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Low Temperature Performance: Performance Modeling

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DOE Vehicle Technologies Program
Annual Merit Review, FY2008
Hybrid Electric Systems
Energy Storage / Applied Battery Research

Vehicle Technologies Program

Outline

- Purpose of Work
- Address Previous Reviewers Comments
- Barriers
- Approach
- Accomplishments and Technical Progress
- Technology Transfer and Publications
- Plans for Next Fiscal Year
- Summary

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Background and Purpose of Work

- Lithium-ion electrodes and cells universally exhibit a dramatic decrease in performance (i.e. increase in impedance) at low temperatures that limits their utility in HEV and PHEV applications
- Potentially more troubling than the high impedance, is the likely possibility of finely divided lithium metal being deposited on low voltage negative electrodes (e.g. graphite) during regen and/or charging at low temperatures
  - Finely divided lithium metal reacts with the electrolyte to produce heat, degrade the SEI characteristics, and reduce cell useable lithium inventory
- Understand the factors that cause lithium deposition and limits the low temperature performance so that improvements can be made
  - Milestone for FY2007: Quantify lithium transport effects at low temperatures in the Gen 3 negative electrode graphitic active material

Address Previous Reviewers Comments from 2006 Annual Merit Review

Reviewers' Comments and Questions	FY2007 Response to Comments and Questions
Why study lithium diffusion in positive electrode active material, while focus should be on negative electrode?	The negative electrode was the focus of this year's work. The earlier study with the much better characterized positive electrode was crucial to learn how to properly apply the GITT technique to lithium-ion composite electrodes.
Consider EIS as an alternative technique to GITT to measure lithium diffusion coefficients in active materials.	Although not fully discussed at the review, a comparison of the two techniques was conducted and is being published.
How are interfacial effects included in composite electrode GITT model?	A detailed description of the model has been published and an article on the application of the model to the GITT technique is being written

Technical Barrier for this Project on Improving Low Temperature Performance of Lithium-Ion Batteries

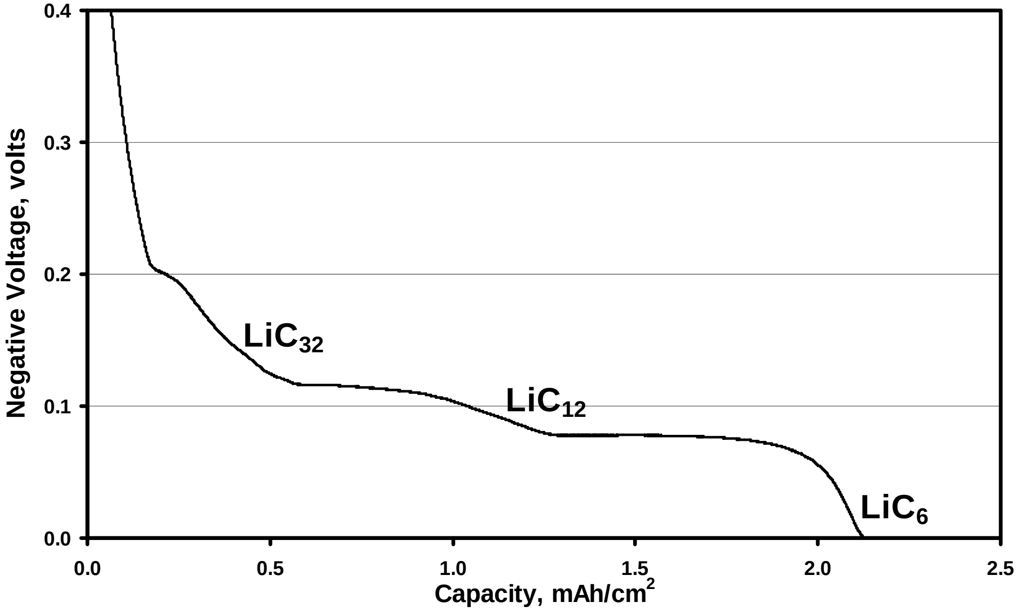
- Understand and quantify lithium metal deposition on graphitic active material in negative electrode
  - Complete electrochemical characterization
  - Quantify lithium metal deposition rates

Multifaceted Approach

- Build on earlier successful positive electrode characterization studies, which used electrochemical modeling studies combined with experimental efforts to gain insights into sources of impedance and aging mechanisms
- Concentrate efforts on the lithium transport in the graphitic active material
- Modify existing electrochemical model to effectively account for graphitic active material negative electrode characteristics
- Develop methodology for quantifying lithium metal deposition rates

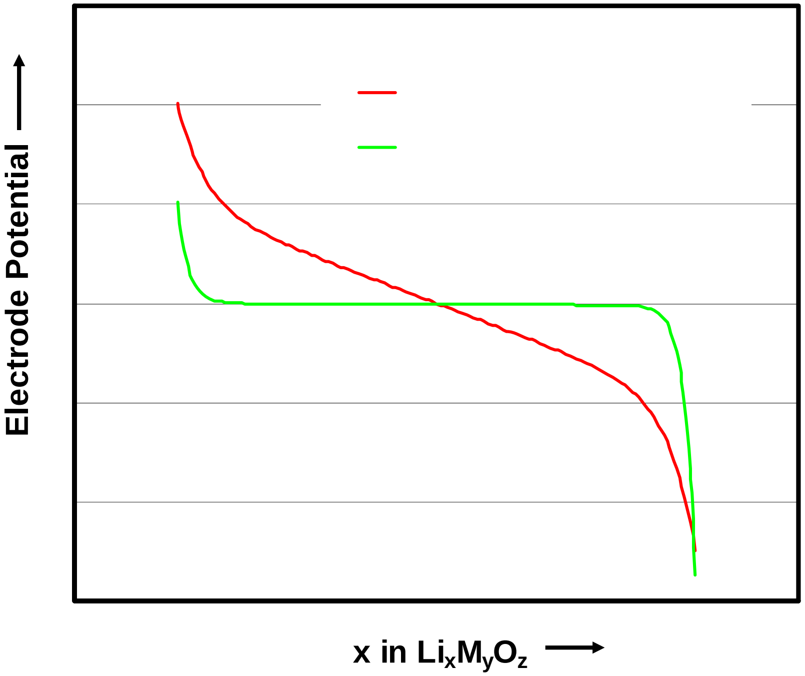
Graphite Gen 3 Negative Electrode Open Circuit Voltage Curve Shows Regions of Single and Two Phase Reactions

Staged lithium intercalation into graphite well established in literature



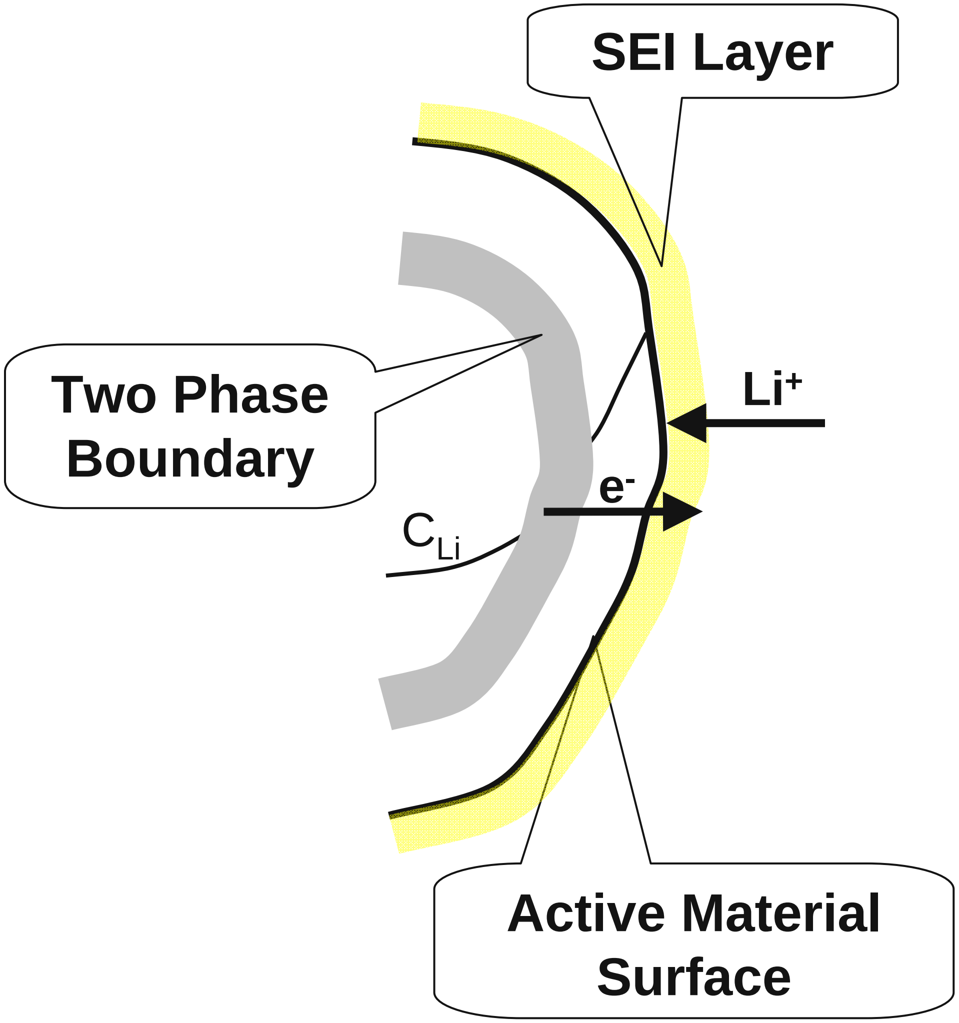
Negative Electrode OCV (~C/50) vs. Lithium

Electrode potential vs. state-of-charge: typical shapes for single and two phase reactions



Factors Influencing Lithium Deposition Rate on Graphitic Active Material in Negative Electrode

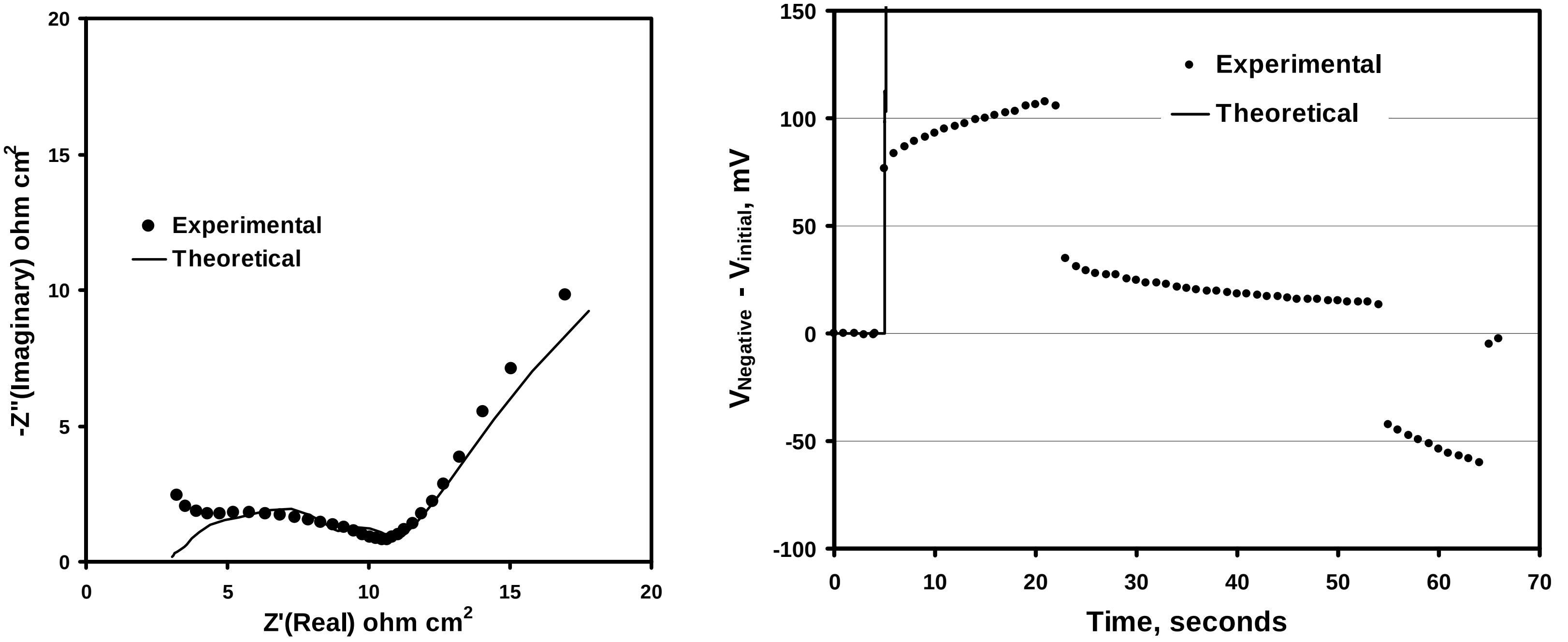
- Thermodynamics for lithium reduction determined by surface concentration of lithium in graphite
  - Controlled by lithium diffusion and phase change
- Transport rates of lithium ions and electrons through the solid electrolyte interface (SEI)
- Electrochemical kinetic rates of lithium insertion into graphite and lithium reduction
- Local concentration of lithium ions in electrolyte



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

Previous Electrochemical Modeling Studies with Gen 2 Technology Cells Indicated that Further Development Work was needed for the Negative Electrode Model

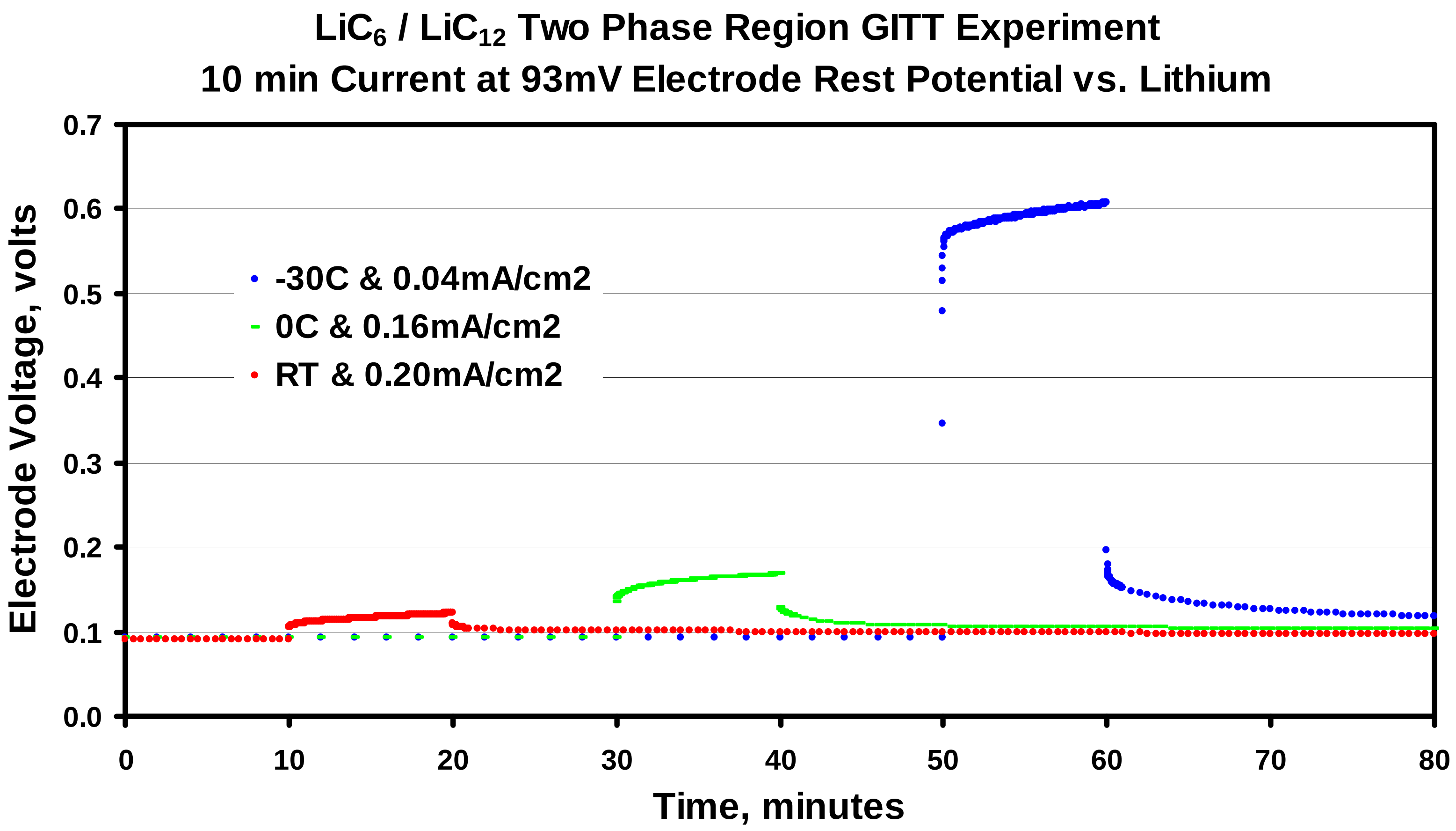


- The electrochemical model could not simulate both the negative electrode’s AC impedance and HPPC test with the same parameter set
- Analysis indicated that potential effects associated with diffusion of lithium in the graphite was not being accurately described (i.e. treating the lithium diffusion in graphite as a single phase process was not adequate)

Major Accomplishments and Technical Progress

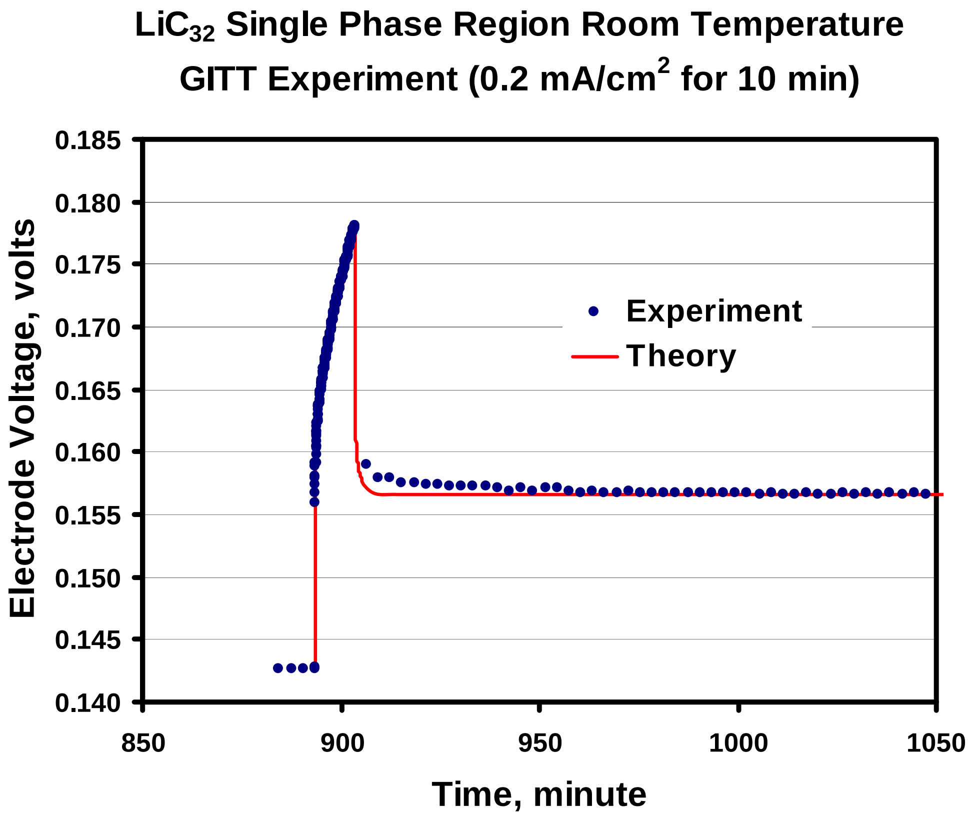
- Experimental Galvanostatic Intermittent Titration Technique (GITT) studies conducted on the Gen 3 negative electrode
  - Reference electrode pouch cell (based on positive electrode studies)
  - Full state-of-charge range from room temperature down to -30°C
- GITT electrochemical model developed for oxide active material composite electrodes was modified and utilized to quantify lithium diffusion in the Gen 3 negative electrode graphite
  - Alternative modeling approaches were examined to accurately and efficiently track the lithium transport in the active material
  - Parameters were established
- Modified cell negative electrode electrochemical model based on GITT modeling studies
  - Applicable to multiphase electrodes where diffusional phenomena dominate over phase equilibrium and phase change effects
- Electrochemical microcalorimetry was explored as a technique to quantify lithium plating at low temperatures

Overlay of GITT Experimental Study on Negative Electrode at 93mV over Temperature Range



- Clear dominance of interfacial over diffusional impedance at low temperature

GITT Experiments Conducted in Single Phase Regions Established Lithium Diffusion Coefficient

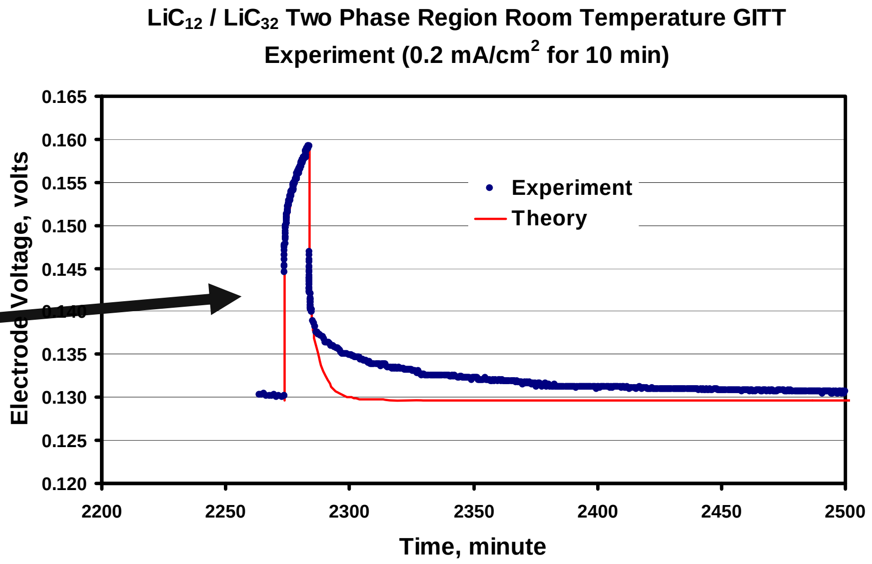


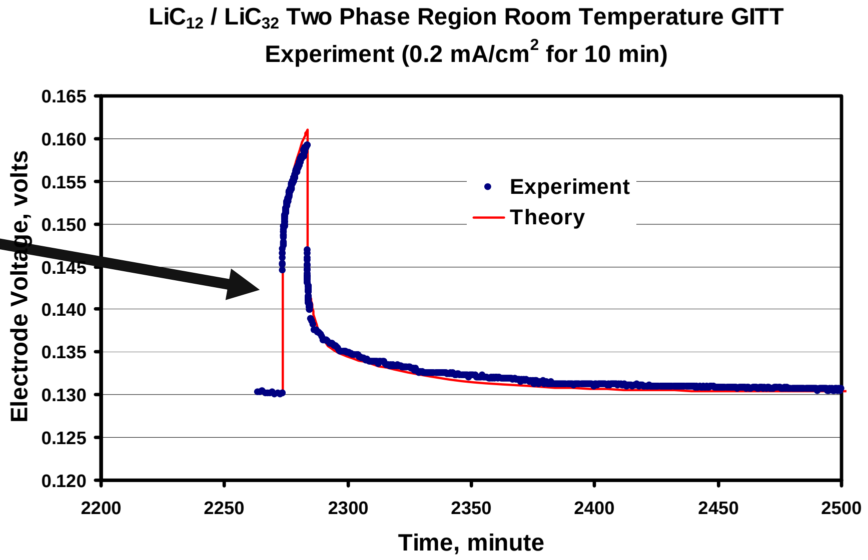
Graphite Phase	D_S in cm²/s	
	Room Temperature	-30°C
LiC_{32}	6.0×10^{-13}	N/A
LiC_{12}	0.7×10^{-13}	0.3×10^{-14}
LiC_6	4.0×10^{-13}	2.0×10^{-14}

- These studies are a direct extension of earlier positive electrode GITT studies using composite electrode electrochemical model
- Simulations indicate that the negative electrode operation is not limited by lithium diffusion at low temperatures

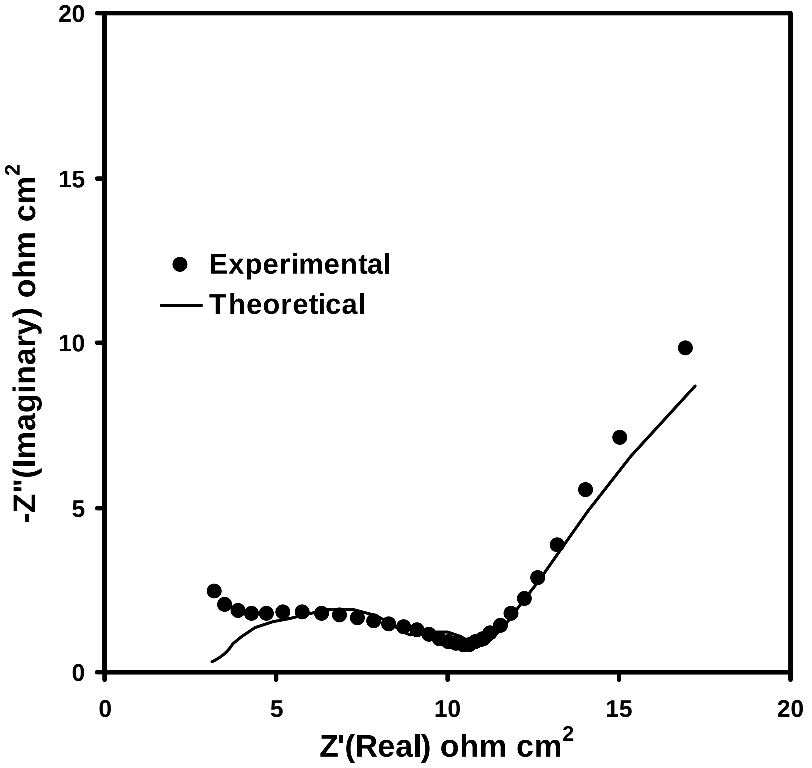
Several Two Phase Active Material Electrochemical Models Examined

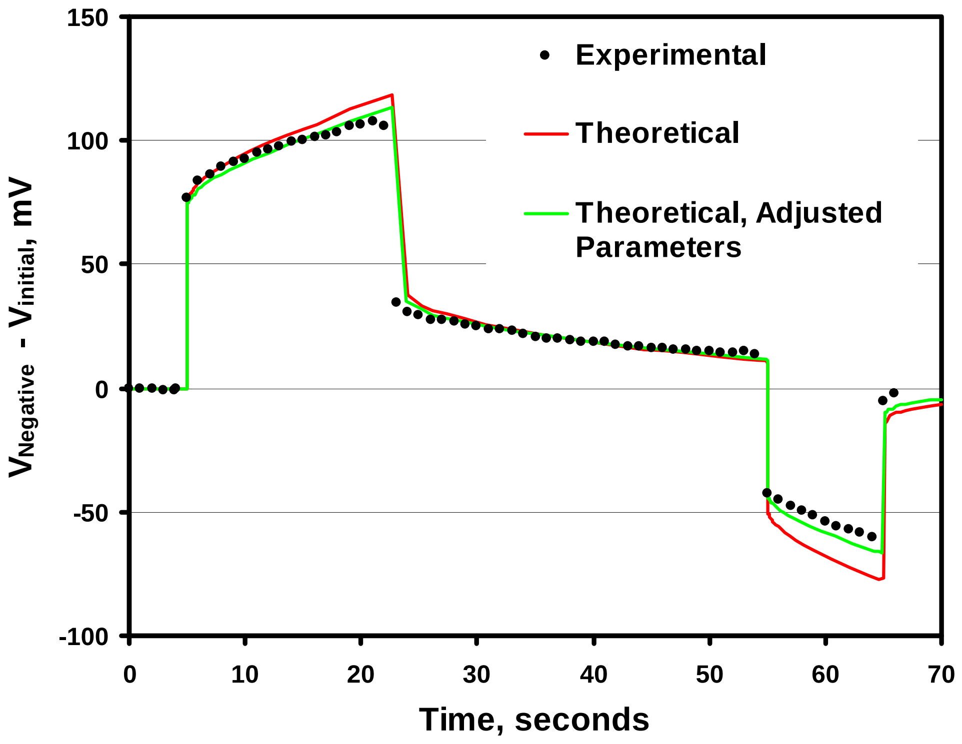
- Shell and core phases in active material particle with lithium diffusion only in outer shell phase and fast phase transition reaction
  - Partial fit of GITT data
- Shell and core phases in active material particle with lithium diffusion in both shell and core phases with finite phase transition reaction and phase equilibrium at interface
  - Good fit of GITT data
- Full two phase reaction diffusion model in active material particle with multiple two-phase boundary layer capability
  - Still under development





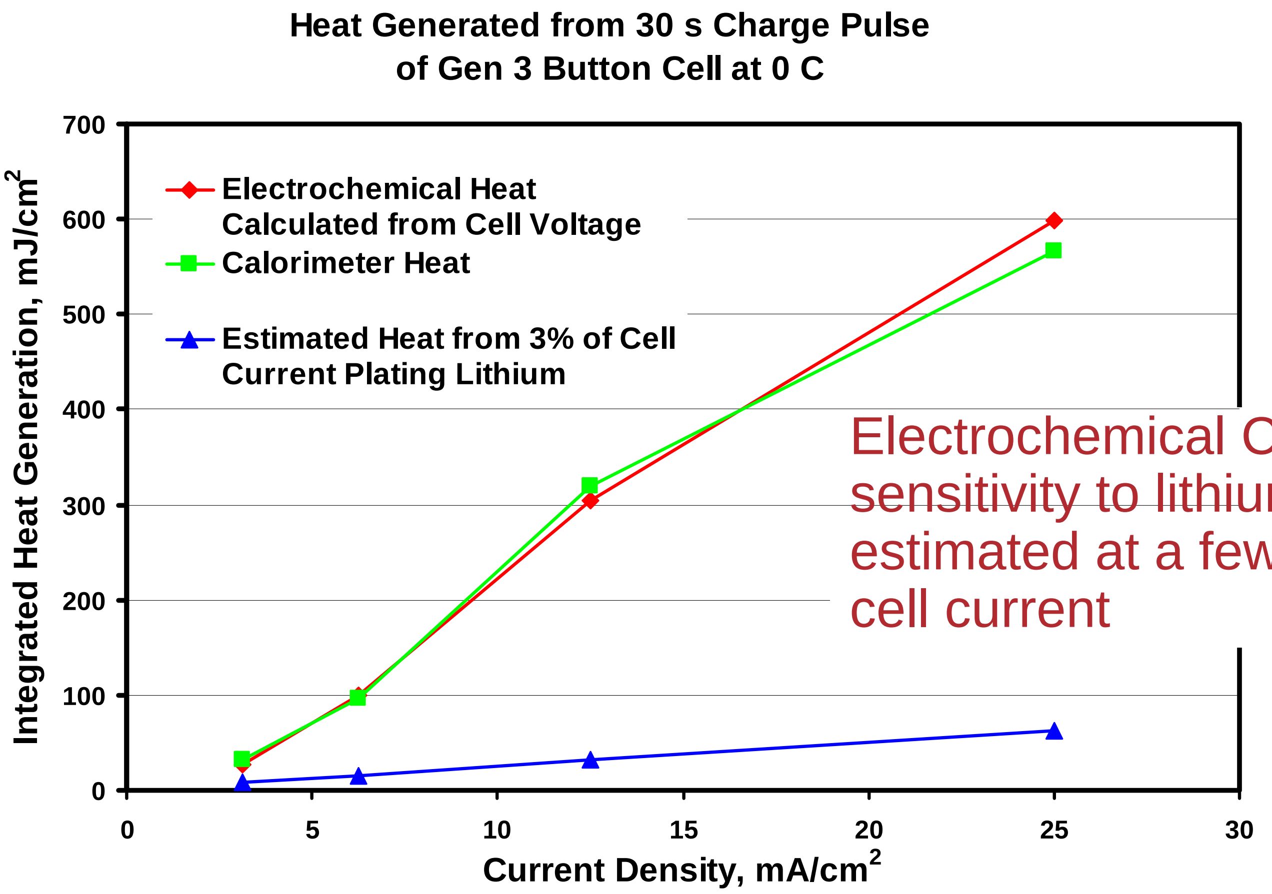
Modified Electrochemical Model Simulation of the Negative Electrode AC Impedance and HPPC Test using the Same Parameter Set





- Adjustment of the model parameters is needed for a better fit because of a poor assumption in the earlier parameter study that could not be tested till now

Electrochemical Microcalorimetry Being Utilized to Examine Lithium Deposition on Negative Electrode at Low Temperatures



Heat Generated from 30 s Charge Pulse of Gen 3 Button Cell at 0 C

Electrochemical Calorimetry sensitivity to lithium plating estimated at a few percent of cell current

No lithium deposition observed during studies at 0° C

Technology Transfer and Recent Publications

- Intellectual property generated under this project is available for licensing through Argonne's Office of Technology Transfer
- Results of our studies are disseminated through a variety of avenues
  - Regular review meetings and discussions with industrial developers
  - Technical reports and journal articles
  - Presentations at technical meetings
  - ATD website (coming soon, thanks to Ira Bloom)
- Recent publications connected with this project
  - "Low-Temperature Study of Lithium-Ion Cells Using a Li_ySn Micro-Reference Electrode, *J. Power Sources*, **174** (2007) 373.
  - "Investigating the Low-Temperature Impedance Increase of Lithium-Ion Cells," *J. Electrochem. Soc.*, **155** (1) A41 (2008).
  - "Theoretical Examination of Reference Electrodes for Lithium-Ion Cells," *J. Power Sources*, **174** (2007) 1001.

Plans for Next Fiscal Year

- With an effective model in-hand for the transport of lithium in the graphitic active material, the emphasis of this work will be shifted towards modifying the interfacial portion of the electrochemical model
  - Lithium deposition and reaction
  - Electronic conductivity through Solid Electrolyte Interface (SEI)
- Conduct electrochemical microcalorimetry studies with Sandia National Laboratory to quantify lithium deposition rates at low temperatures
  - Regen pulse studies at low temperatures
  - High positive-to-negative capacity ratio cells
- Further development of full two phase reaction diffusion model for active material particle
- Milestones for FY2008
  - Completion of interfacial portion of the negative electrode electrochemical model
  - Confirm microcalorimetry technique for quantifying lithium deposition

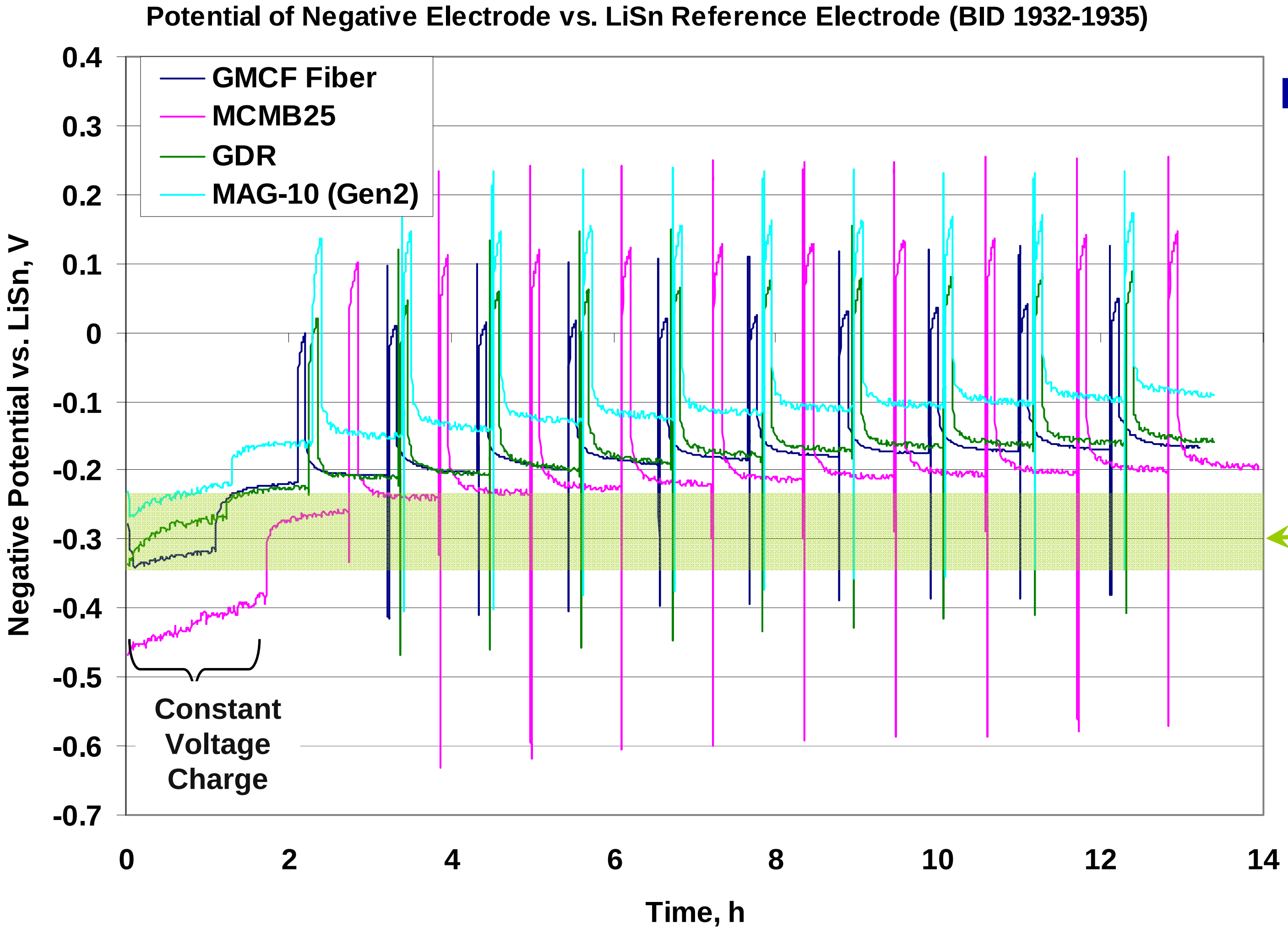
Summary

- Understanding and quantifying lithium metal deposition on the graphitic active material in negative electrodes is crucial to improving the low temperature performance of lithium-ion batteries
- A combined experimental and theoretical approach to meeting this objective is being pursued
- Technical Accomplishments in FY2007
  - Experimental GITT studies conducted
  - GITT electrochemical model modified and utilized to quantify lithium diffusion in negative electrode graphite
  - Modified cell negative electrode electrochemical model based on GITT modeling studies
  - The utility of electrochemical microcalorimetry explored
- Advancements have been reported through a wide variety of technical meetings and literature
- Plans for next year include improvement of the interfacial model and further electrochemical microcalorimetry studies

Reference Materials

- Negative electrode voltage evidence of lithium deposition at low temperatures using reference electrode cell
- Electrochemical model description (3 slides)
- Development of a modified negative electrode electrochemical model for lithium transport in graphitic active material
- Electrochemical microcalorimetery studies designed to measure lithium deposition rates at low temperatures (3 slides)

Lithium Plating is Possible for These Four Graphites During Charging and Regen



HPPC test at -30° C with constant voltage charge at 4.1V, regen pulse up to 4.4V.

Lithium plating is possible below this region.

Methodology for Electrochemical Model

- Models developed for AC impedance and DC studies using same constituent equations
- Combines thermodynamic and interfacial effects with continuum based transport equations
- Lithium diffusion in active particles and multiple particle fractions included
- Volume averaged transport equations account for the composite electrode geometry
- The system of partial differential equations are solved numerically to obtain concentration, potential, and current distributions throughout cell

Electrolyte Concentrated Solution Transport Equations

$$\varepsilon \frac{\partial c}{\partial t} = \frac{\varepsilon}{\tau} \nabla \cdot \left(D \nabla c \right) + \frac{\nabla \cdot \left[\left(1 - c \overline{V}_e \right) \left(1 - t_+^o \right) \vec{i}_2 \right]}{z_+ \nu_+ F}$$

$$\vec{i}_2 = -\frac{\kappa \varepsilon}{\tau} \nabla \Phi_2 - \nu R T \frac{\kappa \varepsilon}{F \tau} \left(\frac{s_+}{n \nu_+} + \frac{t_+^o}{z_+ \nu_+} \right) \left(1 + \frac{\partial \ln f_\pm}{\partial \ln c} \right) \nabla \ln c$$

Current Balance Equations

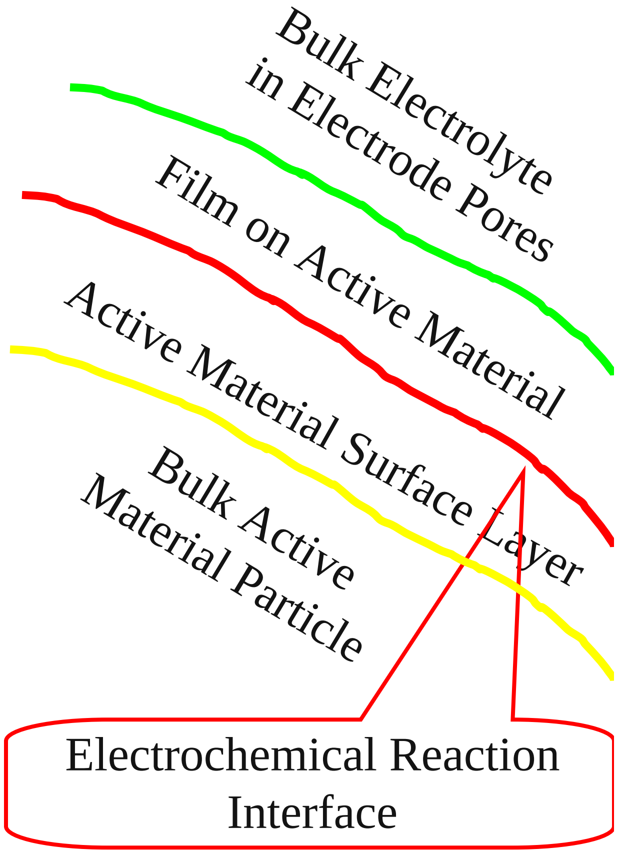
$$\nabla \cdot \vec{i}_2 = F z_+ a j_n \qquad \vec{i}_1 = -\sigma_{eff} \nabla \Phi_1$$

$$\vec{i}_1 + \vec{i}_2 = \vec{I}$$

Lithium Diffusion in Active Materials

$$\frac{\partial c_S}{\partial t} = \nabla \cdot \left(D_S \nabla c_S \right)$$

Model for Active Material / Electrolyte Interfacial Structure



- Film on active particles acts as an electrolyte layer with restricted diffusion and migration of lithium ions

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

- Surface layer of active particle inhibits the diffusion of lithium into the bulk active material

$$\frac{\partial c_{Si}}{\partial t} = \frac{\partial}{\partial y}\left(D_{Si}\frac{\partial c_{Si}}{\partial y}\right)$$

- Electrochemical reaction and double layer capacitance at film/layer interface

$$i_n = i_0 \left(\frac{c_+}{c_{+,ref}}\right)^{\alpha_A} \left(\frac{c_{Ti} - c_{Si}}{c_{Ti} - c_{Si,ref}}\right)^{\alpha_A} \left(\frac{c_{Si}}{c_{Si,ref}}\right)^{\alpha_C} \left\{\exp\left[\frac{\alpha_A F}{RT}\left(\Phi_1 - \Phi_2 - U - \eta_f - U_R\right)\right] - \exp\left[-\frac{\alpha_C F}{RT}\left(\Phi_1 - \Phi_2 - U - \eta_f - U_R\right)\right]\right\}$$

- Particle contact resistance and film capacitance

Electrochemical AC Impedance Model Developed Directly from DC Equations

- Linear perturbation complex analysis applied to constituent equations

$$c = c^0 + \tilde{c} = c^0 + c' e^{j\omega t}$$

$$i_2' = -\frac{\varepsilon\kappa\big|_{c=c^0}}{\tau}\frac{\partial \Phi_2'}{\partial x} - \nu RT\frac{\varepsilon\kappa\big|_{c=c^0}}{F\tau}\left(\frac{s_+}{n\nu_+} + \frac{t_+^o\big|_{c=c^0}}{z_+\nu_+}\right)\left(1 + \frac{\partial \ln f_\pm}{\partial \ln c}\bigg|_{c=c^0}\right)\frac{1}{c^0}\frac{\partial c'}{\partial x}$$

- Analytical equations developed for interfacial impedance and lithium diffusion in active particles

$$j\varepsilon\omega c' = \frac{\varepsilon}{\tau}D\big|_{c=c^0}\frac{\partial^2 c'}{\partial x^2} + \frac{\left(1 - c^0\overline{V}_e\right)\left(1 - t_+^o\big|_{c=c^0}\right)}{z_+\nu_+F}\frac{\partial i_2'}{\partial x}$$

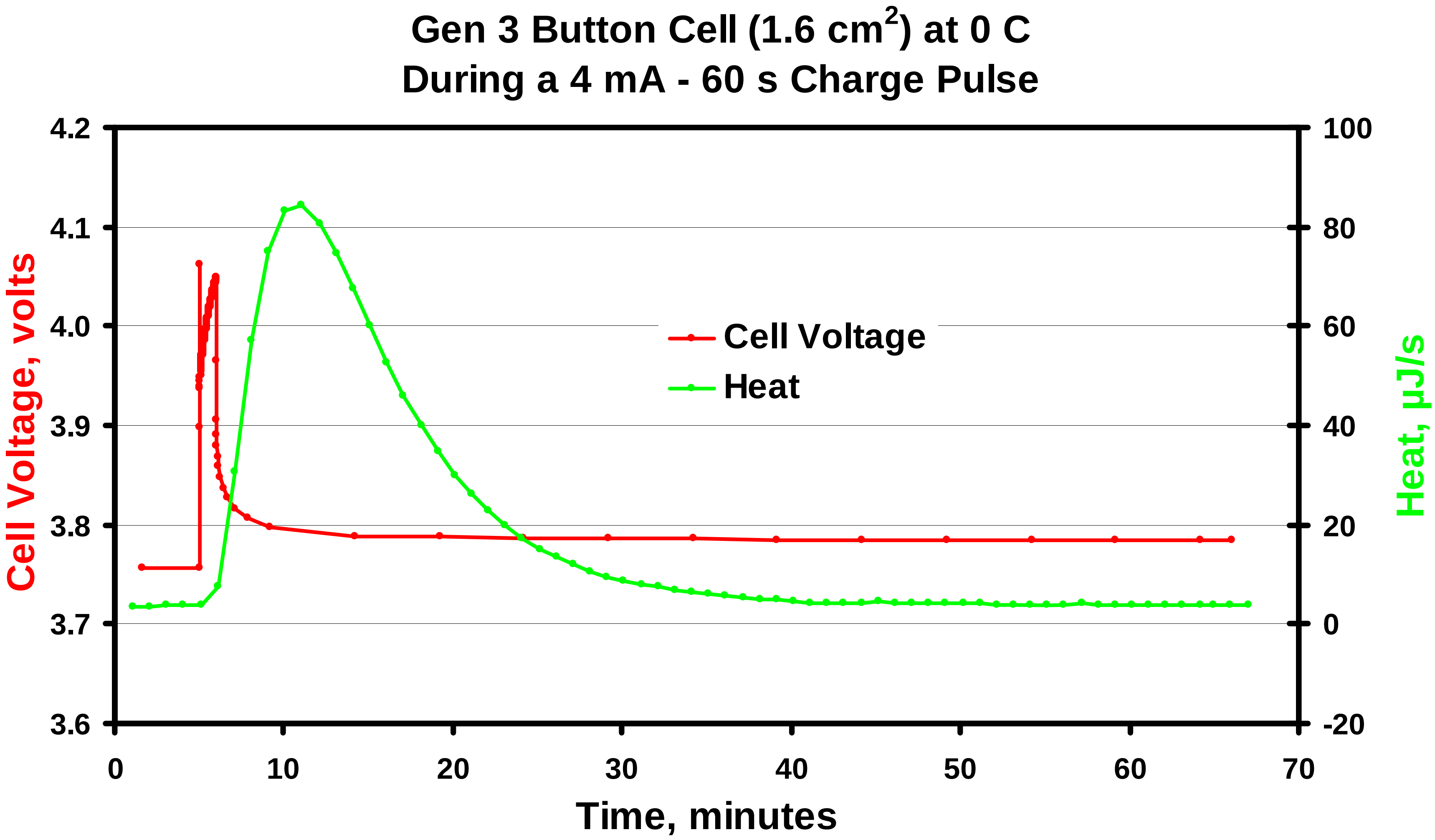
$$Z_s = \left(\frac{-K_s\dfrac{dU_b}{dc_{sb}}}{z_+F\sqrt{D_{si}\,j\omega}}\right)\left(\frac{1 + K_s\sqrt{\dfrac{D_{sb}}{D_{si}}}\tanh\left(\delta_b\sqrt{\dfrac{j\omega}{D_{sb}}}\right)\tanh\left(\delta_i\sqrt{\dfrac{j\omega}{D_{si}}}\right)}{K_s\sqrt{\dfrac{D_{sb}}{D_{si}}}\tanh\left(\delta_b\sqrt{\dfrac{j\omega}{D_{sb}}}\right) + \tanh\left(\delta_i\sqrt{\dfrac{j\omega}{D_{si}}}\right)}\right)$$

- Overall model results in a set of coupled differential equations solved numerically

Development of a Modified Negative Electrode Model

- Ideally, the full two phase reaction diffusion model would most accurately be able to track the lithium transport in the graphitic active material
  - Even fully operational this model would be much slower than the positive electrode portion of the cell electrochemical model
- The two phase modeling studies indicated the importance of lithium diffusional effects in determining the performance of the graphitic active material
- Recognizing the above observations and taking advantage of the non-linear differential equation solver, a simpler lithium transport model was developed for the negative electrode
  - Single phase diffusion equation with a strong concentration dependent diffusion coefficient and open circuit voltage slope
- While it is not possible for the modified negative electrode model to completely account for the transport of lithium in the graphite, it is quite effective for much of the transport phenomena.
  - Including HPPC tests

Electrochemical Microcalorimetry Being Used to Examine Lithium Plating at Low Temperatures



Oxidation of Lithium from Plating will Generate Heat that can be Detected with an Isothermal Microcalorimeter

- From an energy balance on the cell:

$$Q = Q_{\mathrm{Re}versible} + Q_{Irreversible}$$

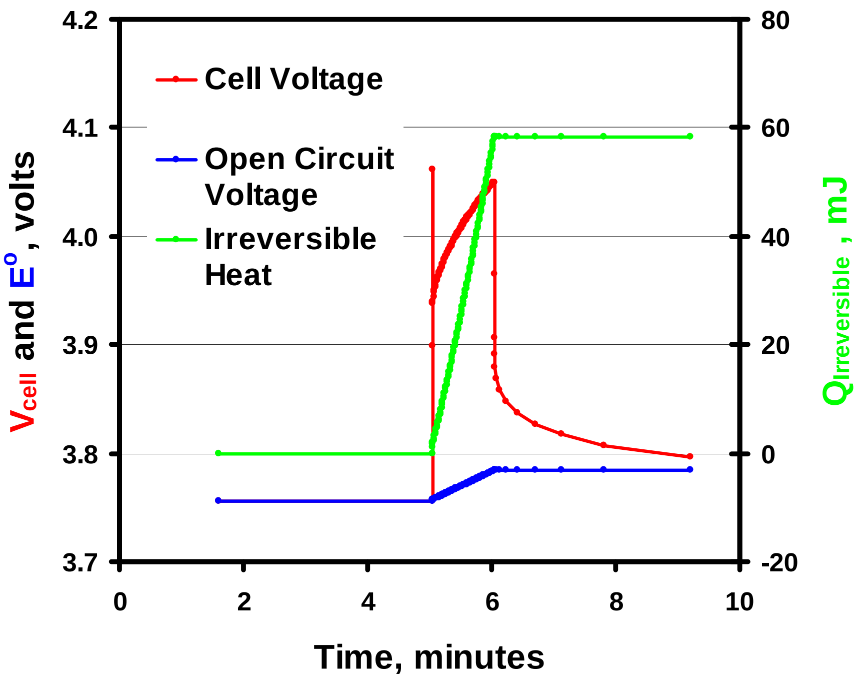
- Where:

$$Q_{\mathrm{Re}versible} = \int T\ \Delta S\left(\frac{I}{nF}\right)dt$$

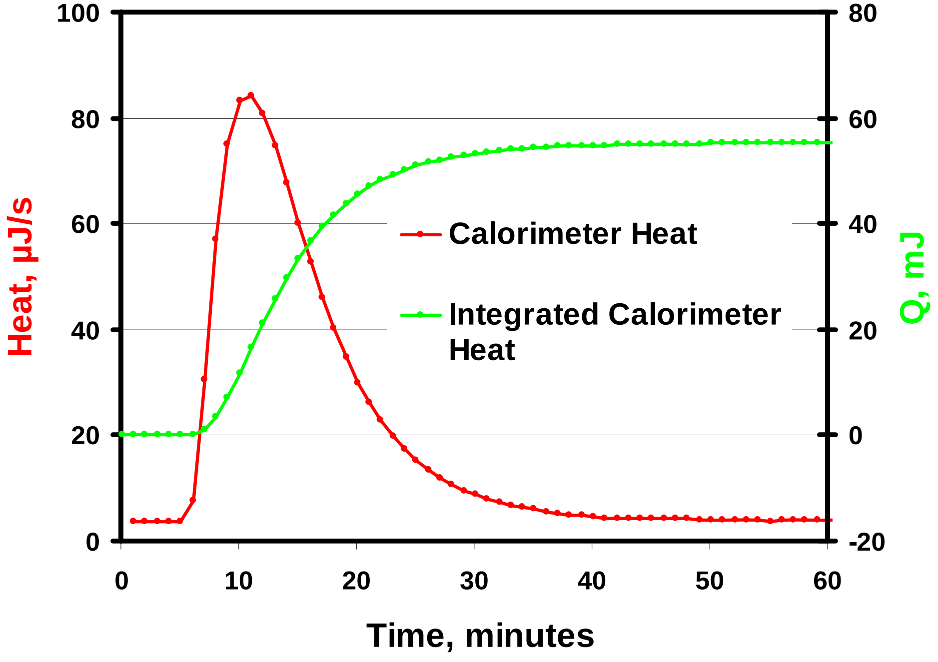
$$Q_{Irreversible} = \int \left(V_{Cell} - E^{0}\right) I\ dt$$

- In lithium ion cells $Q_{Reversible}$ is typically small and in this initial work is neglected
- The measured heat from the cell (Q) can be compared to the electrochemical heat calculated from the cell voltage ($Q_{Irreversible}$)
- Lithium oxidation in the cell is conservatively estimated to generate 270 kJ/mole of lithium

Measured and Calculated Cell Integrated Heats Generally Agree to within Less than 5%



Gen 3 Button Cell (1.6 cm^2) at 0 C
During a 4 mA - 60 s Charge Pulse



Gen 3 Button Cell (1.6 cm2) at 0 C
During a 4 mA - 60 s Charge Pulse