Stress analysis of lithium-based rechargeable batteries using micro and macro scale analysis

Utsav Kumar
Atanu K. Metya
Jayant K. Singh
Department of Chemical Engineering
IIT Kanpur
## INTRODUCTION

**Christensen and Newman, Journal of Electrochemical Society, 2006**
- Estimated stress generation in Li$_y$Mn$_2$O$_4$ and carbon electrodes separately.

**Zhang et al., Journal of Electrochemical Society, 2007**
- Stress distribution inside one single electrode particle using numerical simulation.

**Zhang et al., Journal of Electrochemical Society, 2008**
- Intercalation induced stress and heat generation within single Lithium-Ion battery cathode particles.

**Golmon et al., Computers and Structures, 2009**
- Electrochemical –mechanical interaction phenomena at macro, meso and micro scale.

## OBJECTIVE
- Study of intercalation and thermal stress generation in Li ion rechargeable battery incorporating the effect of Li ion electrode concentration on electrode diffusivity coefficient and stress generation.
STRUCTURE

Source: spectrum.ieee.org

Source: srinivasan et al., 2003
\[ i_s = -\sigma_{s,eff} \nabla \phi_s \]

\[ \frac{\partial c_s}{\partial t} = \nabla \cdot (D_s (\nabla c_s - \frac{\Omega c_s}{RT} \nabla \sigma_h)) \]

Effect of hydrostatic stress on Li ion flux

**Butler-Volmer Reaction**

\[ i_{loc} = i_0 (\exp(\frac{\alpha_c F \eta}{RT}) - \exp(\frac{-\alpha_c F \eta}{RT})) \]

\[ \eta = \phi_s - \Delta \phi_{s,\text{film}} - \phi_l - E_{eq} \]

\[ i_0 = F(k_c)^{\alpha_c} (k_a)^{\alpha_c} (c_{s,\text{max}} - c_s)^{\alpha_a} (c_s)^{\alpha_c} (c_l / c_{l,\text{ref}})^{\alpha_a} \]

Reference: Doyle et al., 1996; Rosas et al., 2011 and Fuel cells and Battery module, COMSOL

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\[ i_l = -\sigma_{l,eff} \nabla \phi_l + \frac{2\sigma_{l,eff} RT}{F} (1 + \frac{\partial \ln f}{\partial \ln c_l})(1 - t_+) \nabla \ln c_l \]

Concentration gradient

\[ \varepsilon_l \frac{\partial c_l}{\partial t} + \nabla \cdot N_l = R_l \]

Flux

\[ N_l = -D_{l,eff} \nabla c_l + \frac{i_l t_+}{F} \]

Diffusion and Migration

\[ R_l = -\sum_m a_{v,m} \frac{v_{Li+} m i_{loc}}{F} \]

Reference: Doyle et al., 1996; Rosas et al., 2011 and Fuel cells and Battery module, COMSOL

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\[ Q_{\text{rev}} = Q_{\text{rea}} \quad Q_{\text{irr}} = Q_{\text{act}} + Q_{\text{ohm}} \]

\[ Q_{\text{rea}} = a_{v,i} i_{\text{loc},i} T \frac{\partial U_i}{\partial T} \]

\[ Q_{\text{act}} = a_{v,i} i_{\text{loc},i} (\phi_{s,i} - \phi_{l,i} - U_i) \]

\[ \kappa_D^{\text{eff}} = \frac{2RT}{F} \kappa^{\text{eff}} (t_+ - 1)(1 + d\ln f / d\ln c) \]

\[ Q_{\text{ohm}} = \sigma_s^{\text{eff}} \nabla \phi_s \cdot \nabla \phi_s + \kappa^{\text{eff}} \nabla \phi_l \cdot \nabla \phi_l + \kappa_D^{\text{eff}} \frac{\nabla c_l}{c_l} \cdot \nabla \phi_l \]

**Thermal Strain** \[ \varepsilon_{\text{thermal}} = \alpha T \]
\[ \frac{\partial c_s}{\partial t} = \nabla \cdot \left( D_s \left( \nabla c_s - \frac{\Omega c_s}{RT} \nabla \sigma_h \right) \right) \]

Effect of hydrostatic stress on Li ion flux

\[ J = -M c_s \nabla \mu \quad \mu = \mu_0 + RT \ln X - \Omega \sigma_h \]

\[ \varepsilon_r = \frac{1}{E} \left( \sigma_r - 2\vartheta \sigma_t \right) + \frac{\Omega}{3} \tilde{c} \]

\[ \varepsilon_t = \frac{1}{E} \left[ (\sigma_t - \vartheta (\sigma_r + \sigma_t)) + \frac{\Omega}{3} \tilde{c} \right] \]

\[ \sigma_r = \frac{2\Omega E}{3(1-\vartheta)} \left( \frac{1}{r_0^3} \int_0^{r_0} \tilde{c} r^2 dr - \frac{1}{r^3} \int_0^r \tilde{c} r^2 dr \right) \]

\[ \sigma_t = \frac{\Omega E}{3(1-\vartheta)} \left( \frac{2}{r_0^3} \int_0^{r_0} \tilde{c} r^2 dr - \frac{1}{r^3} \int_0^r \tilde{c} r^2 dr - \tilde{c} \right) \]

Reference: Zhang et al., 2007; Zhang et al., 2008 and Xiao et al., 2010

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MODELING

Butler Volmer

Electrode & Electrolyte Species/Charge Transport

Electrode Solids State Diffusion

Stress Intercalation and Thermal

Thermal Heat Generation/Transport

MODELING

\[ J \]

\[ C_s \]

\[ \frac{\partial C}{\partial t} + \nabla \cdot (D \nabla C) = \frac{\partial J}{\partial C} \]

\[ \frac{\partial J}{\partial \phi} = \frac{\partial J}{\partial \phi} \]

\[ \frac{\partial T}{\partial t} + \nabla \cdot (K \nabla T) = \frac{\partial \phi}{\partial \phi} \]

\[ \frac{\partial \phi}{\partial t} = \frac{\partial \phi}{\partial t} \]

\[ \frac{\partial i}{\partial t} = \frac{\partial i}{\partial t} \]
\[ D_s \text{ as a function of } C_s? \]

Butler Volmer

Electrode & Electrolyte Species/Charge Transport

Electrode Solids State Diffusion

Stress Intercalation and Thermal

Thermal Heat Generation/Transport

\[ C_s, J \]

\[ D_s (T) \rightarrow D_s (C_s, T) \]

\[ C_s \]

\[ \phi, i \]

\[ T \]
Li$_x$C$_6$ Electrode phase diffusion value (MD Simulation)

INTERACTION PARAMETERS

<table>
<thead>
<tr>
<th>Graphene Layers</th>
<th>AIREBO (Adaptive Intermolecular Reactive Empirical Bond-Order)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>Lorentz-Berthelot combining rules</td>
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</table>

DIFFUSIVITY CALCULATION

Einstein relation - diffusion coefficient is related to the slope of the mean square displacement (MSD) of the particles over time.

$$D = \frac{1}{6} \lim_{t \to \infty} \frac{d}{dt} \left\langle \left[ r_i \left( t + t_0 \right) - r_i \left( t_0 \right) \right]^2 \right\rangle$$
\[ \Delta E = 81.5 \text{ meV} \]

\[
D_{C_s,T} = D_{298K} \times \exp \left( -\frac{\Delta E}{R} \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) \right)
\]

Similarly for LiMn$_2$O$_4$ Wakhira et al., Ionic State Solids, 1996 and Srinivasan et al., Journal of The Electrochemical Society, 2003 gives us the same kind of expression.
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1D electrochemical finite element model (FEM)
- Charge Conservation
- Chemical Kinetics
- Mass Transport (except for electrode particles)
- Heat Transport

2D electrode particle FEM model
- Li ion concentration in electrode particle
- Intercalation and Thermal Stress


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- Current density of **17.5 A/m²** applied
- Charge cycle of **1600s** with **800s** of discharging and charging
- Total number of cycles - **10**
- Anode kept at constant potential

Source: srinivasan et al., 2003
Electrode
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Cs variation

Discharging (200s-600s)

Charging (1100s-1500s)
AVERAGE TEMPERATURE

$Q_{\text{total}}$ is taken as heat generated inside Li ion battery and on the basis of that an average Temperature is calculated and used for further studies including thermal stress.
INTERCALATION STRESS

Anode – Tangential Stress

Cathode – Tangential Stress

\[
\sigma_t = \frac{\Omega E}{3(1 - \nu)} \left( \frac{2}{r_0^3} \int_0^{r_0} \tilde{c}r^2 dr - \frac{1}{r^3} \int_0^r \tilde{c}r^2 dr - \tilde{c} \right)
\]
Electrode Potential

![Graph of Electrode Potential](image)

- **x-axis**: Time (s)
- **y-axis**: Normalized electrode potential

The graph shows the normalized electrode potential over time, indicating periodic fluctuations.
Normalized Stress and Potential

![Graph showing normalized stress and potential over time. The graph compares different types of stress and potential over time.]

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CONCLUSION

• Diffusion coefficient as a function of Temperature and Li ion concentration is developed for electrodes and incorporated into model.

• Effect of Diffusion coefficient as a function of Li ion electrode concentration on stress value can be seen.

• $T_{\text{avg}}$ reaches an asymptotic value as counterbalance between heat generation and heat rejection comes to an equilibrium as time progresses.

• There is an accumulation of stress with continuous use of battery, this may lead to break down of battery if it reaches the break through point limit.

• With continuous use of battery there is a decrease in maximum battery potential, i.e. more charge required for achieving the previous potential value as we keep on using battery.
ACKNOWLEDGEMENT

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Computational Nano Science Group, IIT Kanpur for their help and support

Thank You
**LiₙC₆ Electrode phase diffusion value**
**(MD Simulation)**

**INTERACTION PARAMETERS**

**Graphite**: AIREBO (Adaptive Intermolecular Reactive Empirical Bond-Order).
Stuart et. al, Journal of Chemical Physics, 2000

\[
E = \frac{1}{2} \sum_i \sum_{j \neq i} \left[ E_{ij}^{REBO} + E_{ij}^{LJ} + \sum_{k \neq i, j} \sum_{l \neq i, j, k} E_{kijl}^{\text{tors}} \right].
\]

\[
E_{ij}^{REBO} = V^R r_{ij} + b_i V^A r_{ij}
\]

**Li-Li interaction** - Field Parameter for Intermolecular and Columbic interactions.
Wander and Shuford, Journal of Chemical Physics, 2011

**Graphite-Li interaction** - Lorentz-Berthelot combining rules are employed for the cross interactions
DIFFUSIVITY CALCULATION

The diffusion coefficient can be obtained using two equivalent equilibrium methods.

**Einstein relation** - diffusion coefficient is related to the slope of the mean square displacement (MSD) of the particles over time.

\[
D = \frac{1}{6} \lim_{t \to \infty} \frac{d}{dt} \left\langle \left[ r_i(t) - r_i(t_0) \right]^2 \right\rangle
\]

**Green-Kubo (GK)** - integration over the velocity autocorrelation function

\[
D = \frac{1}{3} \int_0^\infty \left\langle V_i(t) \cdot V_0(t) \right\rangle dt
\]

Green-Kubo gives too much fluctuation as compared to Einstein relation because of low concentration of Li.
Lithium intercalated graphite $\text{Li}_{0.396}\text{C}_6$
(MD Simulation snapshot)

INITIAL CONFIGURATION

FINAL CONFIGURATION (1ns)

SIDE VIEW

NVT Ensemble

TOP VIEW

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DIFFUSIVITY at 298K

\[ D = \frac{1}{6} \lim_{t \to \infty} \frac{d}{dt} \left\langle \left[ r_i (t + t_0) - r_i t_0 \right]^2 \right\rangle \] 

(MSD)
THERMAL ANALYSIS

\[ Q_{\text{irrev}} = Q_{\text{ohm}} + Q_{\text{act}} \]

\[ Q_{\text{rev}} = a_{v,i} i_{loc,i} T \frac{\partial U_i}{\partial T} \]
Anode-Tangential Stress Difference

Tangential Stress for Diffusivity as function of electrode Li ion and Temperature subtracted from Tangential Stress for Diffusivity as function of Temperature only vs. time

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