Battery Safety Science Webinar Series
Advancing safer energy storage through science
June 14, 2021
Multiphysics and Multiscale Modeling of Lithium-ion Battery Safety Issues
Host Dr. Daniel Juarez Robles
Presenter Dr. Jun Xu
Assistant Professor
Department of Mechanical Engineering & Engineering
Science
University of North Carolina at Charlotte

©️ 2021 Underwriters Laboratories Inc. All rights reserved. UL and the UL logo are trademarks of UL LLC.
BACKGROUND

Battery Crash Safety

- Fire/explosion after car crash
- Cell-phone battery explosion after penetration
- Large-scale energy storage system safety

Battery Degradation

- Li-plating
- Li-dendrite

- Mechanical abusive loading
- Li plating
- Li dendrite
- Particle crack

Vehicle Energy & Safety Laboratory (VESL)

Particle Scale

Component Scale

Cell Scale

Pack Scale

Atomic Scale

1 × 10^{-10} ~ 1 × 10^{-8}

1 × 10^{-7} ~ 1 × 10^{-3}

1 × 10^{-4} ~ 1 × 10^{-2}

1 × 10^{-2} ~ 1 × 10^{-1}

1 × 10^{-1} ~ 1 × 10^{0}

Unit: m
Particle Scale

Component Scale

Cell Scale

Pack Scale

Atomic Scale

$1 \times 10^{-10} \sim 1 \times 10^{-8}$

$1 \times 10^{-7} \sim 1 \times 10^{-3}$

$1 \times 10^{-4} \sim 1 \times 10^{-2}$

$1 \times 10^{-2} \sim 1 \times 10^{-1}$

$1 \times 10^{-1} \sim 1 \times 10^{0}$

Unit: m
AN INTERESTING QUESTION

Li diffusion mechanism in Si/C system

Two representative Si/C mixing modes

1. Li diffusion in Si first or C first?
2. How the composite configuration affects diffusion? DFT simulation
3. How the C material affects Li diffusion in Si?
Method

DFT simulation

Si/C with various C layer thicknesses

Si/C(2) 14 Å 2 Å 11 Å
Si/C(3) 14 Å 3 Å 11 Å
Si/C(4) 14 Å 4 Å 11 Å

Two representative Si/C configuration modes

Mixture mode

Core-shell mode

AIMD simulation:

1200 K, 0.01 eV/Å, 10^{-4} eV

(Gao, et al. ACS Applied Material & Interfaces, 2021)
Discussion

Diffusivity analysis

Core-shell mode

Mixed mode

- A thicker C layer slightly decreases the Li diffusivity in Si
- The overall Li diffusivity in mixture mode is almost same
- Li diffusivity in core-shell mode highly depends on the C layer atomic structure
- Li diffusivity in core-shell mode is commonly lower than in mixture mode

<table>
<thead>
<tr>
<th>Type</th>
<th>Bulk c-Si</th>
<th>Si/C (2)</th>
<th>Si/C (3)</th>
<th>Si/C (4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixture mode</td>
<td>7.75e-5</td>
<td>2.097e-4</td>
<td>2.028e-4</td>
<td>2.003e-4</td>
</tr>
<tr>
<td>Core-shell mode</td>
<td>\</td>
<td>1.545e-4</td>
<td>1.953e-4</td>
<td>1.435e-4</td>
</tr>
</tbody>
</table>

(Gao, et al. ACS Applied Material & Interfaces, 2021)
Particle Scale

Unit: m
Si/C composite anode shows a complex multiscale structure property.
PART I: CONTACT BEHAVIOR

**Modeling**: Si-C core-shell particles

- **FEM model settings**
- **Governing equations**

**Symmetry axis**

**Si-C interface**

**C-C interface**

**Vertical constraint**

**R**

**Li flux**

\[
\varepsilon_y^l = \ln(1 + \alpha c) / 3 : \text{Lithiation induced strain}
\]

\[
\varepsilon_y^e = \left[ (1 + \nu)\sigma_y - \nu\sigma_{id}\sigma_y \right] / E : \text{Elastic strain}
\]

\[
\varepsilon_y^p = \lambda S_y^p : \text{Plastic strain increment}
\]

Based on Hooke’s law

\[
\sigma_y = \frac{E \varepsilon_y}{1 - \nu^2} + \frac{E \nu}{1 - 2\nu} \sigma_y
\]

**Structure mechanics**

**Partial differential equation**

\[
\frac{\partial c}{\partial t} - D \nabla \cdot \left( \nabla c - \frac{\Omega c}{RT} \nabla \sigma_h \right) = 0
\]

**Diffusion equation**

\[
\bar{c} = c / c_{\text{max}}
\]

\[
E(\bar{c}) = E_0 + \bar{c}(E_1 - E_0)
\]

\[
\sigma_y(\bar{c}) = \sigma_y^0 + \bar{c} (\sigma_y^1 - \sigma_y^0)
\]

**Mechanical parameters related to Li\(^+\) concentration c**

PART I: CONTACT BEHAVIOR

Simulation: Stress analysis

- Stress evolution and distribution

  - Plastic contact mainly occur in first cycle
  - Tensile stress produced in every cycle end

Parameter definition

\[
\sigma_n^{\text{max}} \quad \text{maximum Si-C interface normal stress}
\]

\[
\sigma_c^{\text{max}} \quad \text{maximum C-C contact stress}
\]

\[
\frac{R - R_0}{R_0} = \frac{R_0 + \Delta R_{\text{max}}}{R_0} \quad \text{maximum Si radius change}
\]

\[
\frac{t(t_0)}{t_0} = \frac{(t_0 + \Delta t_{\text{max}})}{t_0} \quad \text{maximum C thickness change}
\]

PART II: SI/C CORE-SHELL STRUCTURES

Modeling: Si-C core-shell particles

Core-shell structure studied in previous slides

Nano-structure designs

- Yolk-shell
- Dual-shell
- Core-shell
- Hollow core-shell
- Multicore-shell

PART II: SI/C CORE-SHELL STRUCTURES

Modeling: FEM model settings

Geometry and boundary

- Same governing equations were adopted

2D simplification

- Each structure has three different $\lambda$ values

Five structures

(Gao et al., Nano Energy, 2021)
PART II: SI/C CORE-SHELL STRUCTURES

Simulation: Mechanical behavior

- Stress and displacement curve

![Stress and Displacement Curve](image)

- Stress distribution

![Stress Distribution](image)

- Failure modes

![Failure Modes](image)

- The normal stress $\sigma_n$ at the core-shell interface is in compressive stress status and increases during lithiation.

- At the core-shell interface, the maximum normal stress occurs in the contact area of two particles, and the maximum compressive stress is in the center of the C shell.

PART II: SI/C CORE-SHELL STRUCTURES

Simulation: Failure, capacity, design

Shell fracture

Core-shell debonding

- Capacity behavior

Actual Li$^+$ concentration, $c_{\text{act}}$(10$^4$ mol/m$^3$)

Normalized capacity considering debonding, $C^{\text{d}}_{\text{nom}}$

PART III: MULTISCALE-MULTIPHYSICS STUDY

Modeling: Multiphysics coupling strategy

- Constitutive equation in microscale
  \[ \sigma_{ij} = 2G\varepsilon_{ij} + \lambda\varepsilon_{kk}\delta_{ij} - \Omega_{eff}\Delta c_s \frac{E}{1-2\nu} \delta_{ij} \]

- Li diffusion model in microscale
  \[ \frac{\partial c_s}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} r^2 J_s = 0 \]

- Stress-strain model in macroscale
  \[ \Sigma_{ij} = C_{ijkl}(\Psi_{kl} - \Psi_{eigen}\delta_{kl}) \]

- Li flux model in macroscale
  \[ I_e = -\kappa_{eff} \left[ \nabla \Phi_e - \frac{2RT}{F} \left( 1 + \frac{d \ln f_s}{d \ln C_e} \right) (1-t_e) \nabla \ln C_e \right] \]

Governing equations
**Simulation**: Model validation

- Multiscale and Multiphysics coupling model can well predict the voltage and deformation

---

(Gao, et al. *Journal of Power Sources*, 2020)
Vehicle Energy & Safety Laboratory (VESL)

Component Scale

1 × 10^{-4} ~ 1 × 10^{-2}
Experiment: Material test of battery components

- SEM images after tensile test

MECHANICAL BEHAVIOR OF ELECTRODE

**Modeling:** Laminate theory and sandwich model

**Simulation:** Tension and failure analysis

**FAILURE BEHAVIOR OF SEPARATOR**

**Experiment:** Indentation test on anode-separator-cathode stacks

- **Sphere indentation**

- **Cylinder compression**

**Ex-situ** observation of separator morphology

(Yuan et al., Journal of Power Sources, 2020)
**FAILURE BEHAVIOR OF SEPARATOR**

**Simulation:** Separator deformation based short-circuit criteria

- Volumetric strain criterion
- Equivalent strain criterion

Particle Scale
Cell Scale
Component Scale
Pack Scale

Atomic Scale

$1 \times 10^{-10} \sim 1 \times 10^{-8}$

$1 \times 10^{-7} \sim 1 \times 10^{-3}$

$1 \times 10^{-4} \sim 1 \times 10^{-2}$

$1 \times 10^{-2} \sim 1 \times 10^{-1}$

$1 \times 10^{-1} \sim 1 \times 10^{0}$

Unit: m
MECHANICAL BEHAVIOR OF STRUCTURE

**Experiment:** Mechanical test of single cell

- Test platform

- Test samples

- Typical results

(Xu et al. Scientific Reports, 2016)
(Xu et al. Experimental Mechanics, 2018)
**MECHANICAL BEHAVIOR OF STRUCTURE**

**Modeling**: homogenized method and detailed model

- **Homogenized modeling**
  - Elastic property:
    \[ \sigma = 9300 \cdot 10^1 + 0.8 \]

- **Detailed modeling**
  - Plastic:
    \[ R = \begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{bmatrix} \]
  - Mechanical property of each component:
    - Casing: Steel, 7.85e-9, 211000, 740, \(\eta\) related
    - Separator: PP/PE, 1.2e-9, 275, 11.39, 1
    - Anode: Cu/Active material, 2.27e-9, 300, /, /
    - Cathode: A//Active material, 4.69e-8, 720, /, /
    - Winding: Steel, 7.85e-9, 100000, 2430, /
    - Foam: /, 6.5e3, 100, /

- **RVE modeling**
  - RVE Mechanical Model:
    \[ \rho \ddot{u} + \dot{\gamma}^2 = V \dot{q} \]
  - RVE Electrical Model:
    \[ Q_e = j \int \rho_e \dot{q} dt \]

*References*
- Wang et al., *Journal of Power Sources*, 2019
- Jia et al., *Journal of Energy Storage*, 2021
Simulation: various abusive loading conditions

• Simulation results by homogenized model

• Simulation results by detailed model

(Wang et al. Journal of Power Sources, 2019)
Multiphysics modeling strategy

**1D battery model**

- Anode
- Cathode
- Separator

\[ \begin{align*}
\frac{d}{dt} (e^f) &= -D_{e}^f \nabla e^f + \frac{i^f}{F} \\
i^f &= -\kappa_{ef}^r \nabla \phi^r + \frac{2\kappa_{ef}^r R_c^f T}{F} \left(1 + \frac{d \ln F}{d \ln c^f}\right)(1 - t_s) \nabla \ln c^f
\end{align*} \]

\[ Q_{1D} = T_a^{Te} (t) = T_a^{TD} (t) \]

**Short circuit model**

- Anode
- Cathode
- Separator

\[ \begin{align*}
\bar{E} &= -\nabla \phi \\
\bar{j} &= \kappa_s \nabla \phi \\
Q_s &= \frac{j \cdot j}{\kappa_s}
\end{align*} \]

**Thermal model**

\[ d \cdot \rho C_p \frac{\partial T}{\partial t} + d \cdot \rho C_p T \cdot \nabla T + \nabla \cdot q = d \cdot Q \]

\[ Q_s = x_s (t) = x(t) \cdot c(\sigma_i (t) - \sigma_s (t)) \]

\[ R_c^s = z (1 - S_c^s) \]

\[ T^{Te} (t) = T^T (t) \]

\[ T^{Me} (t) = T^{Te} (t) \]

**Thermal runaway model**

\[ Q_{run} = H^s \cdot W_c \cdot A_{set} \cdot \exp \left[ -\frac{E_{set}}{R_c^s T} \right] \cdot c_{set} \]

\[ \frac{dc_{set}}{dt} = -A_{set} \cdot \exp \left[ -\frac{E_{set}}{R_c^s T} \right] \cdot c_{set} \]

**Mechanical model**

\[ \rho \frac{\partial^2 u}{\partial t^2} = \nabla \cdot (F_s S) + F_F \]

MULTIPHYSICS BEHAVIOR OF LIBS

**ISC EVOLUTION**

**Experiment: In-situ particle indentation of a cell**

(Liu and Jia et al. *Journal of Materials Chemistry A*, 2018)

Comparing force/voltage/thermal

Highly repeatable experiment
**ISC EVOLUTION**

**Multiphysics model**

Prediction of mechanical, electrochemical & thermal behavior after short-circuit

### Mechanical model

\[
\rho \frac{\partial^2 u}{\partial t^2} = \nabla \cdot (F_i S) + F_v
\]

Deformation

### Thermal runaway model

\[
\frac{dc_{sei}}{dt} = -A_{sei} \exp\left(-\frac{E_{sei}}{RT}\right) c_{sei}
\]

Heat

### Heat model

\[
\rho C_p \left( \frac{\partial T}{\partial t} + u_{trans} \cdot \nabla T \right) + \nabla \cdot (q + q_r) = Q
\]

Temperature

### Short circuit model

\[
j = \kappa^S \nabla \phi \quad R_{st} = \frac{1}{\kappa^S}
\]

Deformation

### Battery model

\[
\frac{dc_{cell}}{dt} = \frac{\Delta \phi}{R_{sol}} \quad \frac{dc_{cell}}{dt} = \nabla \cdot (-D \nabla c_i)
\]

Current

\[
i_{cell} = \frac{\Delta \phi}{R_{sol}} \quad E_{cell} = \Phi^{pos}_s - \Phi^{neg}_s \quad Q_{h,cell} = Q_{h,pass} + Q_{h,sol}
\]

Voltage

### Detailed components

Separator and current collector melting

### Melting

\[
\frac{dc_{sep}}{dt} = -A_{sep} \exp\left(-\frac{E_{sep}}{R_g T}\right) c_{sep}
\]

Resistance change

\[
\frac{dc_{cc}}{dt} = -A_{cc} \exp\left(-\frac{E_a}{R_g T}\right) c_{cc}
\]

\[
\kappa^{sep} = \kappa^e_{cc} \Phi^{sep} \left(1 - c_{sep}\right) + \kappa^0_{sep}
\]

**ISC EVOLUTION**

**Computation:** Internal short circuit (ISC) analysis

Indications from computational model

(Liu and Jia et al. *Journal of Materials Chemistry A*, 2018)
SAFETY EVALUATION OF DEFECTIVE BATTERY

**Experiment:** Manufacture/test of defective battery

- **Manufacture**
  - Forced displacement
  - Mobile Phone Lithium-ion Battery
  - Indenter: Or
  - Temperature
  - Voltage

- **Test**
  - Compression
  - Bending
  - D = 10mm
  - INSTRON 2345
  - L = 60mm

- **Free Drop**
  - Drop Testing Machine
  - Cameras
  - Data Acquisition 34970A

(Jia et al. Journal of Materials Chemistry A, 2020)

**Modeling:** Mechanical & multiphysics models

- **Mechanical**
  - **Temperature Point**
  - **Loading Point**
  - **Positive Active Material**
  - **Negative Active Material**
  - **Aluminum Collector**

- **Multiphysics**
  - **3 mm**
  - **2 mm**

(Battery model: $E_{bat} = \Phi_{bat} - \Phi_{m} = \frac{\Delta \Phi}{\Delta t} = -D \nabla \Phi$

Short circuit: $\frac{I}{R_{bat} + R_{int}} = Q = I / (R_{bat} + R_{int})$

Thermal model: $\rho c_v \rho c_v \frac{\partial T}{\partial t} + q = \alpha T - \frac{\partial Q}{\partial T}$

Temperature field: Heat sources

Chemical Reaction: $Q_{chem} = N_{e,0} \frac{N_{e,0}}{Z^2} A \exp \left( \frac{-E_a}{kT} \right)$

2021/6/14
Vehicle Energy & Safety Laboratory (VESL)
SAFETY EVALUATION OF DEFECTIVE BATTERY

Simulation: Risk evaluation

- Mechanisms (defection introduction process)
  - Electrochemical-thermal safety evaluation

• Mechanical safety evaluation

- ISC Process

(Jia et al. Journal of Materials Chemistry A, 2020)
STRESS-DRIVEN SHORT-CIRCUITS

Experiment & Simulation: Mechanical behavior characterization of components

- In-plane tension
  - Cathode
  - Anode
  - Separator

STRESS-DRIVEN SHORT-CIRCUITS

Experiment & Simulation: Mechanical behavior characterization of components

- Out-of-plane loading
  - Cathode
  - Anode + separator

STRESS-DRIVEN SHORT-CIRCUITS

Experiment & Simulation: Short-circuit behavior and criteria

- Short-circuit behavior

- PEEQ based short-circuit criteria

(Liu & Duan et al., Journal of Materials Chemistry A, 2021)
Particle Scale

Component Scale

Cell Scale

Pack Scale

Unit: m

Atomic Scale

1 × 10^{-10} ~ 1 × 10^{-8}

Particle Scale

1 × 10^{-7} ~ 1 × 10^{-3}

Component Scale

1 × 10^{-4} ~ 1 × 10^{-2}

Cell Scale

1 × 10^{-2} ~ 1 × 10^{-1}

Pack Scale

1 × 10^{-1} ~ 1 × 10^{0}
HOMOGENIZATION OF BATTERY PACK

**Modeling**: homogenized methodology

- **RVE (Representative Volume Element)** module with periodic boundary conditions
- **Homogenized model**
- **RVE module compression simulation**
  - Stress-strain data
  - Equivalent model for battery pack
Simulation: various packing modes in small scale

- $\theta = 2\pi/3$
- $\theta = \pi$
- $\theta = 3\pi/4$
- $\theta = 5\pi/6$
- $\theta = 11\pi/12$

(Liu et al. *Engineering Failure Analysis*, 2018)
**THERMAL RUNAWAY PROPAGATION**

**Experiment:** penetration caused thermal runaway (TR)

**Modeling:** TR propagation model

(Jia et al. *Journal of Energy Storage*, 2020)

![Image of experiment setup](image)

- **Diagram:** Schematic representation of the thermal runaway propagation model.
Simulation: TR propagation in various stacking modes

(Jia et al. Journal of Energy Storage, 2020)
OUTLOOK

Lithium-ion battery safety research

Physics

Electro-chemistry

Mechanics

Multi-physics Interactions Across Length Scales

Electrode Scale
- Charge balance and transport
- Electrical network in composite electrodes
- Li transport in electrolyte phase

Cell Scale
- Electronic potential & Current distribution
- Heat generation and transfer
- Electrolyte wetting
- Pressure distribution

Module Scale
- Thermal/electrical
- Inter-cell configuration
- Thermal management
- Safety control

System Scale
- System operating
- Conditions
- Environmental conditions
- Control strategy

How to model across the scale?

10^-10 10^-8 10^-6 10^-4 10^-2 10^0 [m]

Atomic Scale
- Thermodynamic properties
- Lattice stability
- Material-level Kinetic barrier
- Transport properties

Particle Scale
- Li diffusion in solid phase
- Interface physics
- Particle deformation & fatigue
- Structural stability

(Abada et al. Journal of Power Sources, 2016)
Thank you for your time.

The following information is provided if you would like to contact the speakers.

Session host          Dr. Daniel Juarez Robles
daniel.juarez-robles@ul.org

Presenter             Dr. Jun Xu
jun.xu@uncc.edu

Learn more about our battery safety science research and initiatives at:

Web:   ul.org/focus-areas/battery-safety
Email: NFP.BatterySafety@ul.org