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Paths of energy changing for electrodes of Li-ion batteries under nonequilibrium process

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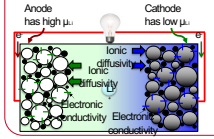
Introduction and background

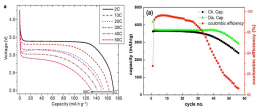
Introduction:

- Lithium-ion batteries are critical to modern and emerging technologies such as electric vehicles, high-power tools.
- It stores and release energy by Li-ion's diffusion between anode and cathode.

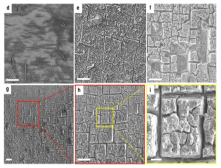


Current Problems of Li-ion battery

(a) Poor power performance under high C-rate[1]
(b) Irreversible capacity loss after cycling and limited lifetime under high C-rate[2]

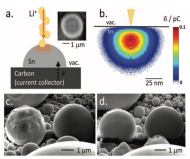


(c) Electrodes' cracks and failure[3]



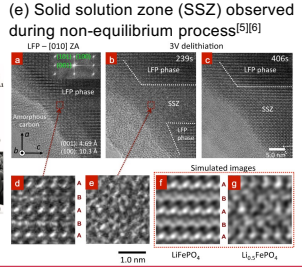
Si anode SEM images after (d) 3, (e) 8, (f) 50 and (g–i) 30 cycles. Scale bar, 20μm (d–h), 3 μm (i).

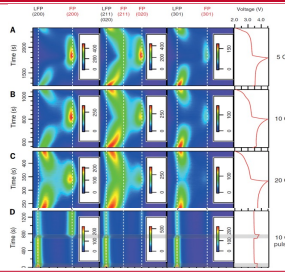
(d) Li-ion diffusion were affected by mechanical deformation[4]



Li-ion diffusion under FIB doping

(e) Solid solution zone (SSZ) observed during non-equilibrium process[5][6]





Objective:

- Describe and predict electrical potential, capacity, stress and strain under high C-rate (dis)charging.
- Present the relation between stress/strain and solid solution zone (SSZ) during non-equilibrium process
- Develop approaches to improve Li-ion battery's cyclic life at high C-rates

Electrodes with finite deformation

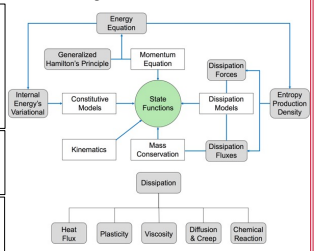
Model Architecture based on Continuum Mechanics and Non-Equilibrium Thermodynamics

Constitutive models

$$\dot{\boldsymbol{\Omega}} = \dot{\boldsymbol{\Omega}}\left(\lambda, G, \rho, \mathbf{g}, \dot{\boldsymbol{\varepsilon}}^{(e)}, \boldsymbol{\sigma}, \dot{\mathbf{e}}, \kappa, x_{(k)}, \boldsymbol{\varepsilon}^{(e)}\right)$$

$$\mu_{(12)} = \mu_{(12)}\left(x_{(k)}, \boldsymbol{\varepsilon}^{(e)}, \rho\right)$$

$$ds = \sum_I -\bar{\gamma}^{(I)} d\bar{\varepsilon}^{(I)}_{(2)ij} + c_{Vx}\frac{dT}{T} + \left(\frac{\partial s}{\partial x_{(\alpha)}}\right)_{T_{(2)},T} dx_{(\alpha)}$$



Momentum equation

$$\rho\frac{d\mathbf{v}}{dt} = \nabla\cdot\mathbf{p} + \sum_k^K \rho_{(k)}\mathbf{F}_{(k)}$$

Dissipation models

$$\lambda^{(P)\pm} = C^{(P)\pm}\exp\left(-\frac{E_A^{(P)\pm}}{RT}\right)$$

$$\tau^{(e)} = \tau^{(e)}\left(\dot{e}^{(e)}, \lambda^{(P)\pm}\right)$$

$$\mathbf{J}_{(k)} = -\frac{\mathbf{L}^{(kq)}}{T}\cdot\nabla T - \sum_k \frac{\mathbf{L}^{(kk')}}{T}\cdot\nabla\left(\psi_{(k')} - \psi_{(n)}\right) - \frac{\mathbf{L}^{(kn)}}{T}\cdot\nabla\phi$$

$$r_+^{(J)} = C_+^{(J)'}\exp\left(\alpha^{(J)}\beta\sum_k \mu_{(k)M}\delta^{(kj)}\right)$$

Kinematics

$$\dot{\varepsilon}_{(2)ij} = \frac{\partial\varepsilon_{(2)ij}}{\partial t} = \frac{1}{2}\frac{\partial g_{(2)ij}}{\partial t}$$

$$\dot{\varepsilon}_{(2)ij} = \dot{\varepsilon}_{ij}^{(e)} + \dot{\varepsilon}_{ij}^{(p)} \qquad \dot{\varepsilon}_{(2)ij} = \frac{1}{2}\left(\nabla_i v^L_{(2)j} + \nabla_j v^L_{(2)i}\right)$$

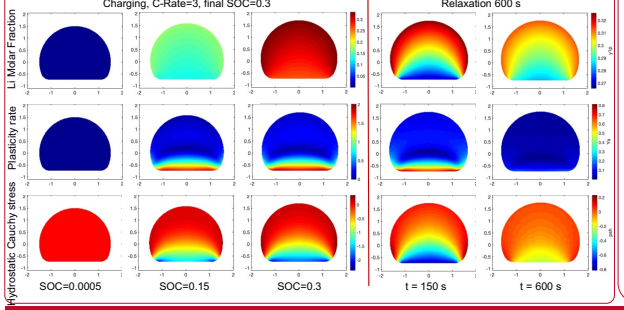
Mass conservation

$$\rho\frac{dx_{(k)}}{dt} + \nabla_i J^i_{(k)} = \sum_j \bar{s}^{(j)}_{(k)} J^{(j)} \qquad F\int_V J_M dV = I$$

Dislocation effects

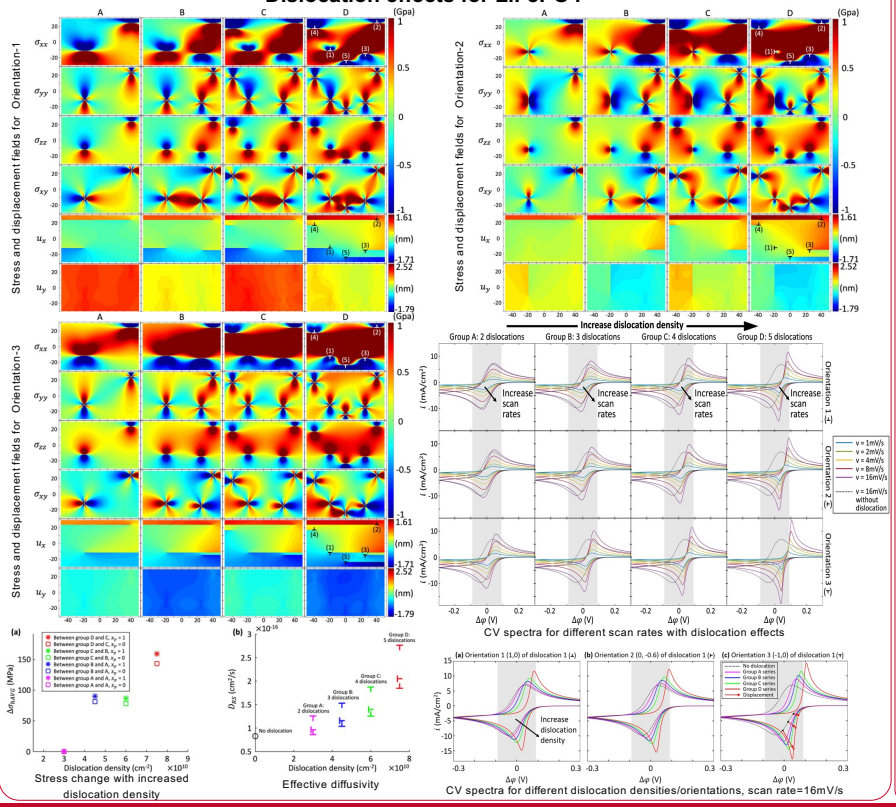
$$\boldsymbol{\sigma}_{DC} = \boldsymbol{\sigma}_{DC}\left(b_x, b_y, r_x, r_y\right) \qquad \mathbf{u}_{DC} = \mathbf{u}_{DC}\left(b_x, b_y, r_x, r_y\right)$$

Li diffusion and particle deformation for Tin particle



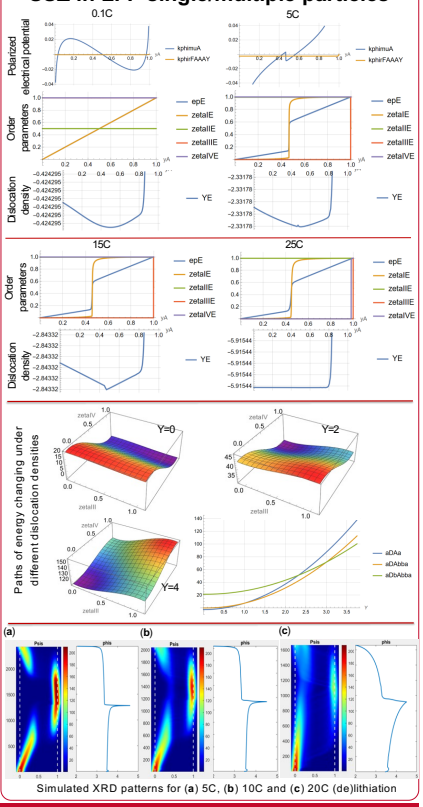
Dislocations and electrochemical performance

Dislocation effects for LiFePO4



SSZ in electrodes

SSZ in LFP single/multiple particles



Future Work

- Simulate whole (dis)charging process and cycling for large deformation of Si anode.
- Investigate the detailed influences of dislocation densities on the evolution of SSZ for multi-particles.
- Damage and irreversible capacity loss modeling.

[1] Kang & Ceder, Nature 458, 190-193; [2] J. Xie et al, doi: 10.1149/2.0091503jes; [3] Shi et al, doi: 10.1038/ncomms11886; [4] Saya Takeuchi et al., doi:10.1149/2.1161606jes; [5] Niu et al., dx.doi.org/10.1021/nl501415b; [6] Liu et al., DOI: 10.1126/science.1252817

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