A novel reformulation of the Pseudo2D battery model coupling large deformations at particle and electrode levels

Weijie Mai, Andrew Colclasure, Kandler Smith
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Si anode has high energy density but suffer from large deformation. 


Si anode + Daxin Binder

4200 mAh/g, 400% volume expansion

Electrode/Cell deformation


Active material (AM) expansion causes electrode deformation and porosity reduction.

A model coupling multi-scale deformations required for better cell design.
Introduction

- **Goal**: consistently incorporate deformations based on the P2D framework
- **Challenge**: infinitesimal deformation assumption inapplicable

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**P2D Newman model**

<table>
<thead>
<tr>
<th>Particle Domain</th>
<th>Electrode Domain</th>
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<td>1D spherical particle model</td>
<td>1D porous electrode model</td>
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\[ j(X) = a(X)i_{surf} \]

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**P2D model coupling large deformations**

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\[ j(x) = a(x)i_{surf} \]
Formulation: large deformation in electrode domain

- Finite strain theory
  - Deformation composed of elastic and inelastic deformations
    \[ F = I + \nabla u \quad F = F_c F_c \]  
    multiplicative decomposition
    \[ u : \text{displacement vector} \]
    \[ F : \text{deformation gradient tensor} \]
  - Isotropic inelastic deformation due to Li insertion/extraction
    \[ F_c = \left(1 + \frac{\Omega_e}{3} \Delta C_{s,\text{avg}} \right) I \]
    \[ \epsilon_e = \frac{1}{2}(F_e^T F_e - I) \]
    \[ \Omega_e : \text{partial molar volume of Li in electrode} \]
    \[ \epsilon_e : \text{elastic strain tensor} \]
  - Displacement can be solved by
    \[ S = J_c F_c^{-T} (C : \epsilon_e) F_c^{-1} \]
    \[ \nabla \cdot (FS)^T = 0 \]
    \[ \sigma = J^{-1} F S F^T \]
    \[ S : \text{Secondary PK stress} \]
    \[ \sigma : \text{Cauchy stress} \]
    \[ C : \text{stiffness tensor} \]
  - The Jacobian of the deformation gradient tensor – change of volume
    \[ J = \det(F) = \frac{dV}{dV_0} \]
Formulation: conservation law in reference frame

- **Eulerian conservation law**

  \[
  \frac{\partial c(\mathbf{x})}{\partial t} = -\nabla_x \cdot \mathbf{N}(\mathbf{x}) + R(\mathbf{x})
  \]

  \[
  \mathbf{N}(\mathbf{x}) = -D \nabla_x c(\mathbf{x}) + c(\mathbf{x}) \mathbf{v}(\mathbf{x})
  \]

  - Volume element (fixed in space)
  - Need to include a convection term
  - Need to explicitly keep track of the deformation

- **Lagrangian conservation law**

  \[
  J = \det(\mathbf{F}) = \frac{dV}{dV_0}
  \]

  \[
  \frac{\partial}{\partial t} \left[ c(\mathbf{X}) J(\mathbf{X}) \right] = -\nabla_X \cdot \mathbf{N}(\mathbf{X}) + R(\mathbf{X}) J(\mathbf{X})
  \]

  \[
  \mathbf{N}(\mathbf{X}) = -J F^{-1} DF^{-1} \nabla_X c(\mathbf{X}) = -D_X \nabla_X c(\mathbf{X})
  \]

  - Approximate field distributions in the undeformed geometry
  - Material volume: \(dV_0(\mathbf{X}) \rightarrow dV(x(\mathbf{X}))\)
  - Effect of deformation on conservation is embodied in deformation gradient tensor \(\mathbf{F}\)
Formulation: P2D with large deformation

- Particle deformation
  - Particle size change from $\mathbb{R}$ to $\mathbb{R}(X)$ after lithiation/delithiation
  - Within each particle, the deformation is characterized by the particle deformation gradient tensor $F_p(R)$

  $$
  F_p = \begin{bmatrix}
  \frac{\partial r}{\partial R} & 0 & 0 \\
  0 & \frac{r}{R} & 0 \\
  0 & 0 & \frac{r}{R}
  \end{bmatrix}
  $$

  - In the current model, we assumed that deformation within particle is uniform

  $$
  \frac{\partial r}{\partial R} = \frac{r}{R} = \lambda \quad \Rightarrow \quad J_p = \frac{V_p}{V_{p,0}} = \det(F_p) = \lambda^3
  $$

  - Alternatively the particle deformation can be expressed in terms of electrode-level variables

  $$
  J_p = \frac{dV_s}{dV_{s,0}} = \frac{\varepsilon_s}{\varepsilon_{s,0}} J
  $$

  - Particle stretch can be expressed as

  $$
  \lambda = \frac{r}{R} = \left( \frac{\varepsilon_s}{\varepsilon_{s,0}} J \right)^{1/3}
  $$

AM expansion affects solid diffusion distance
Formulation: P2D with large deformation

- Solid diffusion in particle
  \[
  \frac{\partial}{\partial t}(J_p c_s) = -\frac{1}{R^2} \nabla_L (R^2 J_L)
  \]

- Charge conservation in electrolyte
  \[
  \nabla_L \cdot \mathbf{i}_l = j J
  \]

- Charge conservation in electrodes
  \[
  \nabla_L \cdot \mathbf{i}_s = -j J
  \]

- Mass conservation in electrolyte
  \[
  (1 - \varepsilon_s) J \frac{\partial c_e}{\partial t} = \nabla_L \cdot \left[ D_l^L \nabla_L c_e - \frac{i_{e+}}{F} \right] + \frac{j}{nF} J,
  \]
  electrolyte modeled as incompressible fluid

- Variation of solid volume fraction
  \[
  \frac{\partial (\varepsilon_s J)}{\partial t} = -\frac{s \Omega_e}{nF} j J
  \]
  \[\varepsilon_e = 1 - \varepsilon_s\]

The new model:
- Approximates two additional fields (electrode displacement, AM volume fraction)
- Conservation laws are formulated in the reference frame
- Only requires minor modifications of the existing P2D governing equations
Additional multiphysics coupling and assumptions

- **Stress-dependent OCP**
  
  Lu et al. Physical Chemistry Chemical Physics (2016)

  \[ E_{Si}^{eq} = E_{Si}^{eq}(SOC) + \frac{\Omega \sigma_R}{F} \]

  Voltage hysteresis of Li\(_x\)Si system due to the effect of stress

- **Porosity-dependent mechanical properties**
  

  \[ E = E_s (1 - \frac{\varepsilon_e}{\varepsilon_0})^n \]

  \[ \nu = \nu_s + \frac{\varepsilon_e}{\varepsilon_1} (\nu_0 - \nu_s) \]

- **Specific surface area**

  \[ a = \frac{3\varepsilon_s}{r(x)} = \frac{3\varepsilon_s}{R} J_p^{-\frac{1}{3}}(x) \]

  Couples particle deformation and porosity reduction

- **Assumptions**

  - All deformations are elastic and nondestructive
  - Uniform and isotropic deformation within each particle
  - Negligible in-plane electrode deformation (thin electrode is well adhered to strong metal foil cc)
  - Electrolyte move out/into a material volume only in the out-of-plane direction
  - Electrode is composed of only active material and electrolyte
Low rate performance (0.02C)

- Si anode/NMC532 cathode; ANL Gen2 electrolyte; 5 mAh/cm² ($L_{cell} = 143.3 \mu m$)
- 0.02C charge to 4.08 V; both ends of the cell are fixed

**Case I: P2D**

- Thickness changes: anode (35.6%↑), separator (20.1%↓), cathode (9.3%↓)
- Porosity reductions: anode (43.8%↓), separator (41.8%↓), cathode (18%↓)
- Uniform porosity within each component
- Negligible impact on cell voltage and capacity
Low rate performance (0.02C, Case II)

- Nonuniform particle expansion and specific surface area increase
- Magnitude of variation is small due to low charge rate
- Average particle expansion close to the analytical value
- Both $\sigma_{xx}$ and $\sigma_h$ in anode are uniform due to relatively uniform Li insertion rate distribution
High rate performance (1C)

Case I: P2D
Case II: P2D+deformations
Case III: Case II+OCP($\sigma_h$)

- Nonuniform porosity reduction and deformations due to faster lithiation rate near anode/separator interface
- Porosity reduction leads to increase of charge overpotential
- The stress effect slightly improve the uniformity of field distributions in anode
Effect of porosity and loading (1C, Case III)

- Optimal volumetric energy density (~900 Wh/L) obtained for $\varepsilon_{a,0} = 0.5$
- The predicted optimal loading is 4 mAh/cm²
- Classic P2D overpredicts cell energy density especially for lower electrode porosity and higher loadings
Si/C anode (half cell, 4 mAh/cm², 0.02 C)

- $\varepsilon_e,0 = 0.5$, $\varepsilon_C,0 = 0.43$, $\varepsilon_{Si,0} = 0.07$
- Sequential lithiation/delithiation of graphite and Si
- Significant reduction of porosity due to Si expansion even though its initial volume fraction is low
Conclusion/Future Work

- The P2D model was reformulated to consistently couple particle and electrode deformations.
- Deformations and porosity reduction significantly affect the accessible capacity of the cell.
- The proposed model shows notable differences in predicting the optimal cell loading and electrode porosity compared with the P2D model.
- The model is under further development to resolve particle-level stress and allow simulating performances of composite anode (Si/C).

P2D Newman model

P2D model coupling large deformations
# Complementary materials

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cathode</th>
<th>Separator</th>
<th>Anode</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R$ ($\mu$m)</td>
<td>1.8</td>
<td>N/A</td>
<td>0.1</td>
</tr>
<tr>
<td>$D_s$ ($m^2/s$)</td>
<td>Appendix B</td>
<td>N/A</td>
<td>1e-16</td>
</tr>
<tr>
<td>$\kappa_s$ (S/m)</td>
<td>100</td>
<td>N/A</td>
<td>100</td>
</tr>
<tr>
<td>$i_0$ ($A/m^2$)</td>
<td>Appendix B</td>
<td>N/A</td>
<td>1</td>
</tr>
<tr>
<td>$\Omega$ ($m^3/mol$)</td>
<td>7.8e-7 [22]</td>
<td>N/A</td>
<td>9.0e-6 [23]</td>
</tr>
<tr>
<td>$C_{s,\text{max}}$ (kmol/m$^3$)</td>
<td>49.6</td>
<td>N/A</td>
<td>333.3</td>
</tr>
<tr>
<td>$\varepsilon_{e,0}$</td>
<td>0.35</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>$L_0$ ($\mu$m) @ 5 mAh/cm$^2$, N:P=1.2</td>
<td>96.4</td>
<td>20</td>
<td>26.9</td>
</tr>
<tr>
<td>Intercalation fraction</td>
<td>(0.3,0.9)</td>
<td>N/A</td>
<td>(0.1,0.6)</td>
</tr>
<tr>
<td>$E_s$ (GPa)</td>
<td>2.5</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>$\nu$</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Bruggeman factor</td>
<td>2.2</td>
<td>2.5</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Table 1: Values of the parameters used in the current model for all example problems unless stated otherwise.
Complementary materials

<table>
<thead>
<tr>
<th>Variable</th>
<th>Governing equation</th>
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<tbody>
<tr>
<td>$c_s$</td>
<td>$\frac{\partial}{\partial t} \left[ \frac{\varepsilon_s}{\varepsilon_{s,0}} (1 + \frac{\partial u}{\partial X}) c_s \right] = \frac{1}{R^2} \frac{\partial}{\partial R} \left[ R^2 D_E \left[ \frac{\varepsilon_s}{\varepsilon_{s,0}} (1 + \frac{\partial u}{\partial X}) \right]^{1/3} \frac{\partial c_s}{\partial R} \right]$</td>
</tr>
<tr>
<td>$\varepsilon_s$</td>
<td>$\frac{\partial}{\partial t} \left[ (1 + \frac{\partial u}{\partial X}) \varepsilon_s \right] = -\frac{s \Omega}{n_F} (1 + \frac{\partial u}{\partial X}) i_E a$</td>
</tr>
<tr>
<td>$\phi_s$</td>
<td>$\frac{\partial i_s}{\partial X} = -(1 + \frac{\partial u}{\partial X}) i_E a$</td>
</tr>
<tr>
<td></td>
<td>$i_s = -\kappa_{s,\text{eff}} \nabla \phi_s$, $\kappa_{s,\text{eff}} = \kappa_s e_s^b / (1 + \frac{\partial u}{\partial X})$</td>
</tr>
<tr>
<td>$\phi_e$</td>
<td>$\frac{\partial i_e}{\partial X} = (1 + \frac{\partial u}{\partial X}) i_E a$</td>
</tr>
<tr>
<td></td>
<td>$i_e = -\kappa_{e,\text{eff}} \nabla \phi_e + \left( \frac{2 \kappa_{e,\text{eff}} R T}{F} \right) (1 + \frac{\partial \ln f^+}{\partial \ln c_e}) (1 - t_+) \nabla \ln c_e$</td>
</tr>
<tr>
<td></td>
<td>$\kappa_{e,\text{eff}} = \kappa_e e_e^b / (1 + \frac{\partial u}{\partial X})$</td>
</tr>
<tr>
<td>$c_e$</td>
<td>$\varepsilon_e (1 + \frac{\partial u}{\partial X}) \frac{\partial c_e}{\partial t} = \frac{\partial}{\partial X} \left( D_{e,\text{eff}} \frac{\partial c_e}{\partial X} - \frac{i_e t_+}{F} \right) + \frac{s}{n_F} (1 + \frac{\partial u}{\partial X}) i_E a$</td>
</tr>
<tr>
<td></td>
<td>$D_{e,\text{eff}} = D_e e_e^b / (1 + \frac{\partial u}{\partial X})$</td>
</tr>
<tr>
<td>$u$</td>
<td>$\nabla (FS)_{XX} = 0$</td>
</tr>
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<td></td>
<td>$(FS)<em>{XX} = (1 + \frac{\partial u}{\partial X}) (1 + \frac{\Omega \Delta C</em>{s,\text{avg}}}{3}) \frac{E(1-\nu)}{2(1+\nu)(1-2\nu)} \left[ \left( \frac{1 + \frac{\partial u}{\partial X}}{1 + \frac{\Omega \Delta C_{s,\text{avg}}}{3}} \right)^2 \right] + \frac{2\nu}{(1-\nu)(1+\frac{\Omega \Delta C_{s,\text{avg}}}{3})^2} - \frac{1+\nu}{1-\nu}$</td>
</tr>
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</table>

Table 3: Explicit forms of the governing equations. Derivatives are defined in the reference configuration.
High rate performance (1C)
Effect of cell fixture condition (5 mAh/cm², \(\varepsilon_{a,0} = 0.5, 1\)C)

- Smaller porosity variation and thus more uniform Si utilization when P=0 psi
- Negligible porosity reduction in cathode and separator
- Separator is compressed more when both ends are fixed due to its lower Young’s module compared to electrodes
Effect of cell fixture condition (5 mAh/cm², $\varepsilon_{a,0} = 0.5, 1C$)

- Higher cell capacity and lower electrode stress when the cell is free to expand.
- Stress in cathode is slightly tensile for $P=0$ psi due to NMC contraction.
- ~9.1% increase of cell thickness, mainly due to Si anode expansion.
Formulation: porosity variation

- AM expansion causes porosity reduction and electrode deformation

\[
\frac{\partial \varepsilon_s}{\partial t} + \nabla \cdot (\varepsilon_s \mathbf{v}) = -\frac{s\Omega_e}{nF} j
\]

- Variation rate of solid volume fraction
- Electrode deformation rate
- Increase rate of AM volume

\(\varepsilon_s\) : volume fraction of solid phase
\(\Omega_e\) : partial molar volume of Li in electrode
\(\mathbf{v}\) : local electrode velocity vector
\(j = a(x)i_{\text{surf}}\) : volumetric current source

- Ratio of porosity reduction and electrode deformation depends on fixture condition
- Reference frame reformulation

\[
\frac{\partial (\varepsilon_s J)}{\partial t} = -\frac{s\Omega_e}{nF} j J
\]

\(\varepsilon_e = 1 - \varepsilon_s\)