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

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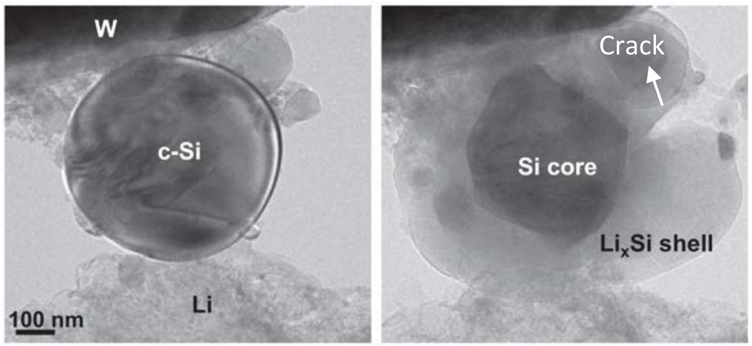
Introduction

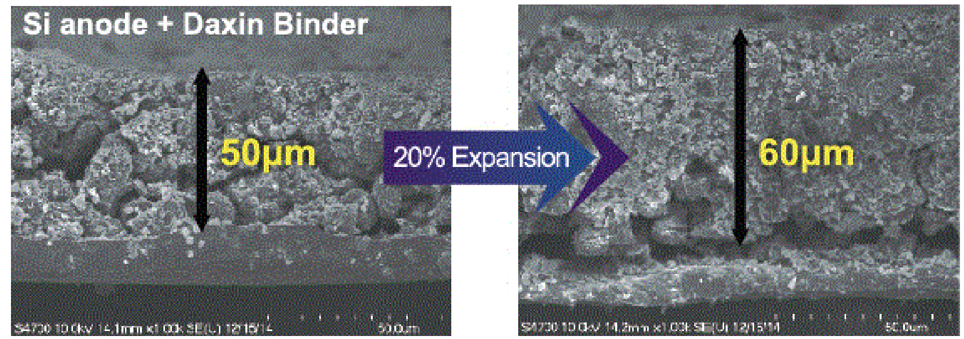
❑ Si anode has high energy density but suffer from large deformation

Huang et al. Acta Materialia (2013)

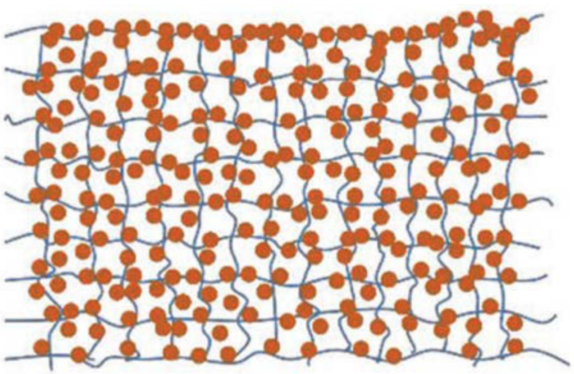


4200 mAh/g, 400% volume expansion

Daxin (http://www.daxinmat.com)

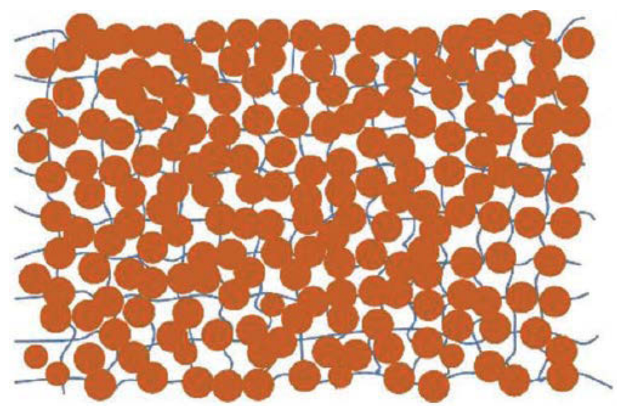


Electrode/Cell deformation



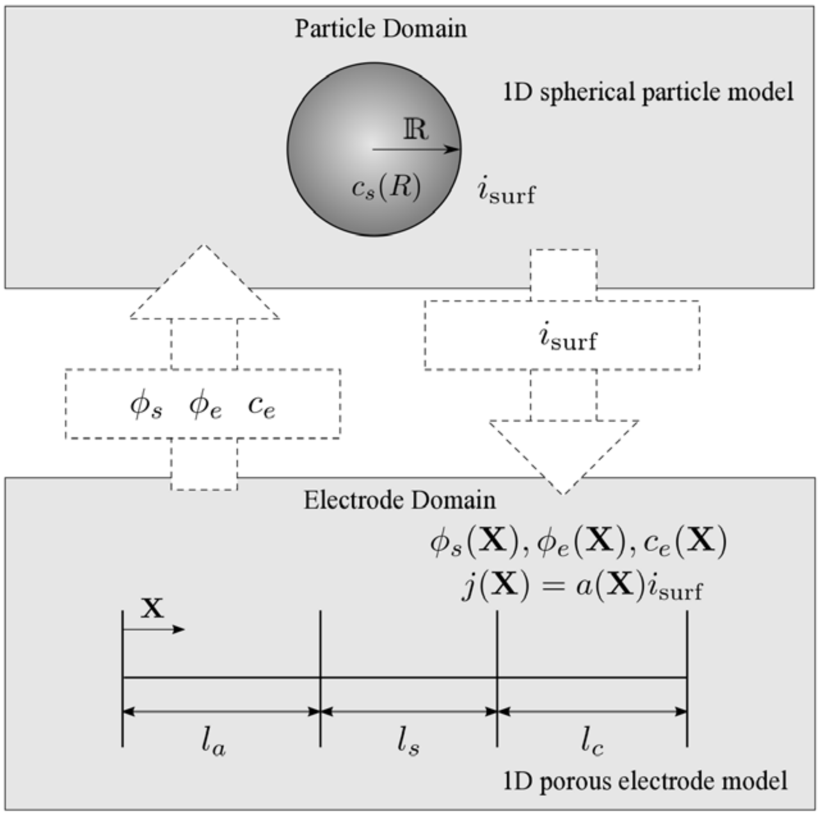
Lithiation

Wang et al. Advanced Energy Materials (2018)

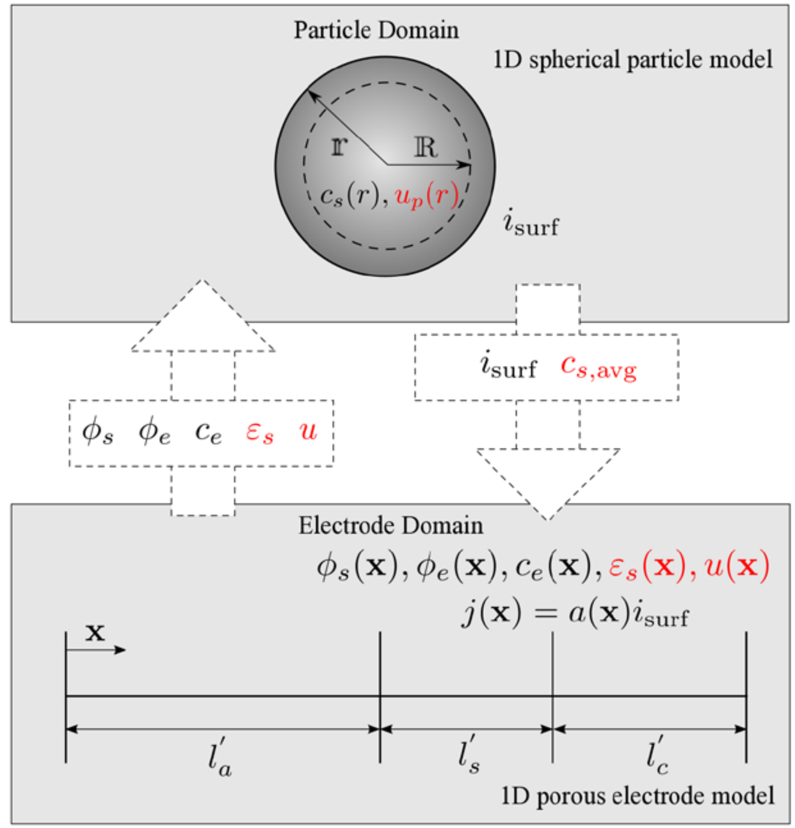


❖ Active material (AM) expansion causes electrode deformation and porosity reduction
❖ A model coupling multi-scale deformations required for better cell design

Introduction



P2D Newman model



P2D model coupling large deformations

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

Formulation: large deformation in electrode domain

❑ Finite strain theory

- Deformation composed of elastic and inelastic deformations

$$\mathbf{F} = \mathbf{I} + \nabla \mathbf{u} \qquad \mathbf{F} = \mathbf{F}_\mathrm{e}\mathbf{F}_\mathrm{c}$$

multiplicative decomposition

$\mathbf{u}$: displacement vector

$\mathbf{F}$: deformation gradient tensor

- Isotropic inelastic deformation due to Li insertion/extraction

$$\mathbf{F}_\mathrm{c} = \left(1 + \frac{\Omega_e}{3}\Delta C_{\mathrm{s,avg}}\right)\mathbf{I} \qquad \epsilon_\mathrm{e} = \frac{1}{2}(\mathbf{F}_\mathrm{e}^\mathrm{T}\mathbf{F}_\mathrm{e} - \mathbf{I})$$

Ω_e: partial molar volume of Li in electrode

ε_e: elastic strain tensor

- Displacement can be solved by

$$\mathbf{S} = J_\mathrm{c}\mathbf{F}_\mathrm{c}^{-\mathrm{T}}(\mathbf{C} : \epsilon_\mathrm{e})\mathbf{F}_\mathrm{c}^{-1} \qquad \nabla \cdot (\mathbf{FS})^\mathrm{T} = 0$$

$$\boldsymbol{\sigma} = J^{-1}\mathbf{FSF}^\mathrm{T}$$

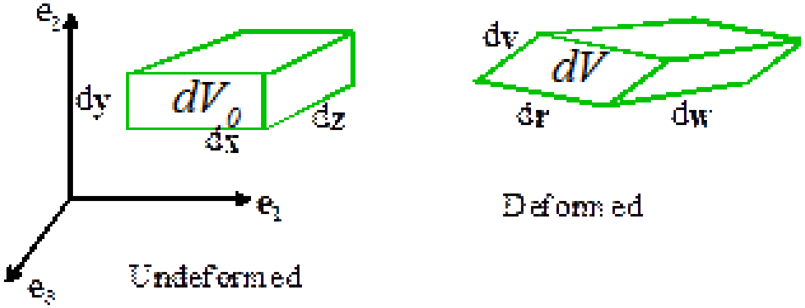
$\mathbf{S}$: Secondary PK stress

σ : Cauchy stress

$\mathbf{C}$: stiffness tensor

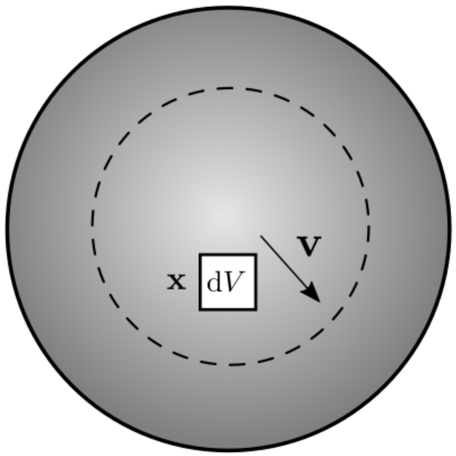
- The **Jacobian** of the deformation gradient tensor – change of volume

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



Formulation: conservation law in reference frame

❑ Eulerian conservation law



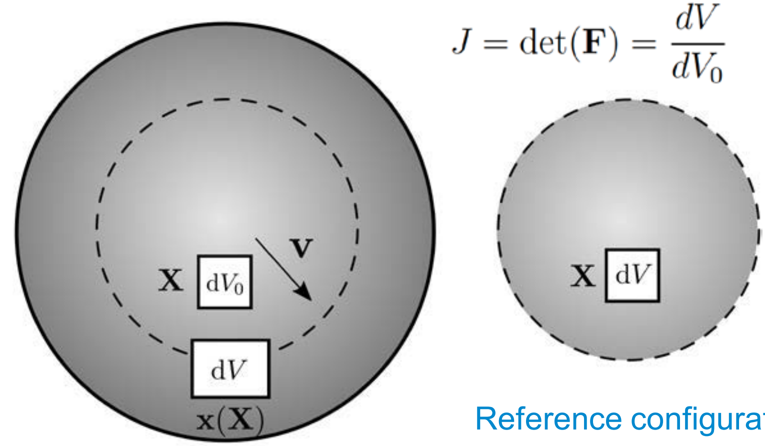
$$\frac{\partial c(\mathbf{x})}{\partial t} = -\nabla_x \cdot \mathbf{N}(\mathbf{x}) + R(\mathbf{x})$$

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

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

❑ Lagrangian conservation law

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



Reference configuration

Deformed configuration

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

$$\mathbf{N}(\mathbf{X}) = -J\mathbf{F}^{-1}D\mathbf{F}^{-T}\nabla_X c(\mathbf{X}) = -D_X \nabla_X c(\mathbf{X})$$

- Approximate field distributions in the undeformed geometry
- Material volume: $\mathrm{d}V_0(\mathbf{X}) \rightarrow dV(\mathbf{x}(\mathbf{X}))$
- 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 $\mathbb{r}(\mathbf{X})$ after lithiation/delithiation
- Within each particle, the deformation is characterized by the particle deformation gradient tensor $\mathbf{F}_p(\mathbf{R})$

$$\mathbf{F}_p = \begin{bmatrix} \frac{\partial r}{\partial R} & 0 & 0 \\ 0 & \frac{r}{R} & 0 \\ 0 & 0 & \frac{r}{R} \end{bmatrix}$$

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

$$\frac{\partial r}{\partial R} = \frac{r}{R} = \lambda \longrightarrow J_p = \frac{V_p}{V_{p,0}} = \det(\mathbf{F}_p) = \lambda^3$$

- 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

$$\frac{\partial}{\partial t}(J_p c_s) = -\frac{1}{R^2}\nabla_L(R^2 \mathbf{J}_L)$$

- Charge conservation in electrolyte

$$\nabla_L \cdot i_l = jJ$$

- Charge conservation in electrodes

$$\nabla_L \cdot i_s = -jJ$$

- Mass conservation in electrolyte

$$(1-\varepsilon_s)J\frac{\partial c_e}{\partial t} = \nabla_L \cdot [D_l^L \nabla_L c_e - \frac{\mathbf{i}_e t_+}{F}] + \frac{j}{nF}J.$$

electrolyte modeled as incompressible fluid

- Variation of solid volume fraction

$$\frac{\partial(\varepsilon_s J)}{\partial t} = -\frac{s\Omega_e}{nF} jJ \qquad \varepsilon_e = 1 - \varepsilon_s$$

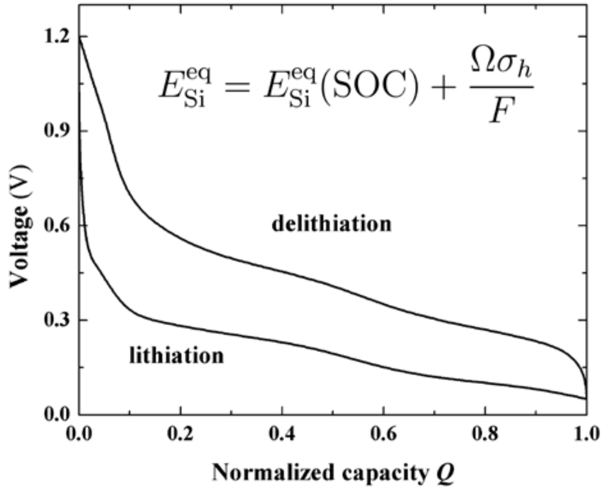
The new model:

- 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)



Voltage hysteresis of LixSi system due to the effect of stress

❑ Porosity-dependent mechanical properties

Kovacik et al. Journal of materials science letters (1999)

$$E = E_s\left(1 - \frac{\varepsilon_e}{\varepsilon_0}\right)^n$$

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

❑ Specific surface area

$$a = \frac{3\varepsilon_s}{\mathrm{r}(x)} = \frac{3\varepsilon_s}{\mathbb{R}} J_p^{-\frac{1}{3}}(x)$$

Couples particle deformation and porosity reduction

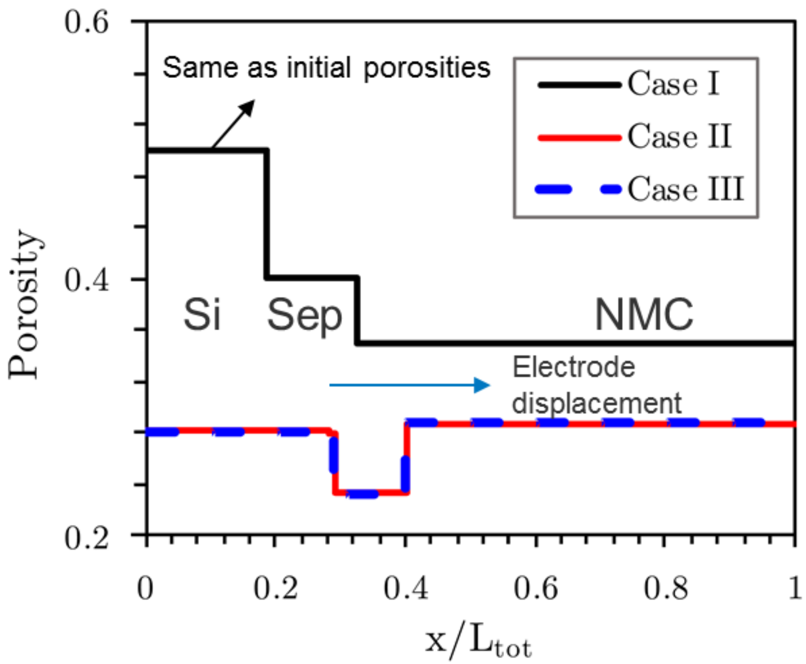
❑ Assumptions

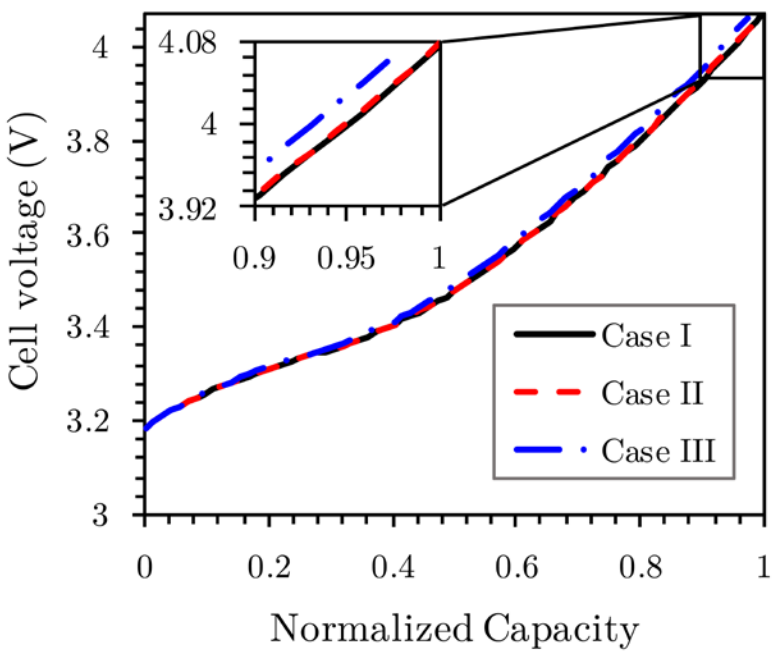
- All deformations are elastic and nondestructive
- Uniform and isotropic deformation within each particle
- Negligible in-plane electrode deformation (thin electrode is well adhered to strong metal foil cc)
- Electrolyte move out/into a material volume only in the out-of-plane direction
- Electrode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

Low rate performance (0.02C)

❖ Si anode/NMC532 cathode; ANL Gen2 electrolyte; 5 mAh/cm^2 ($L_{cell} = 143.3\ \mu$m)
❖ 0.02C charge to 4.08 V; both ends of the cell are fixed

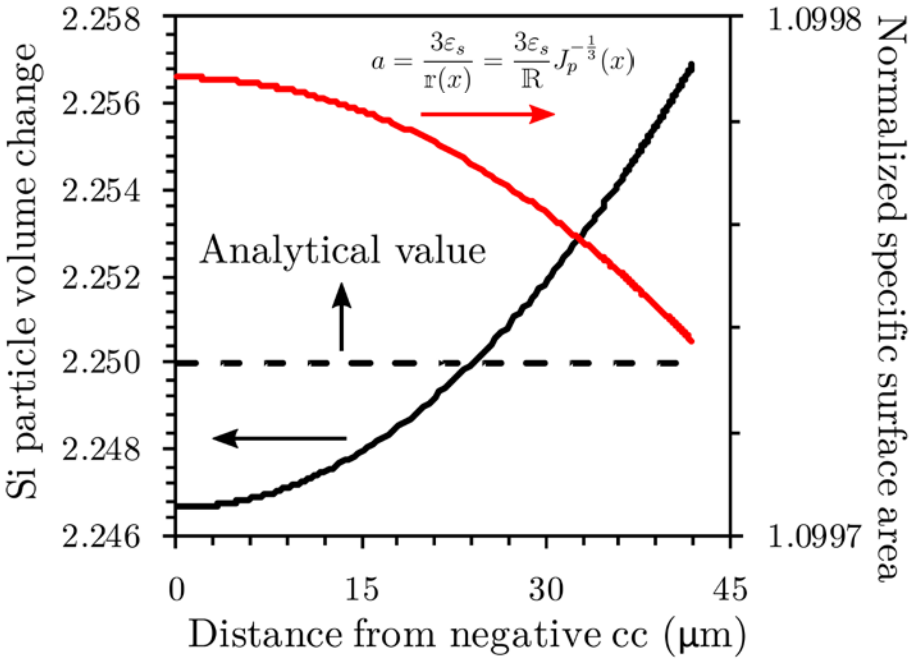
Case I: P2D   Case II: P2D+deformations   Case III: Case II+OCP(σ_h)

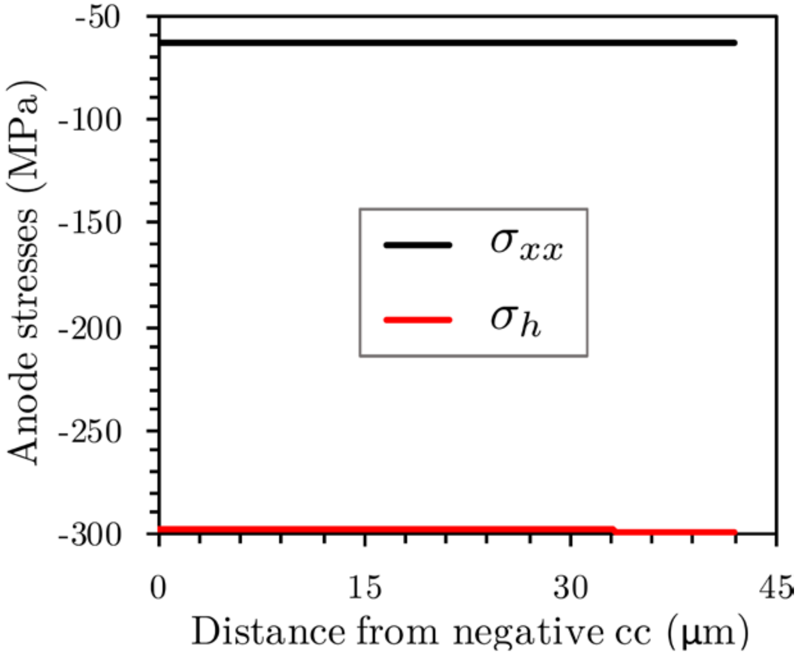




- Thickness changes: anode (35.6%↑), separator (20.1%↓), cathode (9.3%↓)
- Porosity reductions: anode (43.8%↓), separator (41.8%↓), cathode (18%↓)
- Uniform porosity within each component
- Negligible impact on cell voltage and capacity

Low rate performance (0.02C, Case II)

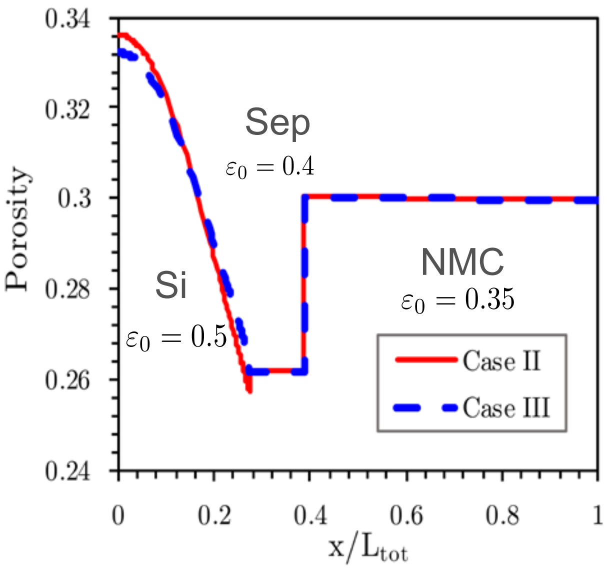


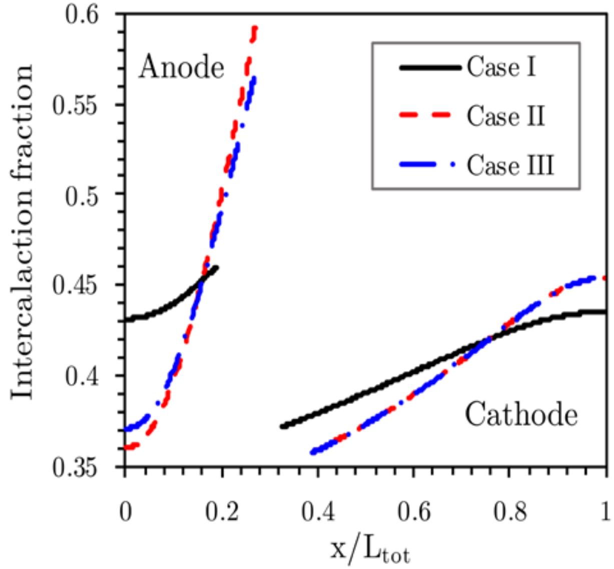


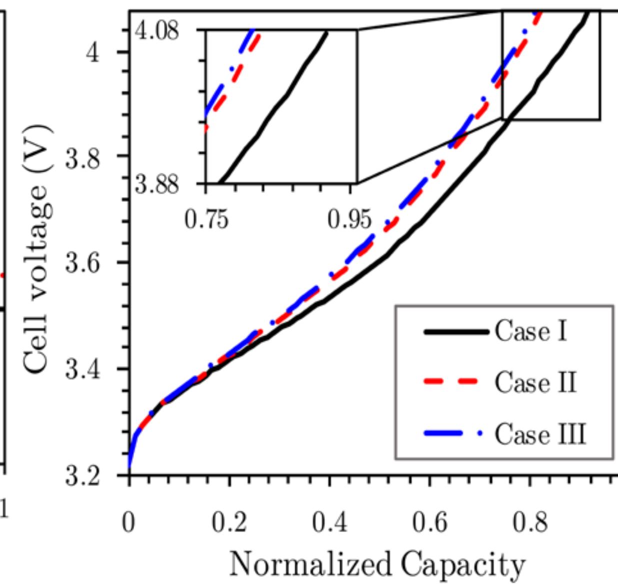
- Nonuniform particle expansion and specific surface area increase
- Magnitude of variation is small due to low charge rate
- Average particle expansion close to the analytical value
- Both σ_{xx} and σ_h in anode are uniform due to relatively uniform Li insertion rate distribution

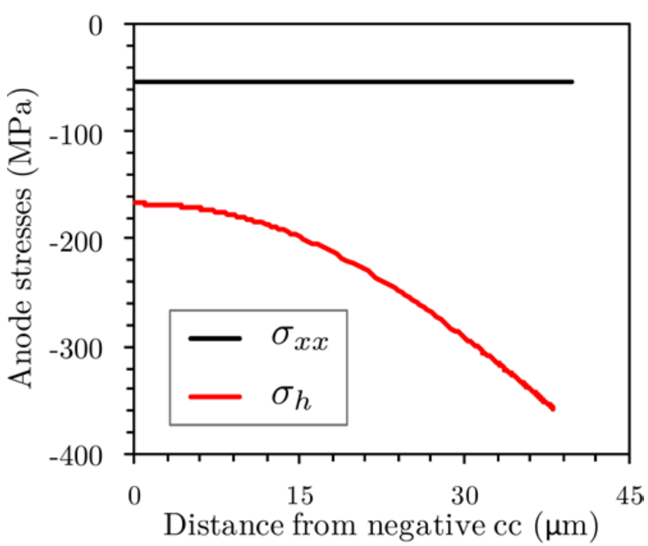
High rate performance (1C)

Case I: P2D　　Case II: P2D+deformations　　Case III: Case II+OCP(σ_h)



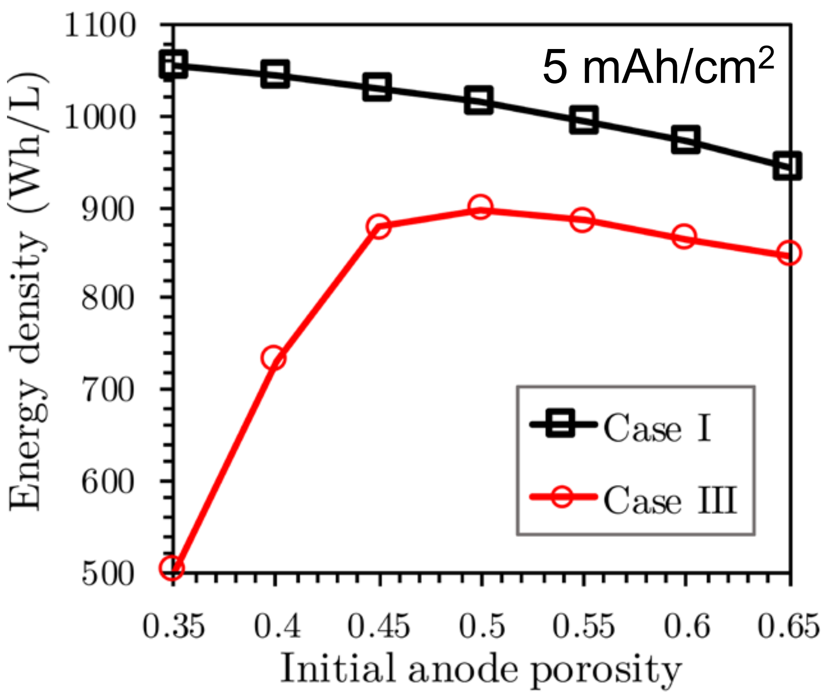


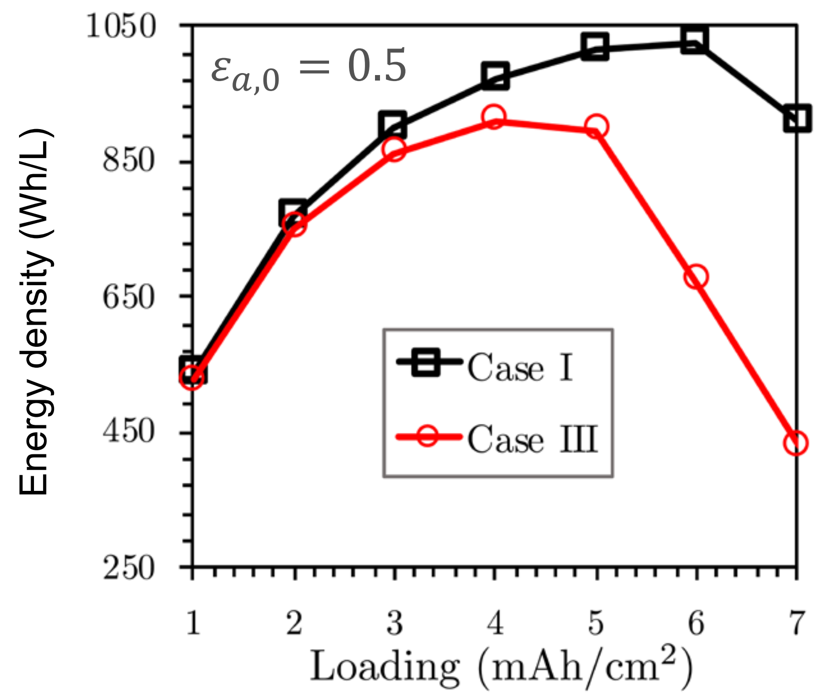




- Nonuniform porosity reduction and deformations due to faster lithiation rate near anode/separator interface
- Porosity reduction leads to increase of charge overpotential
- The stress effect slightly improve the uniformity of field distributions in anode

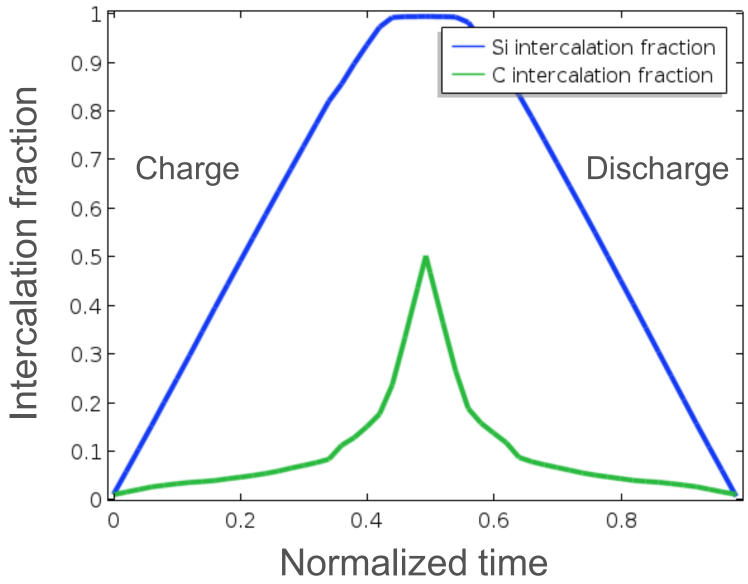
Effect of porosity and loading (1C, Case III)

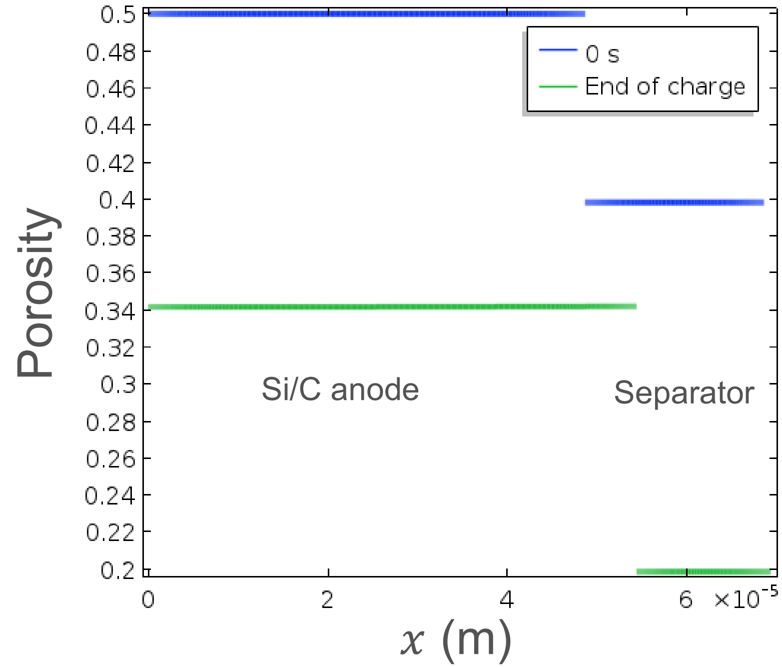


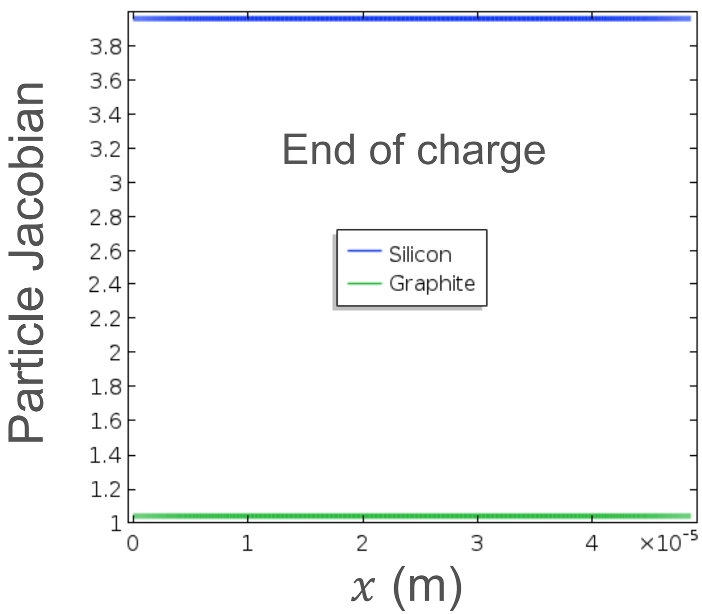


- Optimal volumetric energy density (~900 Wh/L) obtained for $\varepsilon_{a,0} = 0.5$
- The predicted optimal loading is 4 mAh/cm^2
- Classic P2D overpredicts cell energy density especially for lower electrode porosity and higher loadings

Si/C anode (half cell, 4 mAh/cm^2, 0.02 C)



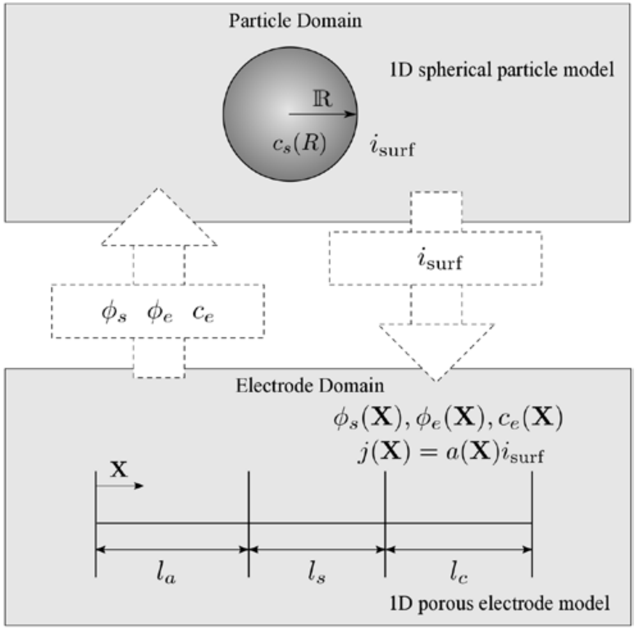




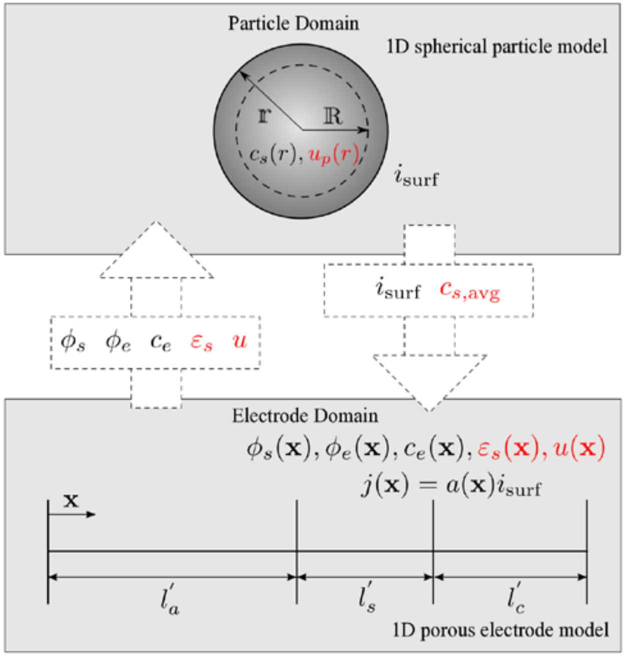
- $\varepsilon_{e,0} = 0.5$, $\varepsilon_{C,0} = 0.43$, $\varepsilon_{Si,0} = 0.07$
- Sequential lithiation/delithiation of graphite and Si
- Significant reduction of porosity due to Si expansion even though its initial volume fraction is low

Conclusion/Future Work

- The P2D model was reformulated to consistently couple particle and electrode deformations
- Deformations and porosity reduction significantly affects the accessible capacity of the cell
- The proposed model shows notable differences on 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

Q&A

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NREL/PR-5400-73985

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Complementary materials

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

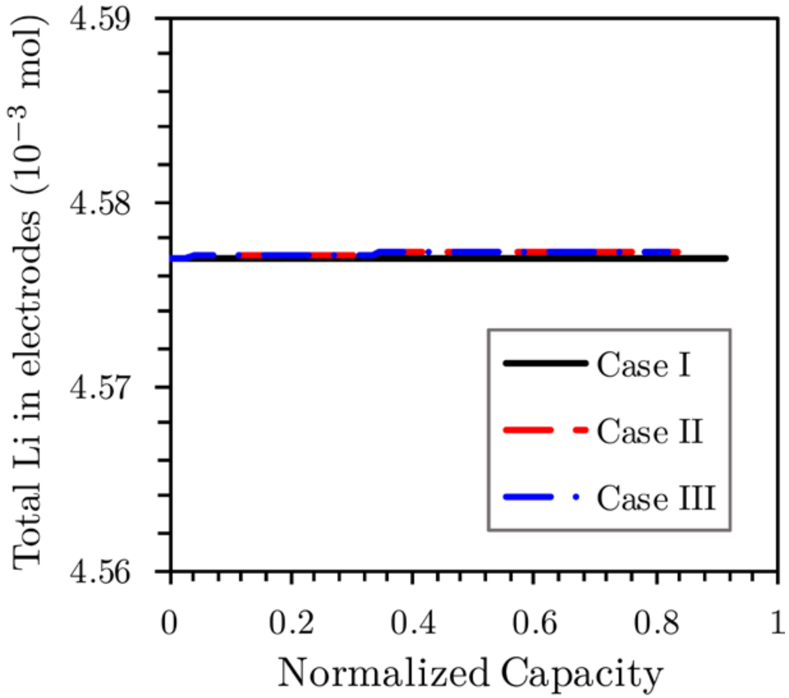
Table 1: Values of the parameters used in the current model for all example problems unless stated otherwise.

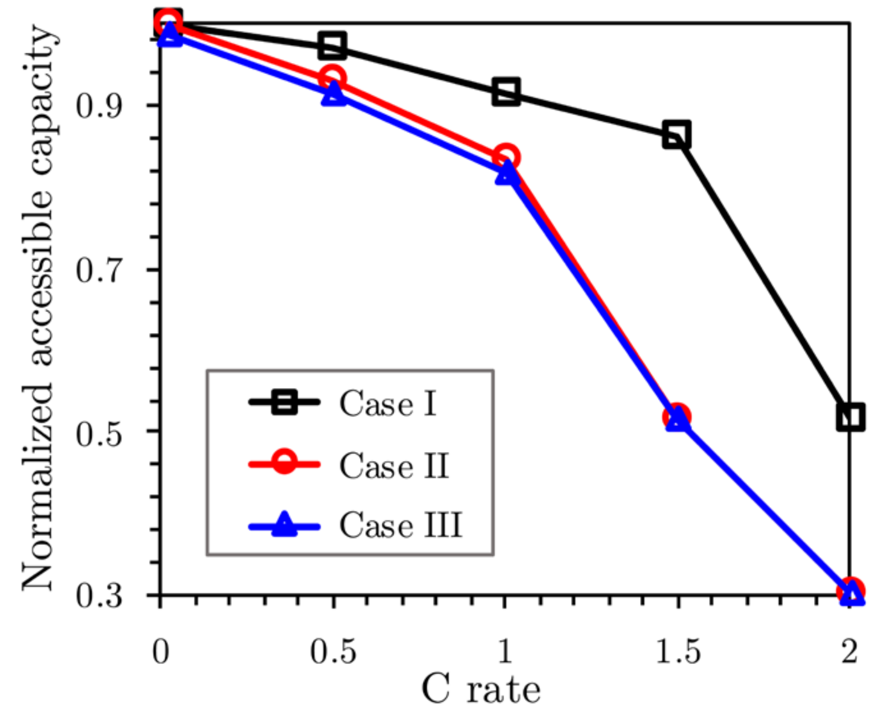
Complementary materials

Variable	Governing equation
c_s	$\frac{\partial}{\partial t}\left[\frac{\varepsilon_s}{\varepsilon_{s,0}}(1+\frac{\partial u}{\partial X})c_s\right] = \frac{1}{R^2}\frac{\partial}{\partial R}\left[R^2 D_E\left[\frac{\varepsilon_s}{\varepsilon_{s,0}}(1+\frac{\partial u}{\partial X})\right]^{1/3}\frac{\partial c_s}{\partial R}\right]$
ε_s	$\frac{\partial}{\partial t}\left[(1+\frac{\partial u}{\partial X})\varepsilon_s\right] = -\frac{s\Omega}{nF}(1+\frac{\partial u}{\partial X})i_E a$
ϕ_s	$\frac{\partial i_s}{\partial X} = -(1+\frac{\partial u}{\partial X})i_E a$ $i_s = -\kappa_{s,\text{eff}}\nabla\phi_s,\ \kappa_{s,\text{eff}} = \kappa_s\varepsilon_s^b/(1+\frac{\partial u}{\partial X})$
ϕ_e	$\frac{\partial i_e}{\partial X} = (1+\frac{\partial u}{\partial X})i_E a$ $i_e = -\kappa_{e,\text{eff}}\nabla\phi_e + \left(\frac{2\kappa_{e,\text{eff}}RT}{F}\right)\left(1+\frac{\partial \ln f_\pm}{\partial \ln c_e}\right)(1-t_+)\nabla \ln c_e$ $\kappa_{e,\text{eff}} = \kappa_e\varepsilon_e^b/(1+\frac{\partial u}{\partial X})$
c_e	$\varepsilon_e(1+\frac{\partial u}{\partial X})\frac{\partial c_e}{\partial t} = \frac{\partial}{\partial X}(D_{e,\text{eff}}\frac{\partial c_e}{\partial X} - \frac{\mathbf{i}_e t_+}{F}) + \frac{s}{nF}(1+\frac{\partial u}{\partial X})i_E a$ $D_{e,\text{eff}} = D_e\varepsilon_e^b/(1+\frac{\partial u}{\partial X})$
u	$\nabla(\mathbf{FS})_{XX} = 0$ $(\mathbf{FS})_{XX} = (1+\frac{\partial u}{\partial X})(1+\frac{\Omega\Delta C_{\text{s,avg}}}{3})\frac{E(1-\nu)}{2(1+\nu)(1-2\nu)}\left[\left(\frac{1+\frac{\partial u}{\partial X}}{1+\frac{\Omega\Delta C_{\text{s,avg}}}{3}}\right)^2 + \frac{2\nu}{(1-\nu)(1+\frac{\Omega\Delta C_{\text{s,avg}}}{3})^2} - \frac{1+\nu}{1-\nu}\right]$

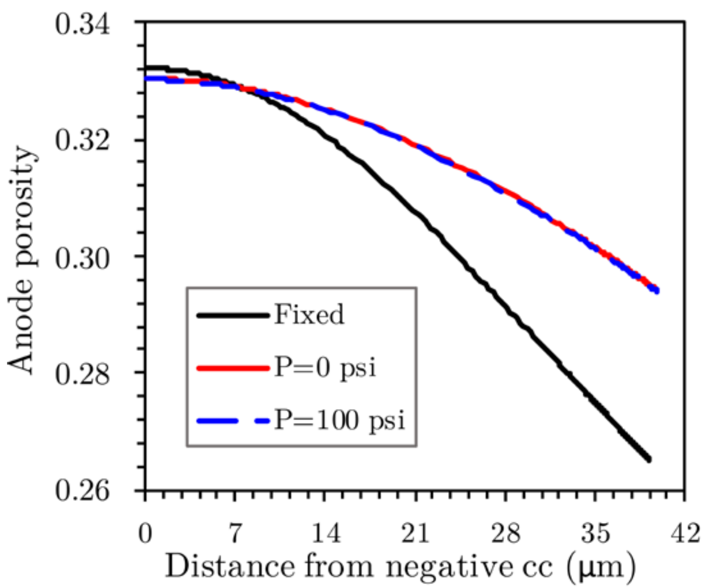
Table 3: Explicit forms of the governing equations. Derivatives are defined in the reference configuration.

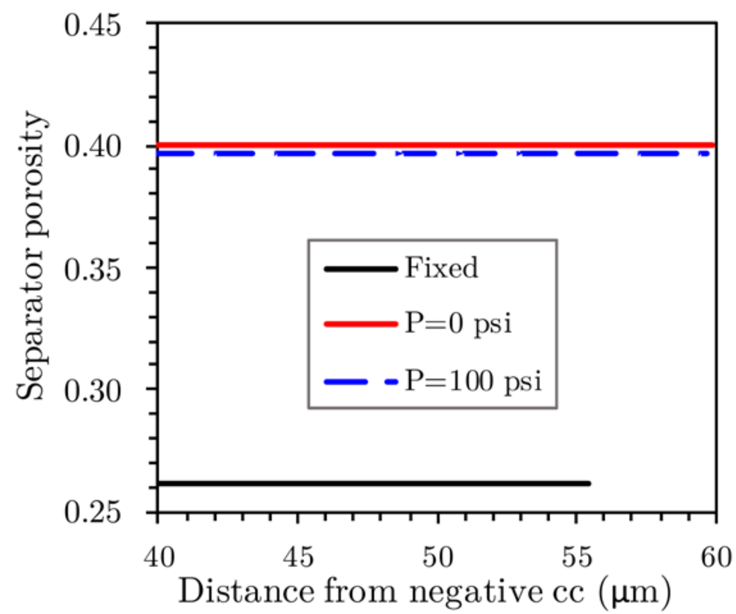
High rate performance (1C)

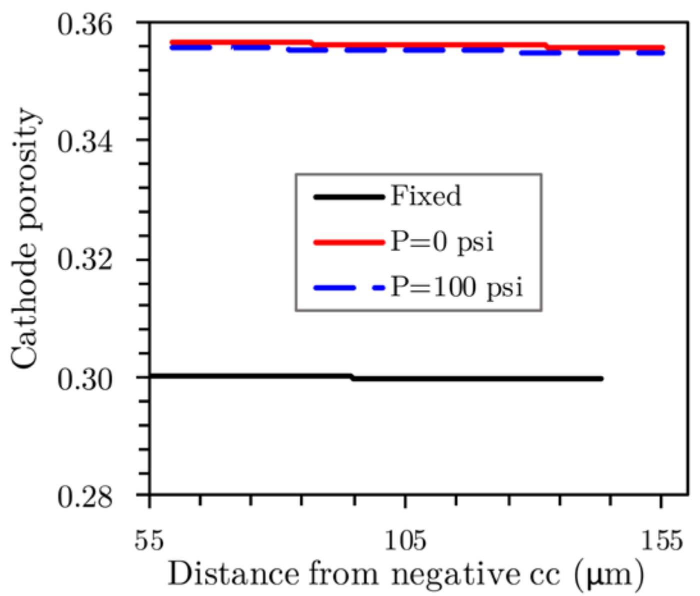




Effect of cell fixture condition (5 mAh/cm^2, $\varepsilon_{a,0} = 0.5$, 1C)

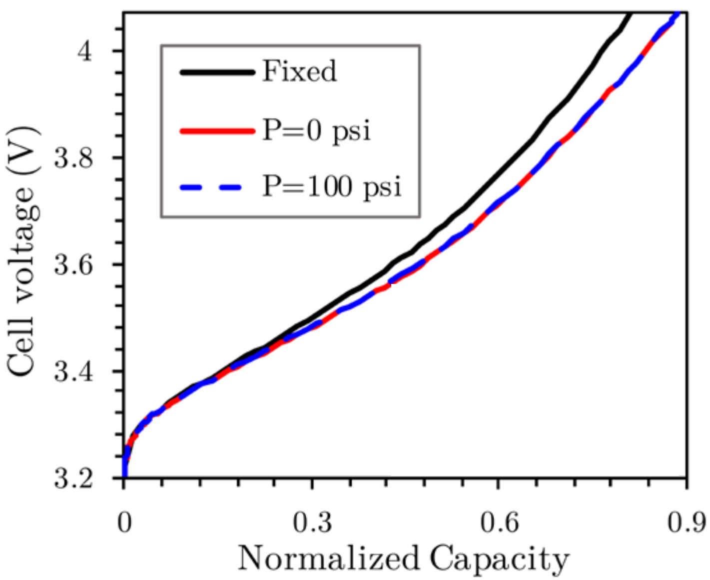


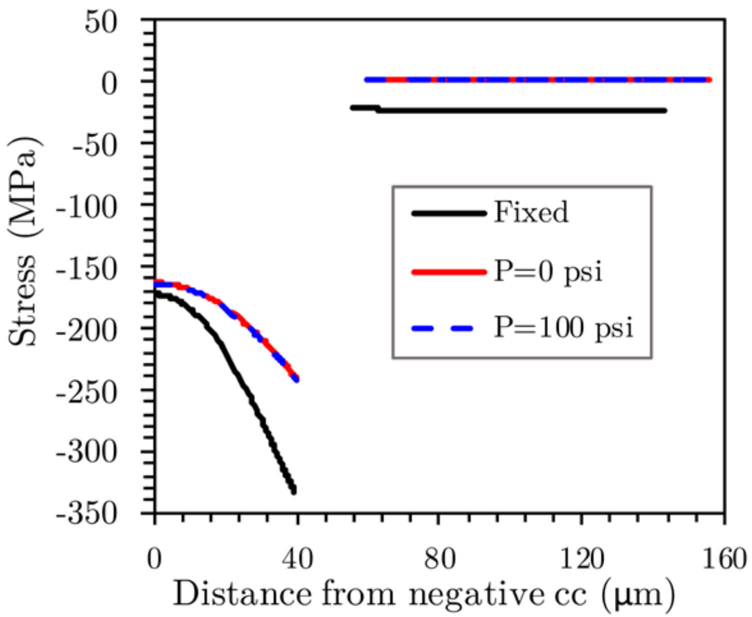


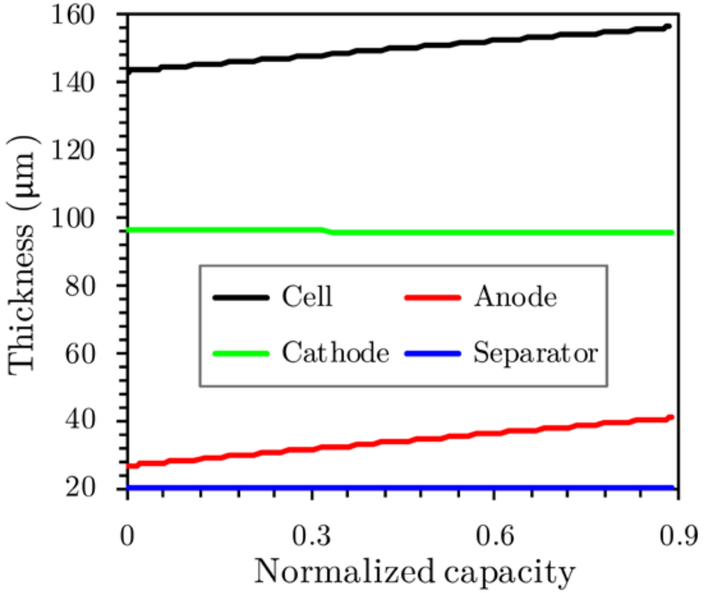


- Smaller porosity variation and thus more uniform Si utilization when P=0 psi
- Negligible porosity reduction in cathode and separator
- Separator is compressed more when both ends are fixed due to its lower Young's module compared to electrodes

Effect of cell fixture condition (5 mAh/cm^2, $\varepsilon_{a,0} = 0.5$, 1C)



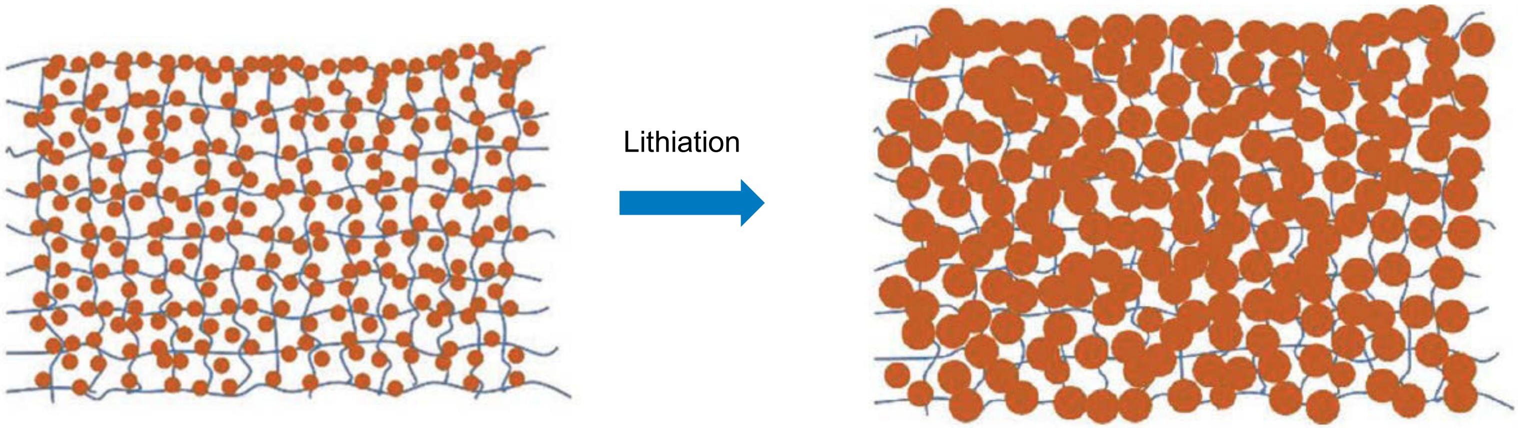




- Higher cell capacity and lower electrode stress when the cell is free to expand
- Stress in cathode is slightly tensile for P=0 psi due to NMC contraction
- ~9.1% increase of cell thickness, mainly due to Si anode expansion

Formulation: porosity variation

Wang et al. Advanced Energy Materials (2018)



- AM expansion causes porosity reduction and electrode deformation

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

$\frac{\partial \varepsilon_s}{\partial t}$: Variation rate of solid volume fraction

$\nabla \cdot (\varepsilon_s \mathbf{v})$: Electrode deformation rate

$-\frac{s\Omega_e}{nF} j$: Increase rate of AM volume

ε_s : volume fraction of solid phase

Ω_e: partial molar volume of Li in electrode

$\mathbf{v}$: local electrode velocity vector

$j = a(\mathbf{x}) i_{\mathrm{surf}}$: volumetric current source

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

$$\frac{\partial \left(\varepsilon_s J\right)}{\partial t} = -\frac{s\Omega_e}{nF} j J$$

$$\varepsilon_e = 1 - \varepsilon_s$$