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Calendar Life Studies:
Gen 3 Cell Model

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DOE Vehicle Technologies Program
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Hybrid Electric Systems
Energy Storage / Applied Battery Research

This presentation does not contain any proprietary or confidential information.

Outline

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

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Purpose, Barriers, and Approach

- The purpose of this work is to correlate analytical diagnostic results with the electrochemical performance of advanced battery technologies
  - Link experimental efforts through electrochemical modeling studies
  - Identify performance limitations and aging mechanisms
  - Milestone for FY2007: Significant expansion of Gen 3 technology electrochemical model capabilities and data base
- Technical barriers in this project to reach the goal of 15 year battery calendar life for HEV and PHEV applications include:
  - Interpreting complex cell electrochemical phenomena
  - Identification of cell degradation mechanisms
- Approach in FY2007
  - Build on earlier successful Gen 2 positive electrode characterization studies in extending modeling studies to Gen 3 technology

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

Address Previous Reviewers Comments from 2006 Annual Merit Review

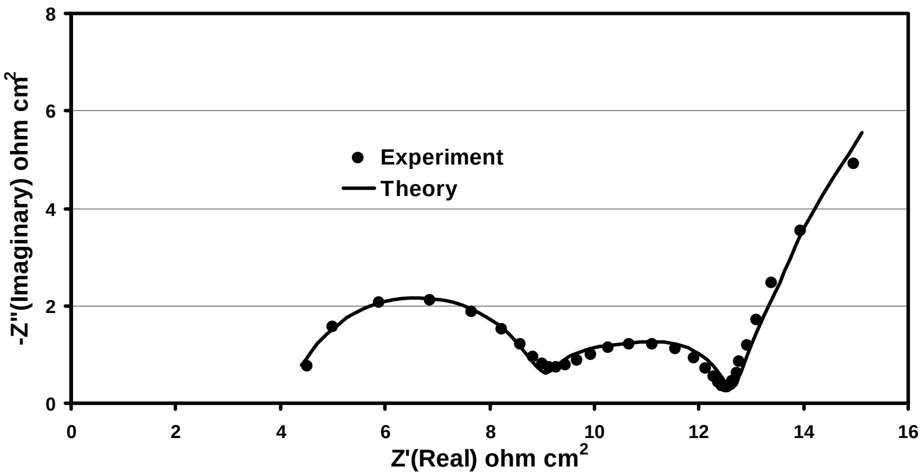
Reviewers' Comments and Questions	FY2007 Response to Comments and Questions
Test the model by modeling electrodes with different properties (thickness, loading, porosity, …).	The model has been extensively tested, but continued testing is important and the number of Gen 3 electrodes available from various suppliers does afford us the opportunity to conduct some of these types of tests.
Can model be used to investigate issues with Gen 3 electrodes?	Yes, in fact the focus of efforts this year has been on examining performance issues with Gen 3 electrodes.
Apply these results to actual cell building to predict life.	The model was used in Gen 2 studies to help elucidate cell degradation mechanisms and these types of studies will be continued for Gen 3 and future cell designs.

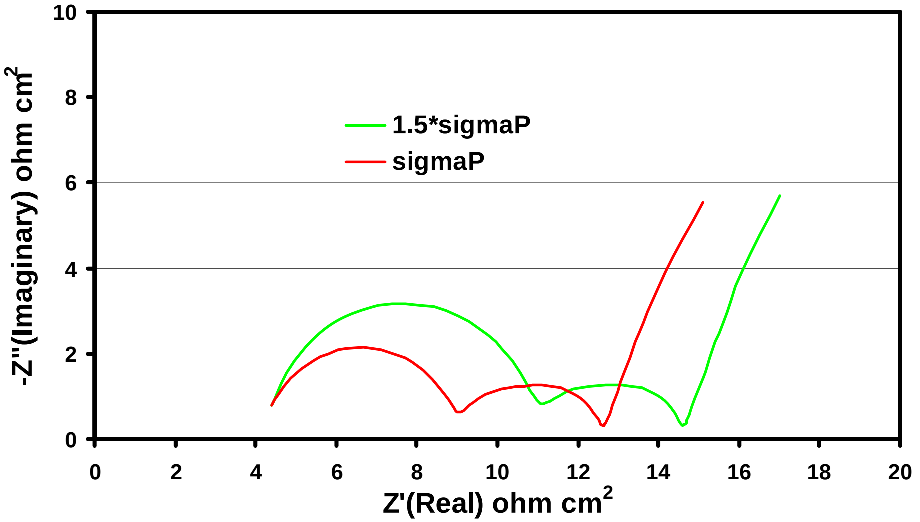
Major Accomplishments and Technical Progress

- Analysis and parameter estimation for Gen 3 technology cells continued
- Aging effects in Vendor D Gen 3 positive electrodes examined
  - Parametric analysis using AC impedance electrochemical model identified electrode electronic conductivity loss
- Four probe resistance measurement technique used to examine the electronic conductivity of various oxide based electrodes
  - Electrodes examined with different manufacturers, active materials, conductive carbon additives, and coating processes
  - Multi-layer three-dimensional model, based on Laplace’s equation, developed to interpret electrode conductivity measurements complicated by current collector foil
- Examined impact of electronic conductivity on electrode performance
  - Parametric study using DC electrochemical model to simulate Hybrid Pulse Power Characterization (HPPC) tests
- Methods to streamline parameter fitting considered

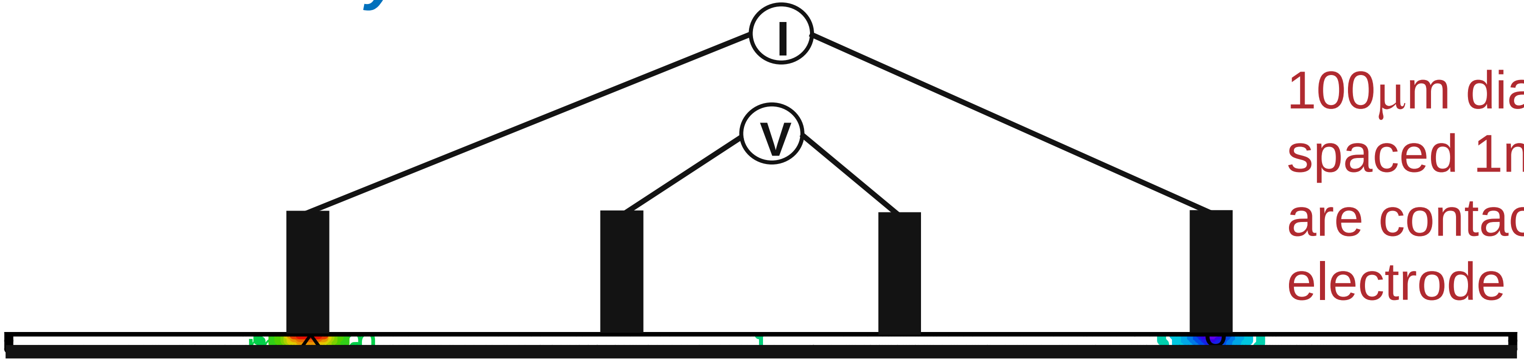
AC Impedance Electrochemical Model Simulation of Vendor D Gen 3 Positive Electrode: Increasing Size of the High Frequency (~10 kHz) Interfacial Arc during Aging

- Majority of high frequency interfacial arc associated with electronic contact resistance between oxide active material and conducting carbon additive
- Above assumption suggests that the high frequency arc impedance increase results from a loss of the electronic contact between active and conductive particles
- Because of the high characteristic frequency of the arc the possibility that an electronic contact resistance at the electrode/current collector interface cannot be eliminated





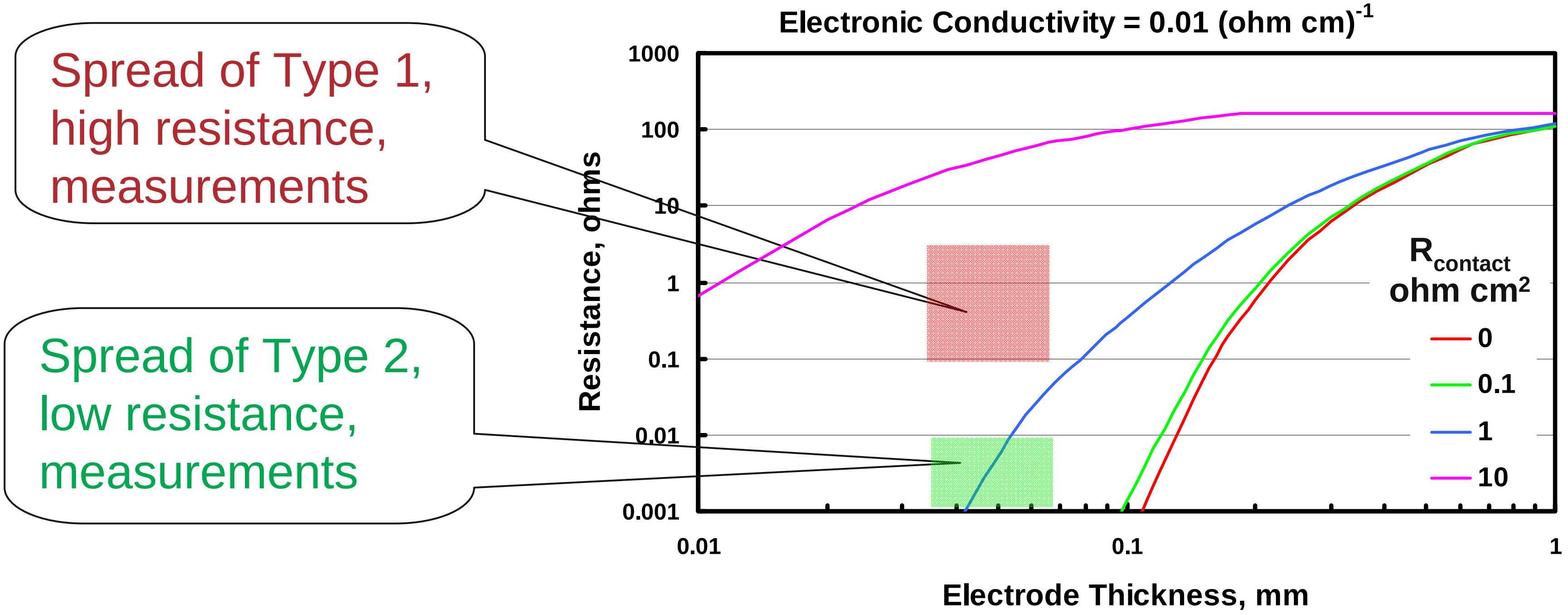
Four Probe DC Resistance Measurements taken on a Series of Dry Electrode Laminates



100µm diameter pins, spaced 1mm apart, are contacted to the electrode

- With the thin (<100µm) resistive electrode coating on metallic foil, most of the current passes through the coating and travels along the foil
- In general the coatings gave two types of resistance values.
  - Type 1 where the resistance is ~0.1 ohms or greater
  - Type 2 where the resistance is << 0.1 ohms
- The high resistance (Type 1) measurements correlated with coatings that exhibited a high frequency impedance circular arc.
- Gen 3 coatings with Super-P carbon conductive additive had a high resistance (Type 1).
- Gen 3 coatings with TB5500 carbon conductive additive showed a low resistance (Type 2).

Simulation of Four Probe Resistance Technique used to Interpret Experimental Results



Spread of Type 1, high resistance, measurements

Spread of Type 2, low resistance, measurements

- The four probe technique cannot be used to accurately determine the effective electronic conductivity of the electrode laminates
- Having a low resistance does not guarantee a good performing electrode or even a good electronically conducting electrode
- Having a high resistance is a clear sign of a poor electronically conducting electrode and/or a high current collector contact resistance

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
  - "Modeling the Impedance Versus Voltage Characteristics of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$," *Electrochim. Acta*, **53** (2008) 2121.
  - "Theoretical Examination of Reference Electrodes for Lithium-Ion Cells," *J. Power Sources*, **174** (2007) 1001.

Plans for Next Fiscal Year

- Improve electrochemical model parameter fitting methods
  - Faster parameter fitting critical for keeping pace with experimental efforts
- Continue analysis and parameter estimation for Gen 3 technology cells
  - Alternative Gen 3 technology electrodes
  - Temperature, electrolytes, and SOC
- Develop electrochemical model for alternative two-phase active materials (e.g. $LiFePO_4$, $LiMn_2O_4$, $Li_4Ti_5O_{12}$)
- 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 FY2008
  - Develop an efficient parameter fitting technique for model
  - Apply model parameter fitting technique to Gen 3 electrodes

Summary

- The purpose of this work is to correlate analytical diagnostic results with the electrochemical performance of advanced battery technologies
- The approach is to build on earlier successful Gen 2 positive electrode characterization studies in extending modeling studies
- Technical Accomplishments in FY2007
  - Analysis and parameter estimation for Gen 3 technology cells continued
  - Aging effects in Vendor D Gen 3 positive electrodes examined
  - Four probe resistance measurement technique used to examine the electronic conductivity of various oxide based electrodes
  - Examined impact of electronic conductivity on electrode performance
- Advancements have been reported through a wide variety of technical meetings and literature
- Plans for next year include improved parameter fitting methods and model development

Reference Materials

- Electrochemical model description (3 slides)
- Electronic conductivity studies on oxide active material electrodes (4 slides)
- Impact of electronic conductivity on electrode performance for Gen 3 positive electrodes (4 slides)

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

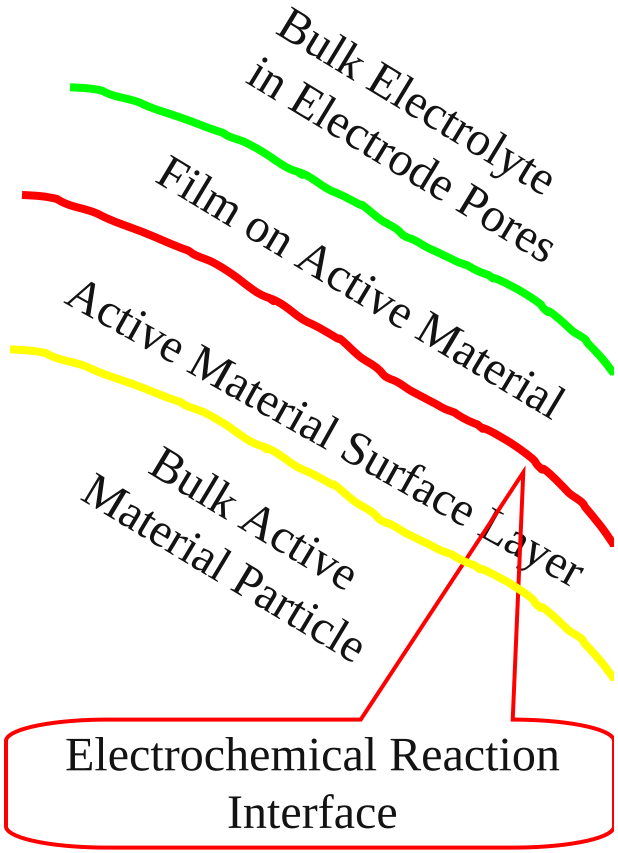
$$\nabla \cdot \vec{i}_2 = F z_+ a j_n \qquad \vec{i}_1 = -\sigma_{eff} \nabla \Phi_1$$

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

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



Bulk Electrolyte in Electrode Pores

Film on Active Material

Active Material Surface Layer

Bulk Active Material Particle

Electrochemical Reaction Interface

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

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

- 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

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

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

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

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

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

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

Electronic Current in Oxide Active Material Electrode

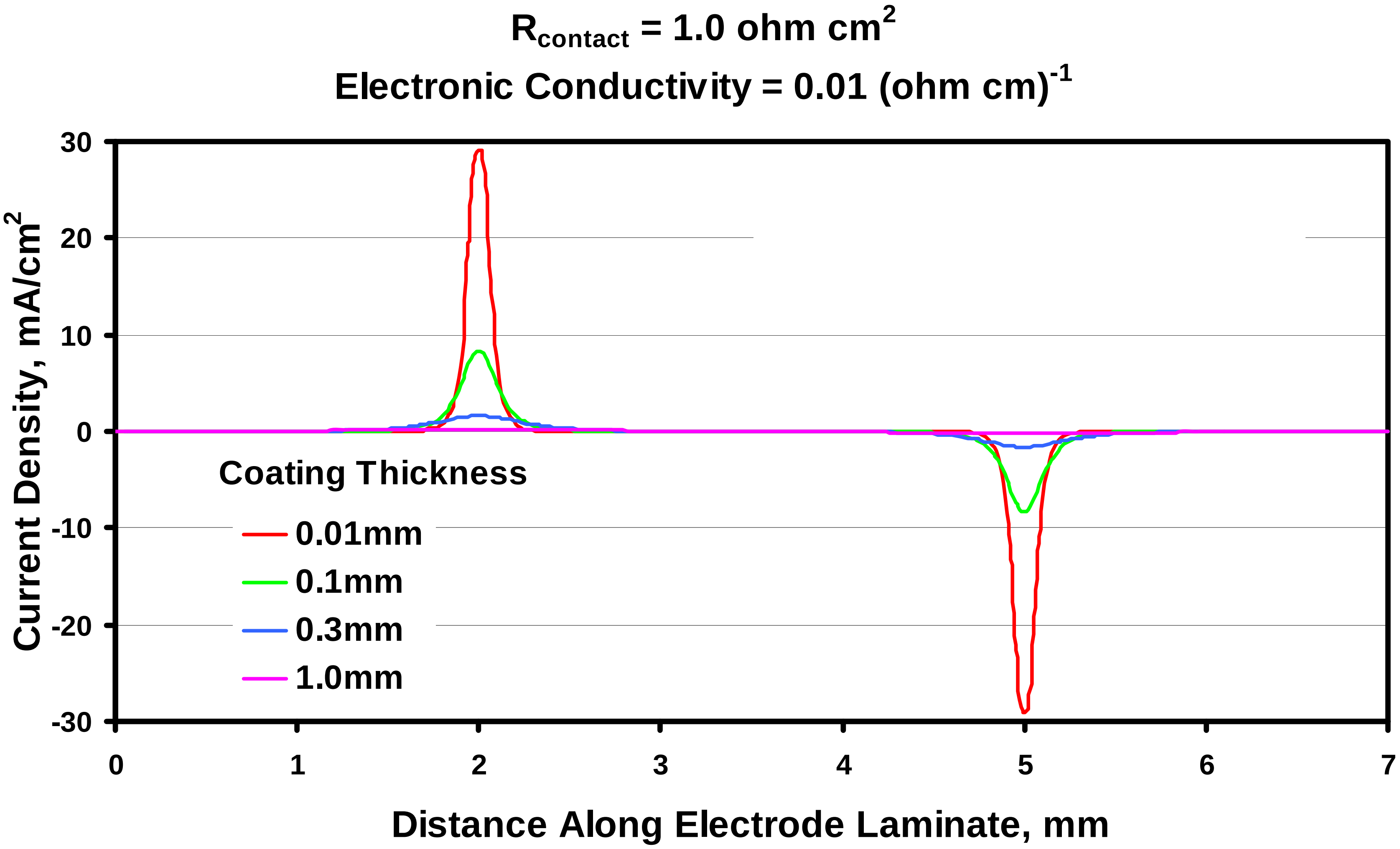
- Electronic current enters/leaves the electrode through the current collector foil and leaves/enters the electrode as an ionic current through the electrolyte
- Because oxide active materials are not very electronically conductive, a carbon and/or graphite conductive material is added to oxide electrodes
  - Carbon > 100 $(\text{ohm cm})^{-1}$
  - Graphite > 700 $(\text{ohm cm})^{-1}$
  - Typical Oxide < 10^{-4} $(\text{ohm cm})^{-1}$
  - Organic Liquid Electrolyte ≅ 0.01 $(\text{ohm cm})^{-1}$
- The current takes a rather ill-defined path (i.e. path of least resistance) as it travels through the electrode, which includes both conductive additive and oxide phases
- The size of a contact resistance can vary with just about everything, but the SEI, PVDF binder, electrolyte, oxide on the aluminum foil, and general lack of contact pressure would all tend to enhance the contact resistance

Four Probe Resistance Measurements on a Wide Variety of Oxide Electrode Laminates

Electrode Description	Coating	Manufacturer	Conductive Additive	Resistance ohms
Gen 3 Positive	single	Vendor F	TB5500	0.001
Mn Spinel	single	Vendor D	Super-P	0.003
Gen 3 Positive	double	Vendor B	TB5500	0.005
Gen 3 Positive (Seimi)	double	Vendor C	TB5500	0.007
Ti Spinel	single	Argonne	Gen 2 Mix	0.007
Gen 3 Positive	double	Vendor D	TB5500	0.008
Gen 2 Positive	single	Quallion	Gen 2 Mix	0.010
Gen 3 Positive	double	Vendor D	Super-P	0.12
Mn Spinel	single	Argonne	Gen 2 Mix	0.33
Gen 3 Positive	single	Vendor D	Super-P	0.42
NMC with 1/9 Co	single	Argonne	Gen 2 Mix	1.61
NMC with 2/9 Co	single	Argonne	Gen 2 Mix	3.02
NMC with no Co	single	Argonne	Gen 2 Mix	3.45
NMC with 3/9 Co	single	Argonne	Gen 2 Mix	4.26

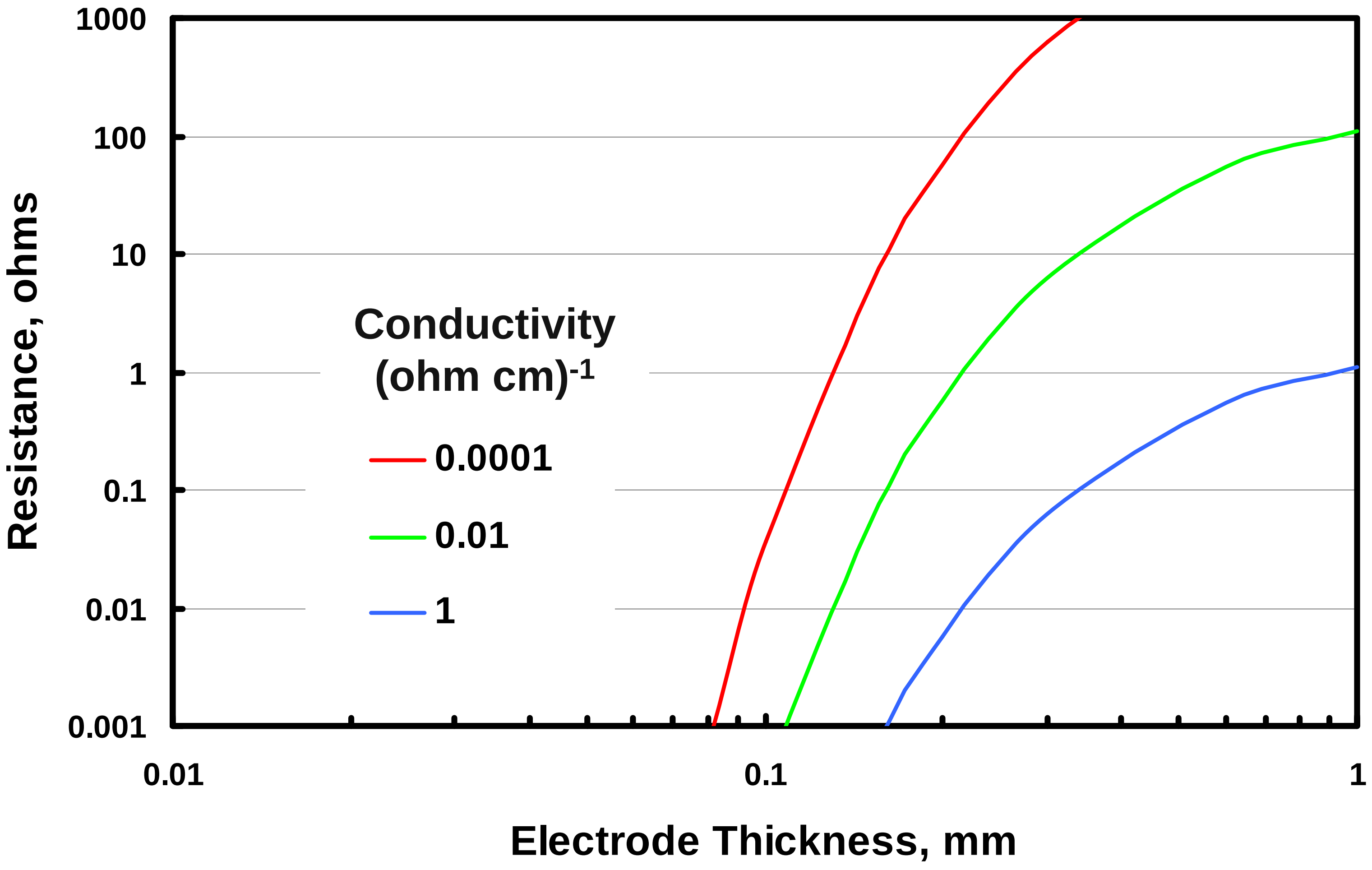
Gen 2 Mix: SFG-6 Graphite and Carbon Black

Current Distribution Simulation at Foil/Coating Interface During Four Probe Resistance Measurement

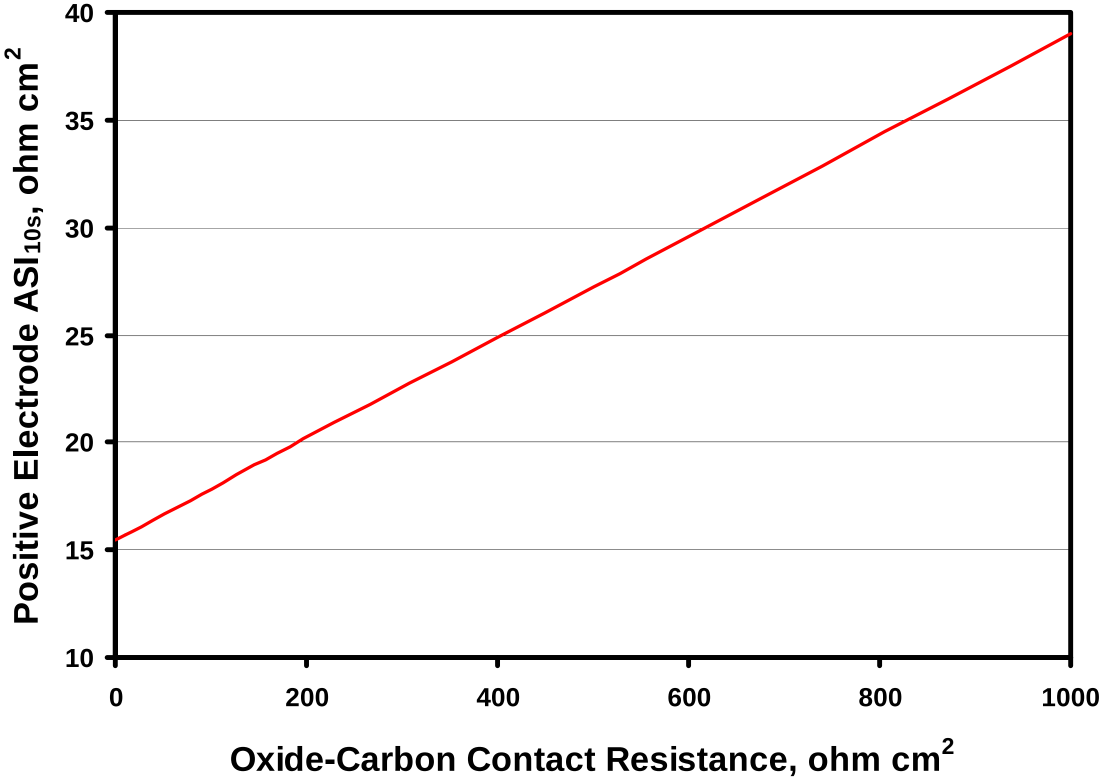


Four Probe Electrode Resistance Simulation

No contact resistance between electrode coating and current collector foil

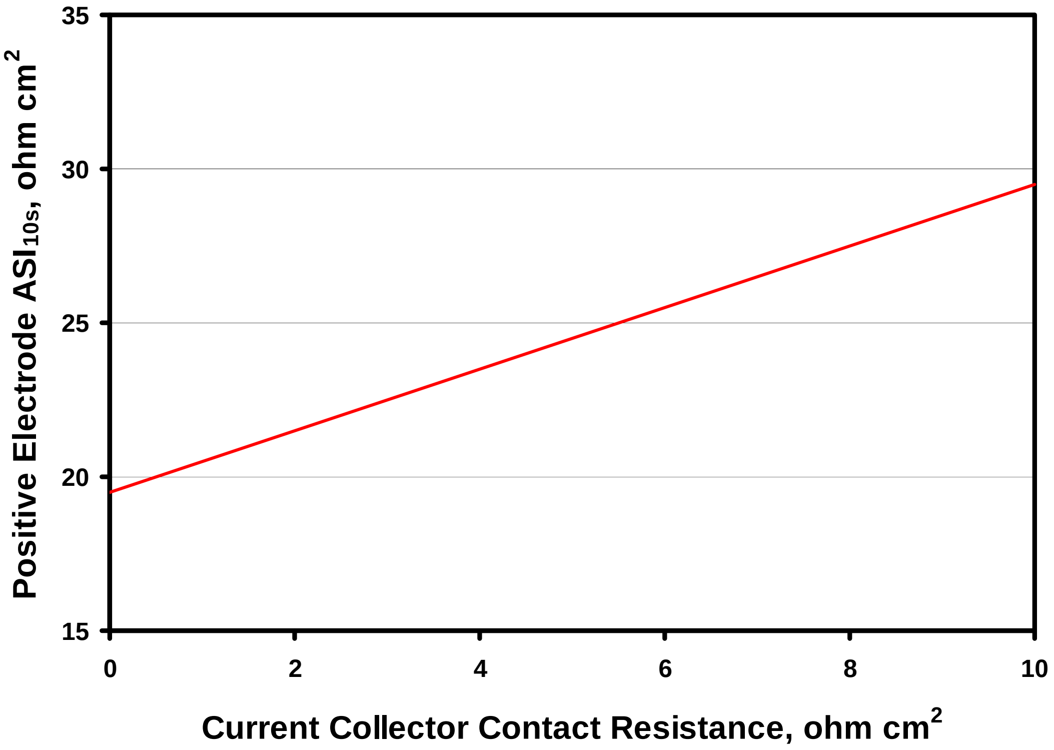


Simulation of Gen 3 Positive Electrode 5C HPPC Discharge Impedance: Impact of Oxide-Carbon Contact Resistance



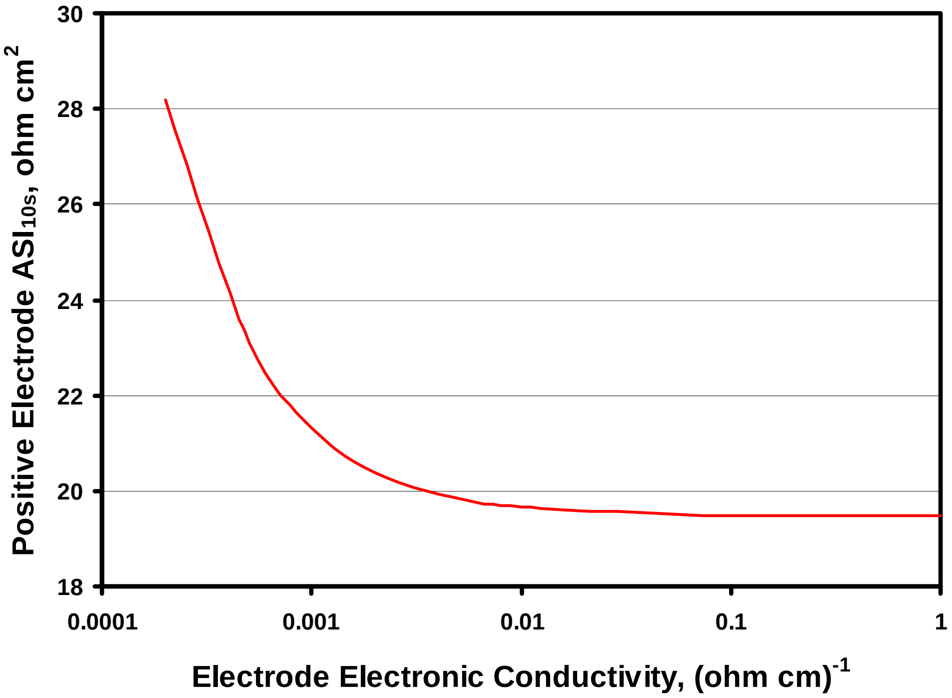
- Linear relationship is indicative of the dominance in electrode’s interfacial impedance over other electrode impedance effects (e.g. ionic conductivity, electronic conductivity, electrolyte salt diffusion, …)
- Slope of curve is equal to the ratio of the electrode’s geometric area to its electrochemically active area

Simulation of Gen 3 Positive Electrode 5C HPPC Discharge Impedance: Impact of Current Collector Contact Resistance



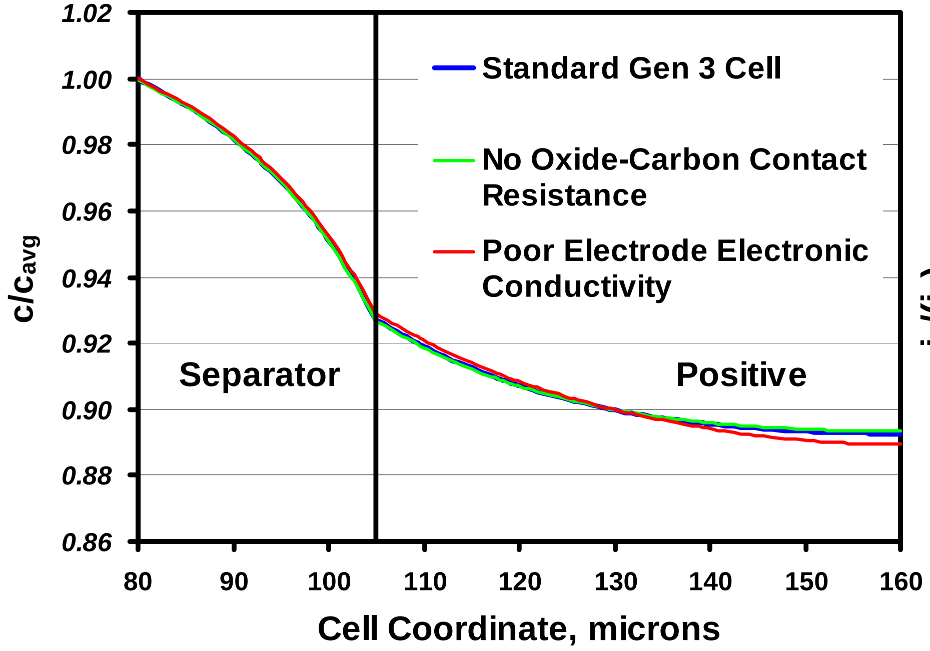
- The 1:1 slope and linear behavior results from the current collector resistance being in series with the other electrode impedance effects
- This simulation does not take into account any non-uniformity of the electrode’s current distribution across the face of the current collector resulting from the high contact resistance

Simulation of Gen 3 Positive Electrode 5C HPPC Discharge Impedance: Impact of Electrode Electronic Conductivity

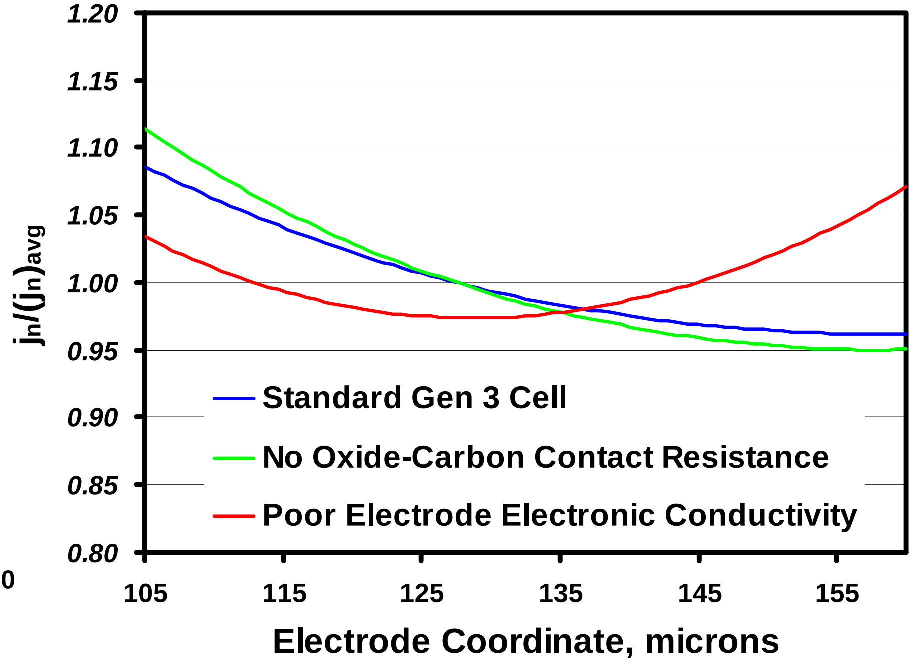


- >0.01 (ohm cm)$^{-1}$: electronic conductivity is much greater than the ionic conductivity and does not impact electrode impedance
- 0.001-0.01 (ohm cm)$^{-1}$: electronic conductivity is comparable to the ionic conductivity
- <0.001 (ohm cm)$^{-1}$: electronic conductivity is much less than the ionic conductivity and significantly impacts electrode impedance

Simulation of Gen 3 Positive Electrode 5C HPPC Test: Distributions at 10s into the Discharge Pulse



Electrolyte Salt Concentration Distribution



Positive Electrode Reaction Distribution

- Electronic conductivity effects has minimal impact on the salt distribution
- Eliminating the oxide-carbon contact resistance, effectively reduces the interfacial impedance and increases the change in the reaction rate
- The concave reaction rate curve is typical of an electrode where the electronic and the ionic conductivities are comparable