharge



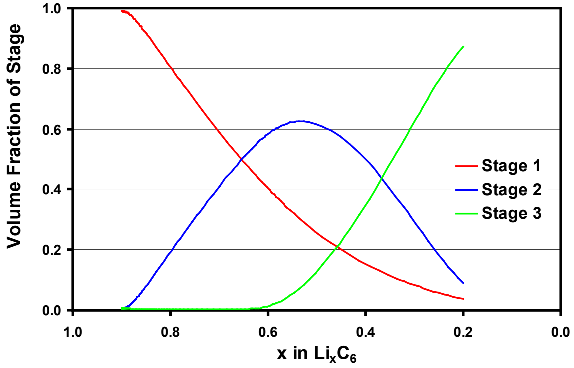
Graphite Particle during C/20 Discharge



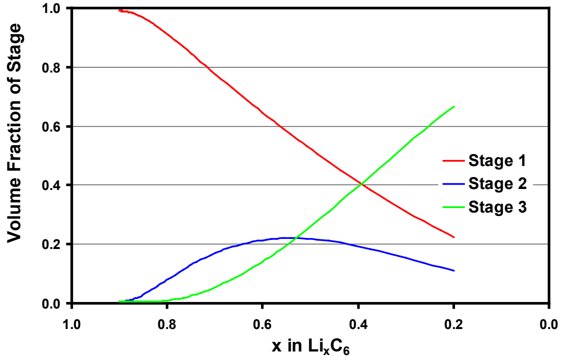
Graphite Particle during C/10 Discharge



Graphite Particle during C/5 Discharge

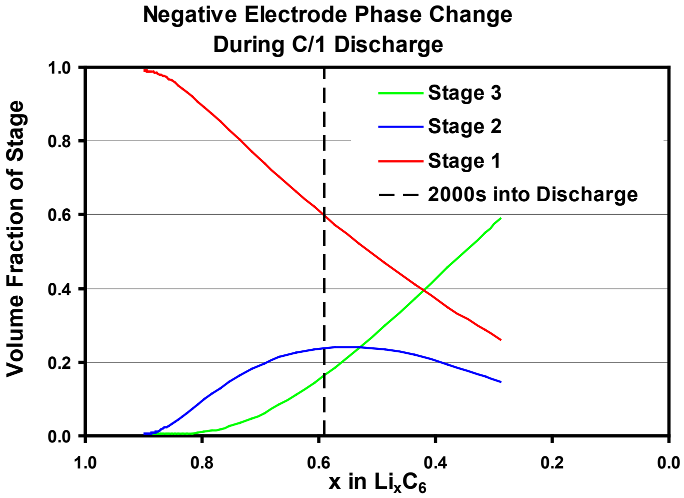


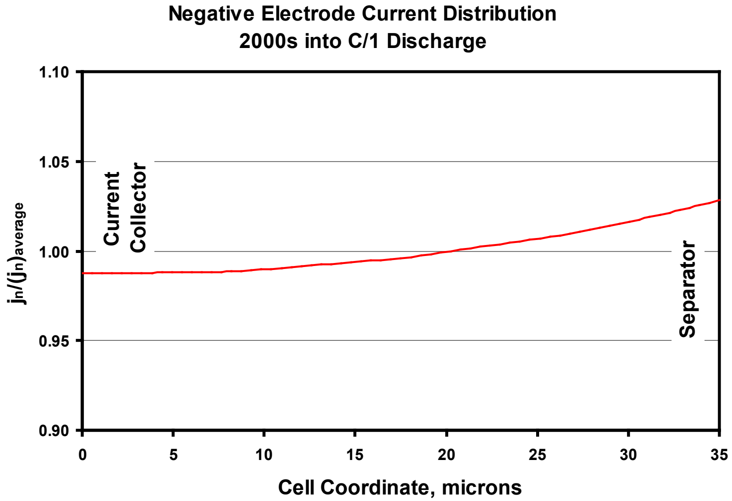
Graphite Particle during C/1 Discharge

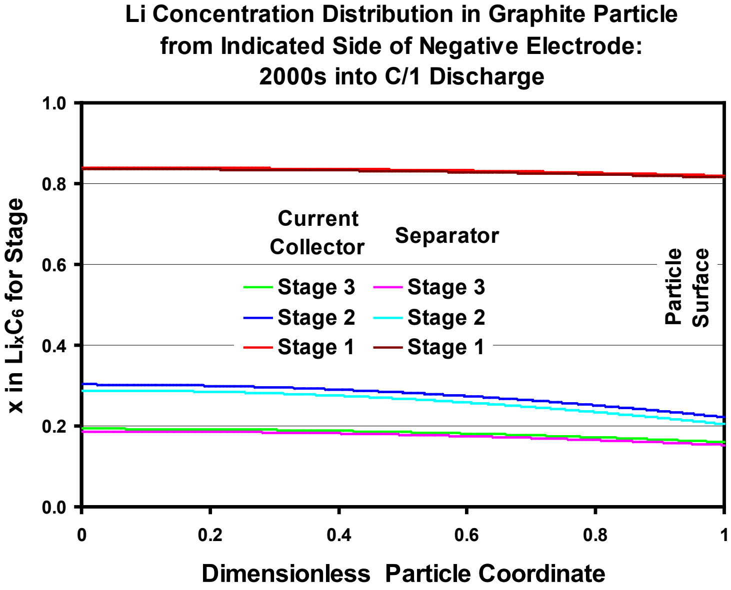


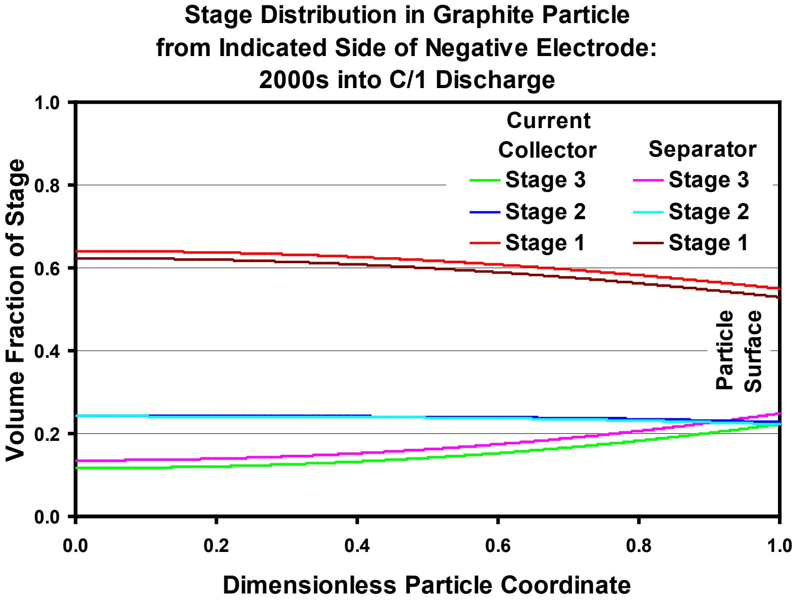
- Coexistence of all three stages indicates that equilibrium is not attained even at a C/50 rate
- Three phase width increases with discharge rate and Stage 2 maximum decreases

Negative Electrode Current and Phase Distributions Relatively Uniform During a C/1 Discharge

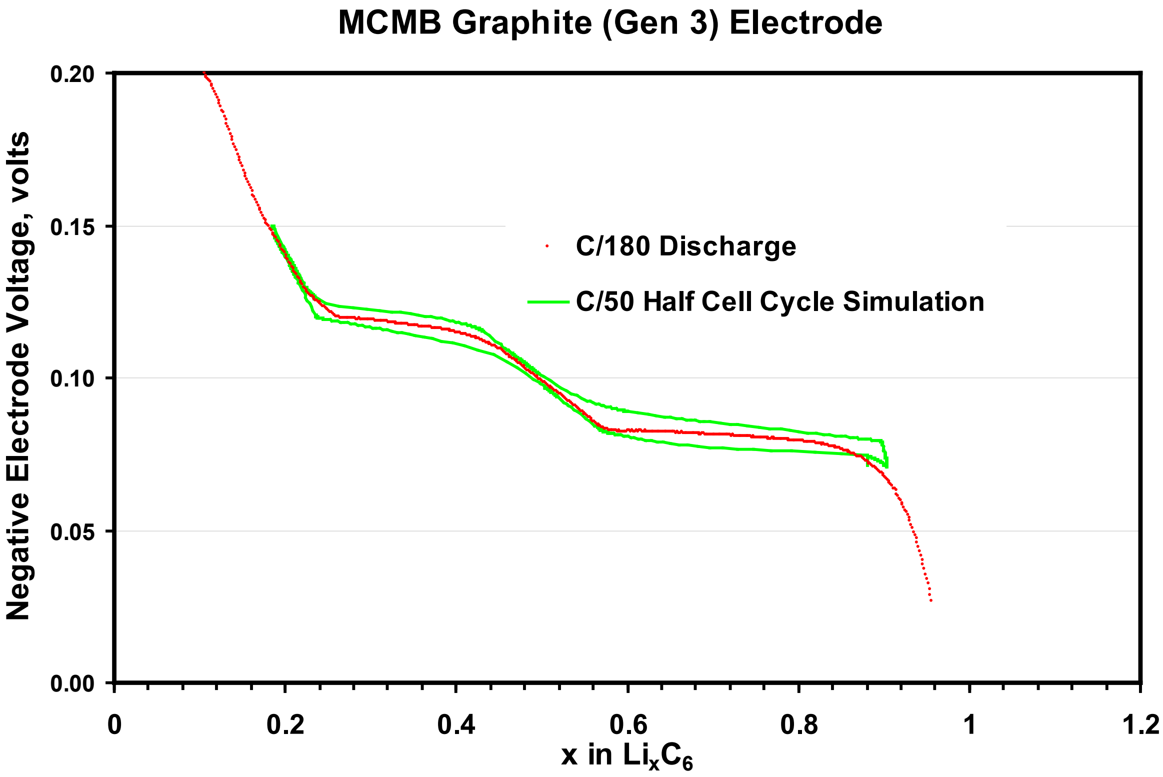

Negative Electrode Phase Change During C/1 Discharge

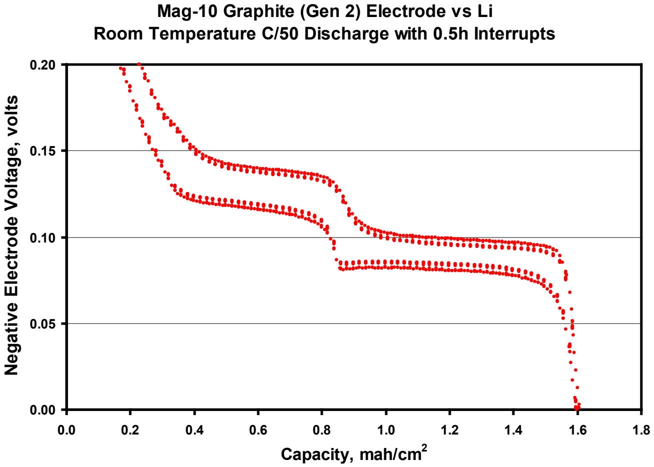

Negative Electrode Current Distribution 2000s into C/1 Discharge


Li Concentration Distribution in Graphite Particle from Indicated Side of Negative Electrode: 2000s into C/1 Discharge


Stage Distribution in Graphite Particle from Indicated Side of Negative Electrode: 2000s into C/1 Discharge

Graphite Negative Electrode Phase Transition Diffusion Model Accounts for Observed Hysteresis





- Slow cycling hysteresis may be useful technique to estimate phase transition rate constant

- Faster lithium diffusion allows for high lithium transport rates (i.e. electrode able to support high currents)
- The slow phase transition rate constant accounts for the electrode’s apparent sluggishness to reach equilibrium

Future Plans

- Advance development of electrochemical model for two phase active materials focusing on impedance effects
  - Develop AC impedance two phase model and integrate SEI model
  - Continue examination of baseline PHEV negative electrode
- Continue development of PHEV focused electrochemical models
  - Advance SEI growth model to examine capacity loss degradation mechanisms
  - Alternative materials, higher electrode loadings, and different testing protocols
- Continue support of other ABR projects
- Milestones for next year
  - Initiate development of AC impedance two phase model
  - Integrate SEI growth model into full cell 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
  - Further development and evaluation of phase transition lithium diffusion transport model for two phase electrode active materials
  - Initiated development of capacity loss degradation model
  - Supported other development efforts in program
- Future plans include development of a full cell AC impedance two phase active material model and advance an SEI growth model to examine capacity loss degradation mechanisms, as well as continued support of other ABR projects

Acknowledgment

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