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A Generalized method of modeling evolution process for a continuous solid-solution system in lithium-ion batteries

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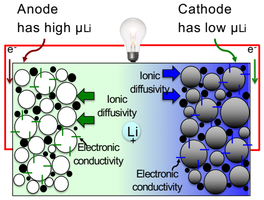
Introduction and Background

Introduction:

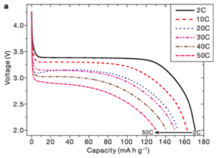
- Lithium-ion batteries are critical to modern and emerging technologies such as electric vehicles, high-power tools.
- It stores and release energy by Li-ion's diffusion between anode and cathode.

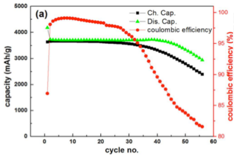


Current Problems of Li-ion battery

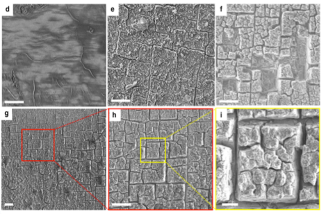
(a) Poor power performance under high C-rate[1]

(b) Irreversible capacity loss after cycling and limited life time under high C-rate[2]



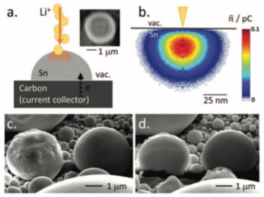


(c) Electrodes' cracks and failure[3]



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]



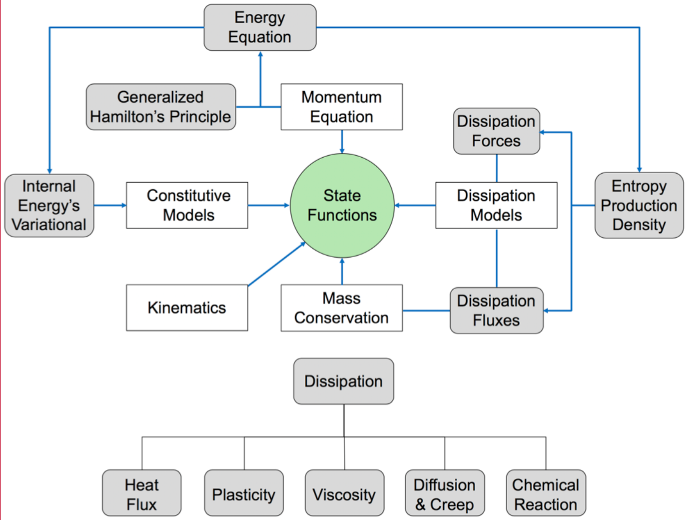
Li-ion diffusion under FIB doping

Objective:

- Describe and predict electrical potential, capacity, stress and strain under high C-rate (dis)charging.
- Predict Li-ion battery performance under various C-rates.
- Develop approaches to improve Li-ion battery's cyclic life at high C-rate

Methods and Current Results

Model Architecture based on Continuum Mechanics and Non-Equilibrium Thermodynamics



Constitutive models

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

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

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

Momentum equation

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

Kinematics

$$e_{(2)ij}=\frac{\partial\varepsilon_{(2)ij}}{\partial t}=\frac{1}{2}\frac{\partial g_{(2)ij}}{\partial t}$$

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

Dissipation models

$$f=\left(\tau^{(p)ij}-\frac{1}{3}\tau^{(p)k}{}_{k}g^{ij}_{(2)}\right)\left(\tau^{(p)}_{ij}-\frac{1}{3}\tau^{(p)k}{}_{k}g_{(2)ij}\right)-\frac{8}{3}\Upsilon^{2}$$

$$\dot{\boldsymbol{\tau}}^{(e)}=\boldsymbol{\eta}\dot{\boldsymbol{e}}$$

$$\boldsymbol{J}_{(k)}=-\frac{\boldsymbol{L}^{(kq)}}{T}\boldsymbol{\cdot}\underline{\nabla}T-\sum_{k}\frac{\boldsymbol{L}^{(kk')}}{T}\boldsymbol{\cdot}\underline{\nabla}(\psi_{(k')}-\psi_{(n)})-\frac{\boldsymbol{L}^{(ke)}}{T}\boldsymbol{\cdot}\underline{\nabla}\phi$$

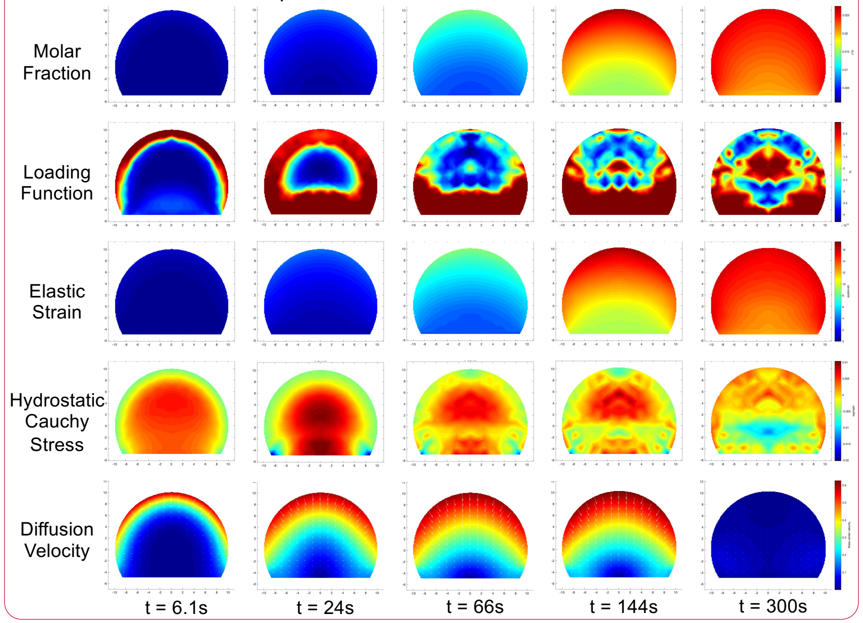
$$r^{(j)}_{+}=C^{(j)\prime}_{+}\exp\left(\alpha^{(j)}\beta\sum_{k}\mu_{(k)M}\delta^{(kj)}\right)$$

Mass conservation

$$\rho\frac{dx_{(k)}}{dt}+\nabla_i J^{i}_{(k)}=\sum_{j}\xi^{(j)}_{(k)}J^{(j)}$$

Numerical Simulation

Lithiate a Tin anode particle for 0~150s with 0.5 C-rate, then relax for 150~300s



Future Work

- Understanding the loss of power density and capacity involving interdisciplinary theories and models.
- Use the finite different method to obtain stress evolutions with phase transformation during cycling.
- Developing algorithms to simulate continuous plasticity-elasticity interface. 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

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Dislocation Based Stresses during Electrochemical Cycling and Phase Transformation in Li-ion Batteries

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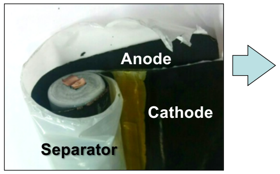
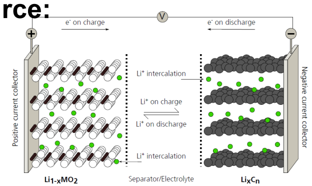
Introduction and Background

Promising Power Source: Lithium-ion Batteries





Lithium De/intercalation (LiFePO4)

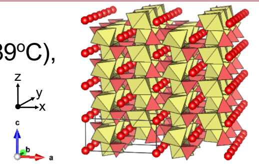
$$Fe_xPO_4 + xLi^+ + e^- \underset{charge}{\overset{discharge}{\rightleftarrows}} Li_{1-x}FePO_4$$

Lithium-Iron-Phosphate ($LiFePO_4$) as a Cathode Material:

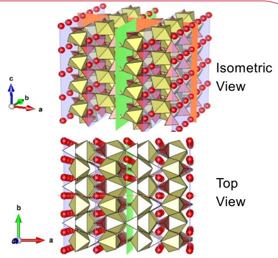
- High volumetric energy (970 WhL^{-1}), low exothermic peak temperature (289°C), and low heat flow (-6 Wg^{-1}).
- One dimensional lithium diffusion (along y-direction, *i.e.*, b-direction)
- Li-poor phase ($FePO_4$) → Li-rich phase ($LiFePO_4$); volume expansion.

Motivations:

- Defects in materials are inevitable, can be used to tailor material properties as per needs.
- A need for model incorporating combined effects of phase transformation and Electrochemical behavior in a material having linear defects called dislocations.



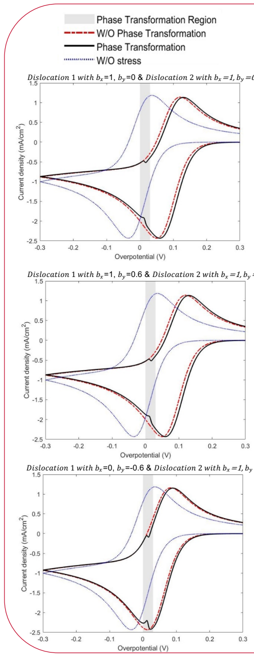
LiFePO4 Crystal Structure



Edge dislocation with bx= 1, by= 0 in LiFePO4

Results

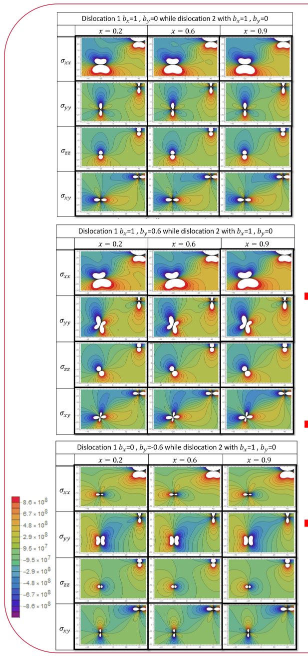
Phase Transformation On Cyclic Voltammogram



- **Presence** of **dislocations changes** the **electrochemical performance** of electrodes dramatically → **shift** in shape of **CV** curve (Blue Dotted Curve & Red dashed curve) →**attributed** to presence of **stresses around dislocations.**
- **Phase Transformation causes** further **change** in **electrochemical behavior** (Red Dashed curve & Black solid curve).
- The amount of **increase or decrease** in value of **current** at an applied overvoltage **depends** on the **orientation of dislocations.**

$$i = i_0\left(\frac{C_0(0,t)}{C_0^*}e^{-\alpha\frac{F(E-E^{0'})-\sigma_h\Omega}{RT}} - \frac{C_R(0,t)}{C_R^*}e^{(1-\alpha)\frac{F(E-E^{0'})-\sigma_h\Omega}{RT}}\right)$$

Stresses During Phase Transformation

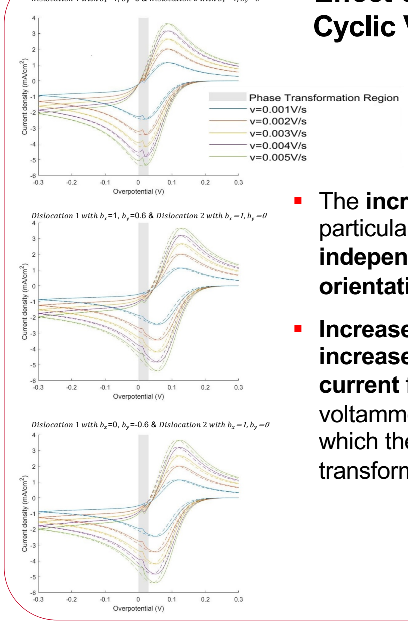


$$[C_{ij}] = (1-x)\left[C_{ij}\right]_{FeO_4} + x\left[C_{ij}\right]_{LiFeO_4}$$

FePO4		**LiFePO4**	
C11	137.4 GPa	C11	164.3 GPa
C22	146.0 GPa	C22	162.9 GPa
C33	132.0 GPa	C33	181.1 GPa
C44	40.8 GPa	C44	40.8 GPa
C55	38.2 GPa	C55	40.5 GPa
C66	42.1 GPa	C66	43.9 GPa
C12	41.0 GPa	C12	61.1 GPa
C13	29.1 GPa	C13	54.9 GPa
C23	29.1 GPa	C23	67.7 GPa

- **Stresses** inside $LiFePO_4$ **change** (increase or decrease) during **phase transformation**.
- **Variations** in stress **depends** on the **orientation** of **dislocations**.
- All components of stress do not change equally, **change** in **particular component depends** upon **orientation** of **dislocations.**

Effect of Scan-rate on Cyclic Voltammogram



- The **increase** in **current** for a particular overvoltage is **independent** of the **orientation of dislocations.**
- **Increased scan rates** show **increased deviation** of **current** from a cyclic voltammogram for material in which there is no phase transformation.

Conclusion

- The stresses around dislocations vary during phase transformation and the variations (increase or decrease) depends on orientation of dislocations.
- Presence of dislocations (*e.g.*, density and orientation) changes the electrochemical behavior of the electrode material by shifting the cyclic voltammograms.
- Increased scan rate shows increase deviation of current from a cyclic voltammogram for material in which there is no phase transformation.

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Nonequilibrium thermodynamics of rate-capacity lost phenomena for Li-ion battery

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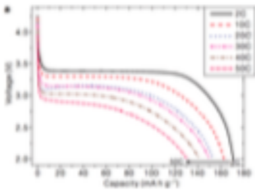
Introduction and Background

Introduction:

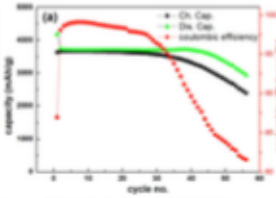
- Lithium-ion batteries are critical to modern and emerging technologies ranging from electric vehicles, high-power tools and wearable electronics to prosthetic limbs and exoskeletons for the physically disabled.

Current Problems of Li-ion battery

- Poor power performance under high C-rate
- Irreversible capacity loss after cycling and limited life time under high C-rate

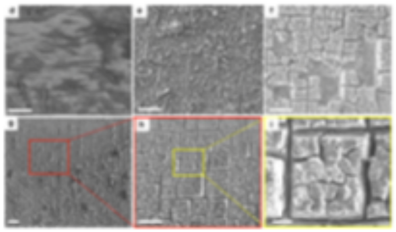


Kang & Ceder, Nature 458, 190-193 (03/12/2009)



J. Xie et al, doi: 10.1149/2.0091503jes

Electrodes' cracks and failure



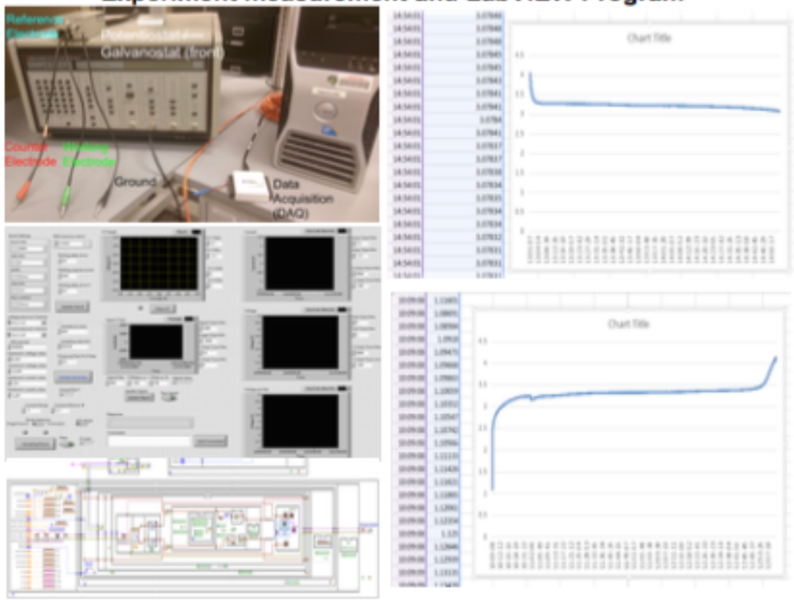
Si anode SEM images after (d)3, (e) 8, (f) 50 and (g–i) 30 cycles. Scale bar, 20μm (d–h), 3 μm (i).
[F. Shi et al, doi: 10.1038/ncomms11886.]

Objective:

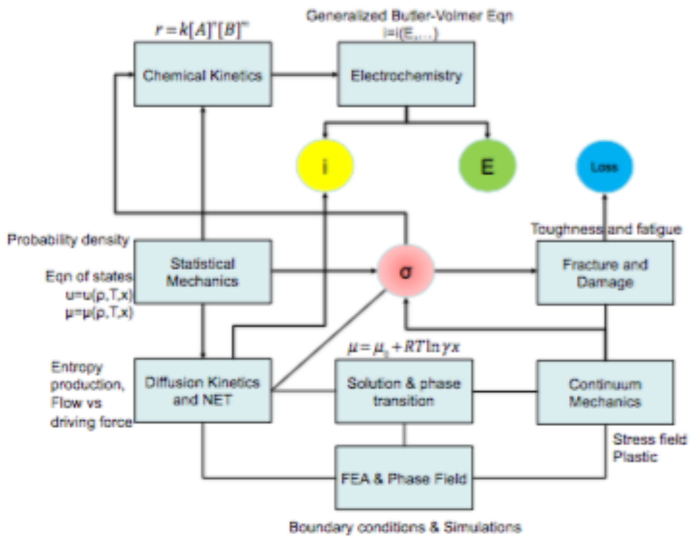
- Describe and predict electrical potential and capacity characteristic under high C-rate (dis)charging.
- Predict Li-ion battery's lifetime under different C-rates.
- Develop approaches to improve Li-ion battery's cycling time and high C-rate performance.

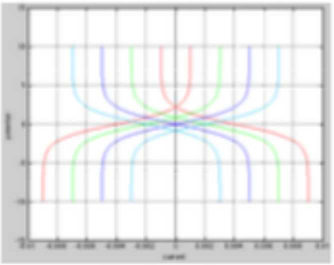
Methods and Current Results

Experiment measurement and LabVIEW Program

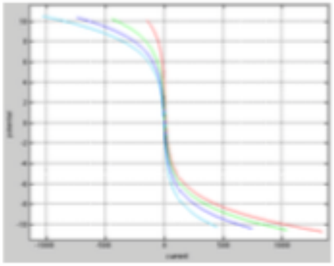


Theory Architecture based on Non-Equilibrium Theory





With diffusion effect



Without diffusion effect

Conclusion and Future Work

- Understanding the loss of power density and capacity involves interdisciplinary theories and models.
- Develop more comprehensive model with less assumption to achieve accurate prediction.
- Model the equations of states: Chemical potentials and specific internal energy incorporating density, fractions and temperature as independent variables.
- Solve equation groups from the above theory architecture and conduct finite element analyses and phase field simulations.
- Damage and capacity loss modeling.

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Investigations of Mechanical Stresses in FIB/SEM Reconstructed Battery Materials

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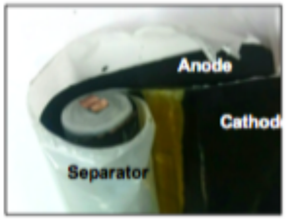
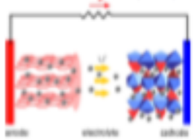
Introduction and Background

Promising Power Source: Lithium-ion Batteries



ref. J. Molenda (2011)



Lithium De/Intercalation ($LiFePO_4$)

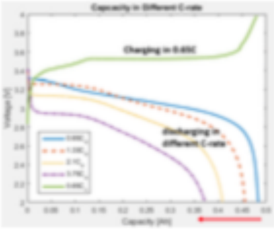
$$Fe_xPO_4 + xLi^+ + e^- \underset{charge}{\overset{discharge}{\rightleftarrows}} Li_{1-x}FePO_4$$

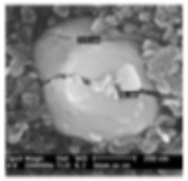
Lithium-Iron-Phosphate ($LiFePO_4$) as a Cathode Material:

- High volumetric energy (970 WhL^{-1}), low exothermic peak temperature (289°C), and low heat flow (-6 Wg^{-1}).
- One dimensional lithium diffusion (along y-direction)
- Li-poor phase ($FePO_4$) → Li-rich phase ($LiFePO_4$); volume expansion.

Motivations:

- Significant capacity loss during high charging/discharging current-rate (C-rate).
- Higher stress in the electrode → particle fracture → short circuit.
- A need for computational models considering reconstructed geometry



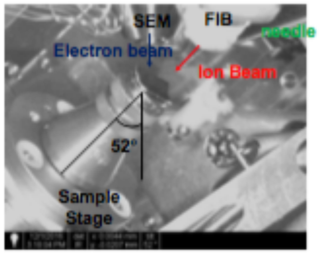


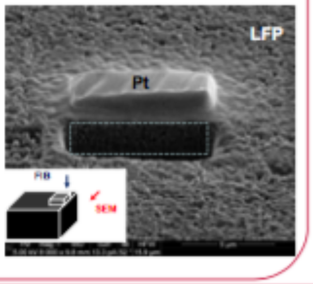
ref. Wang et al. (2005)

Methods

Reconstructed Geometry via FIB/SEM

- **FIB/SEM (NCSU AIF)** was used for sequential FIB (Focused Ion Beam) milling in conjunction with high resolution SEM images.
- Protective layer (Pt) is deposited to ensure **less curtaining effects.**
- After getting sequential images, **image was processed** by ImageJ.
- **3D reconstructed geometry** from 2D images can be imported in both COMSOL and ANSYS

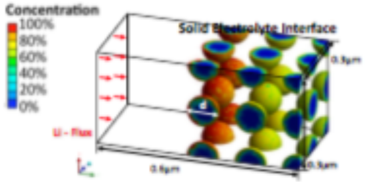


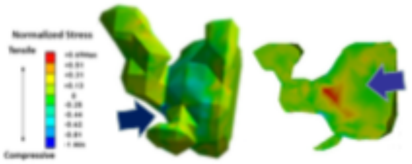


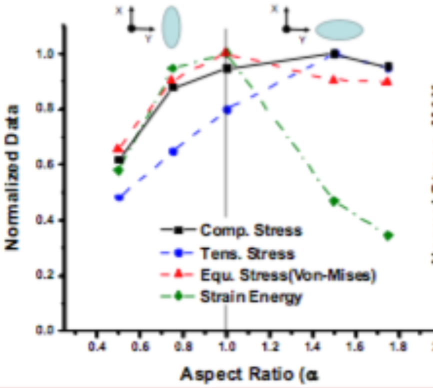
Results

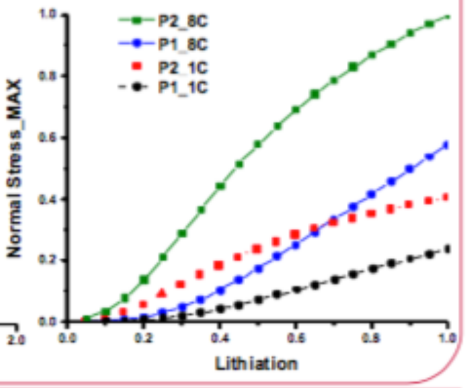
Effect of Geometry Configuration on Mechanical Stress in $LiFePO_4$ Particles

- Material property changes are coupled with **C-rate dependent lithiation stage** during discharging.
- **Tensile stresses** (diffusion induced stress) are highly affected by C-rate; **compressive stresses** (electrolyte) are highly affected by particle geometry.
- Effect of **aspect ratio** is not symmetry in our model due to anisotropic analysis.
- Length along **y-direction** is preferred to be smaller than that along x or z direction.
- Complicated **surface configurations** increase compressive stress rather than tensile stress.









Discussions and Conclusion

- We investigate mechanical stress evolutions during lithiation(discharging) with different C-rates and particle geometry in a half-cell battery system.
- Our simulations demonstrate that both electrode and electrolyte material properties have greater effects when studying mechanical stresses.
- These computational models would aid on mitigating higher stresses in cathode particles to ensure longer battery cycle life.
- Thermal effects will be investigated with reconstructed geometry in the future work.

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Mechanical Stresses at Electrode-Electrolyte Interface in Lithium Batteries

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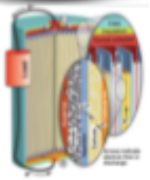
Introduction and Background

Promising Power Source; Lithium-ion Batteries :

- Low cost, toxicity, high thermal stability, electrochemical performance, and high specific capacity.
- Good potential for electronic devices and transportation (HEV, PHEV, and EV)

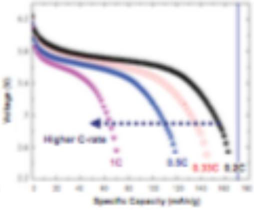


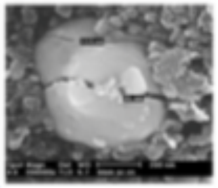
Lithium-Iron-Phosphate ($LiFePO_4$) as a Cathode Material :

- High volumetric energy (970 WhL^{-1}), low exothermic peak temperature (289°C), and heat flow (-6 Wg^{-1}).
- One dimensional lithium diffusion.
- Li-poor phase ($FePO_4$) → Li-rich phase ($LiFePO_4$) ; volume expansion.

Motivations:

- Significant capacity loss during high charging/discharging current-rate (C-rate).
- Higher stress in the electrode → particle fracture → short circuit.
- A need for computational models considering electrode and electrolyte: ***Fluid-Structure Interactions***.



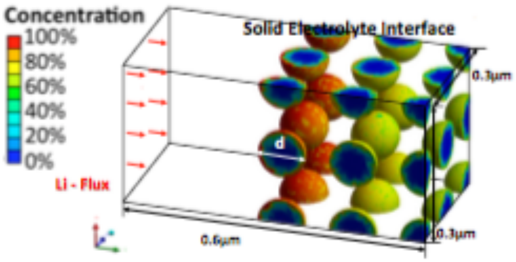


Methods and Results

Phase Transformation during Discharging

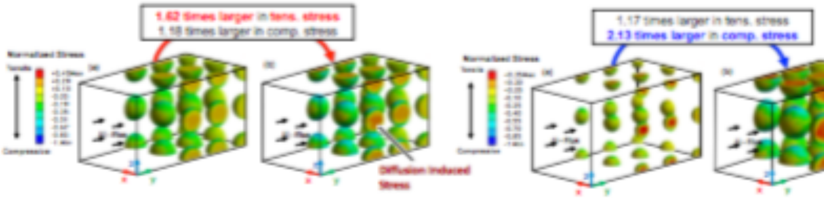
- Diffusion in electrode and electrolyte governed by Fick's second law
- Shrinking-core model for electrode; Li^+ transported from surface to center of particles.
- Material property changes coupled with C-rate dependent lithiation stage during discharging.
- Lithiation stage :

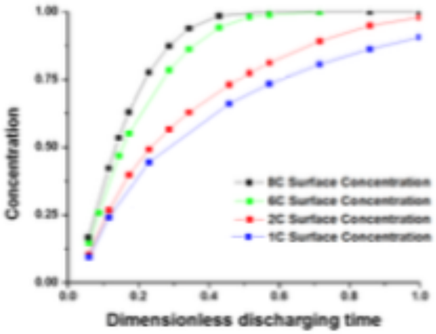
$$\sum_i V_i\left(\frac{\sum_{j=1}^{j=10}\phi_j}{10}\right)\Big/V_T$$

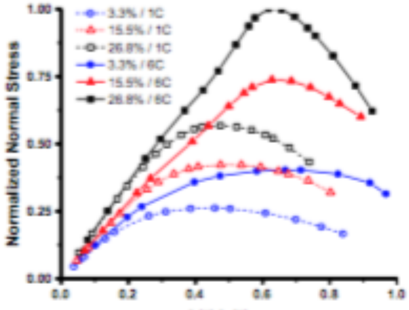


Effect of C-rate and Volume Fraction on Mechanical Stress at the Electrode-Electrolyte Interface

- Tensile stresses are mainly caused by volume expansion; compressive stress mainly caused by electrolyte fluid pressure
- Tensile stresses are highly affected by C-rate; compressive stress highly affected by volume fraction (i.e., particle size).
- Increase in volume fraction and C-rate increase both compressive and tensile stresses.
- Stress increases initially, followed by a decrease after reaching peak values during lithiation due to concentration gradient (similar trends observed in $LiCoO_2$).
- A need to relief stresses on the electrode-electrolyte interface







Discussions and Conclusion

- We investigate mechanical stress evolution during lithiation with different particle sizes, C-rates in a half-cell battery system.
- Our simulations demonstrate that both electrode and electrolyte material properties have greater effects when studying mechanical stresses on the electrode-electrolyte interface
- These computational models would aid on mitigating higher stresses in cathode particles to ensure longer battery cycle life.

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Design a Cyclic Voltammetry Experiment of Lithium-ion Battery via LabVIEW

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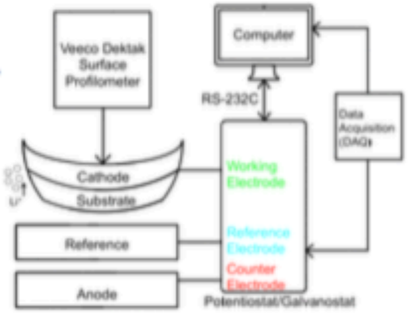
Introduction and Background

Introduction:

- Lithium-ion batteries are critical to modern and emerging technologies ranging from electric vehicles, high-power tools and wearable electronics to prosthetic limbs and exoskeletons for the physically disabled.

Objective:

- To control C-rate and associated voltages for lithium-ion batteries during (dis)charging via Labview.
- Obtain the relationships between C-rate and residual stresses inside electrode materials during (dis)charging.

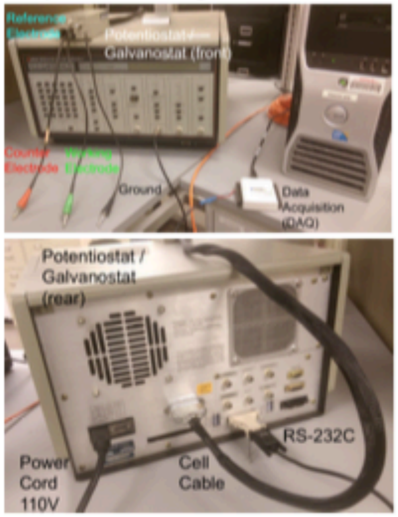


Equipments and Materials:

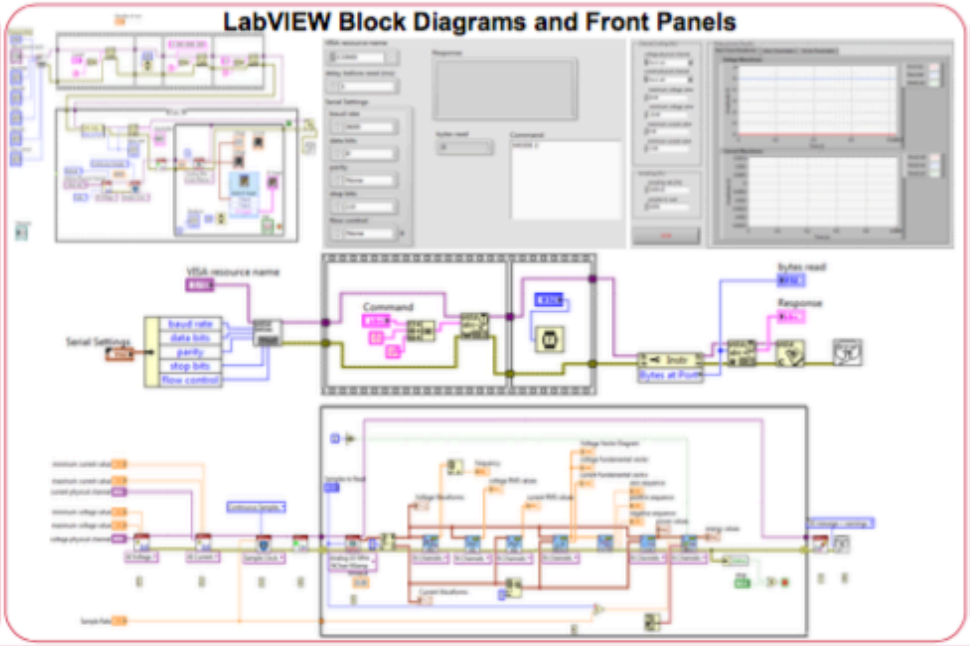
- A Potentiostat/ Galvanostat Model 273:
  - Aid in conducting electrolysis experiments.
  - Controls voltage and current applied to a battery cell.
  - Three electrodes:
    - Working – studied material.
    - Reference – set zero potential.
    - Counter – completes circuit, current flow exits .
- DAQ 6009 from National Instruments.
- Computer Interface: modified RS 232C cable (serial cable) with USB connection and a 25 to 9 pin adapter.

Methods and Results

Equipment:
EG&G Princeton Applied Research 273 potentiostat / galvanostat



LabVIEW Block Diagrams and Front Panels



Detailed experimental Setup

1. Connect potentiostat/galvanostat to resistors and a customized Li-ion thin-film batteries. Three different electrodes are used to establish a better connection with the battery.
2. Establish communications between the potentiostat/galvanostat with the computer via the RS 232C cable.
3. Utilize a data acquisition device DAQ 6009 to transfer analog data to digital ones from the potentiostat/galvanostat to the computer
4. Build a LabVIEW program to control and receive feedbacks from the potentiostat/ galvanostat. Several LabVIEW blocks are presented to demonstrate our capability of better controlling the potentiostat/galvanostat.

Future Study

Connect with nanofabricated lithium-ion batteries to conduct residual stress measurements.

Discussions and Conclusion

- The completed research provides a solid interface and good structure upon which further research on lithium ion batteries will be allowed to take place
- Complete control of Potentiostat/Galvanostat from a host computer is made possible through LabVIEW programming;
- Proper usage of Potentiostat/Galvanostat Model 273 requires much research and detailed knowledge of inner workings and command list
- Improvements must be made to Labview program and hardware for more ideal results- RS 232C replaced with GPIB, higher DAQ system
- Modify program to be able to satisfy diverse control method and test approach.

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Lithium-Oxygen Batteries - A Comprehensive Finite Element Model

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Introduction and Background

The Needs for Li-O_2 Batteries:

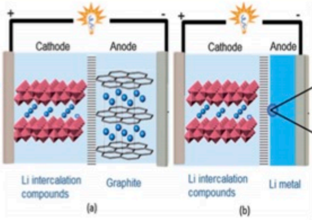
- Li-O_2 batteries possess 6-10 times greater energy densities compared to Li-ion batteries.
- Great for electric vehicles (EVs) or plug-in hybrid vehicles (PEHVs)
- Many energy potential energy storage uses.

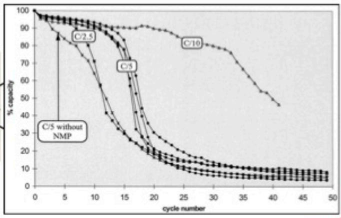
Motivations:

- Dendrite structures grow on anode surfaces.
- Precipitate growth in cathode leads to passivation.
- Identify determinant factors affecting battery performance.

Characteristics of Lithium-Oxygen Batteries:

- Utilizes a lithium metal anode.
- Carbon nanotube cathode structure.
- Oxygen enters and exits the cathode through an oxygen permeable membrane as needed.





Methods and Results

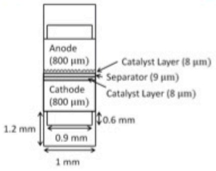
Fuel Cell Module ➔ Lithium-Oxygen Model

Anode Reactions

$$H_2 \longleftrightarrow 2H^+ + 2e^- \qquad 2Li \longleftrightarrow 2Li^+ + 2e^-$$

Cathode Reactions

$$\frac{1}{2}O_2 + 2e^- + 2H^+ \longleftrightarrow H_2O \qquad O_2 + 2e^- + 2Li^+ \longleftrightarrow Li_2O_2$$

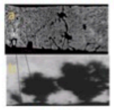


- Construct models of Li_2O_2 batteries with Fuel Cell module within ANSYS Fluent.
- Create models with dendrite growths of different lengths on anode surface.

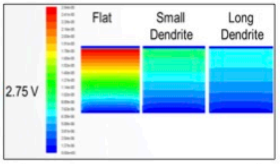
A Comprehensive Finite Element Model

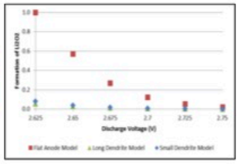
- Simulated discharge in theoretical models to observe several battery parameters such as anode homogeneity, mass fraction of oxygen, mass flow rate of oxygen, and cathode porosity, and their effects on battery discharge.
- Theoretical battery cells discharged at different voltages and their characteristics and performance were compared.
- Total of 150 battery finite element models tested from 2.75 V to 2.6 V.

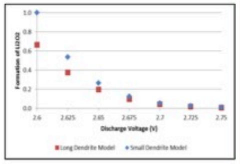
Anode Homogeneity:

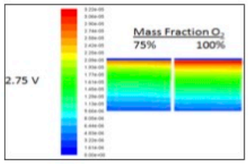


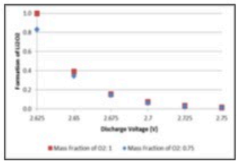
Mass Fraction of O_2:

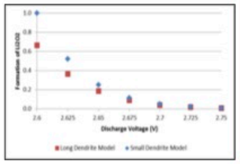












Discussions and Conclusion

- Found the anode homogeneity affected the discharge parameters of our lithium-oxygen battery greater than porosity or mass fraction of O_2.
- Cathode parameters (mass flow rate of O_2, mass flow rate, porosity) affected the performance of the battery cell to a lesser degree compared to the anode homogeneity.
- Lithium dendrite growth continues to pose a significant problem in the commercial development of lithium-oxygen batteries.
- Model can be further developed to incorporate differing reaction rates, different dendrite structures, dendrite spacing, and cell cycling (charging and discharging).

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Modeling C-rate Dependent Diffusion-Induced-Stresses in Lithium-Ion-Battery Materials

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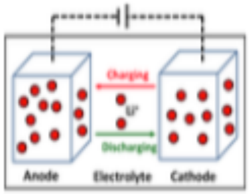
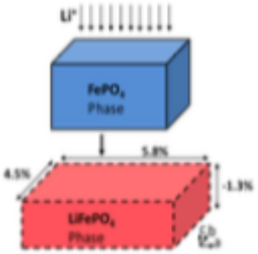
Background and Objectives

- **The needs for high C-rate lithium-ion batteries.**
- **Lithium insertion during charging/discharging → Diffusion-Induced-Stress.**

Li-ion batteries for electric vehicles

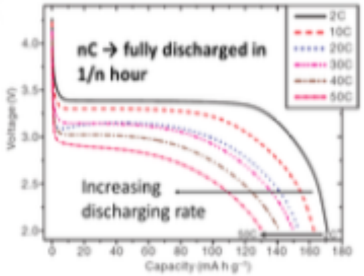


How Li-ion battery works

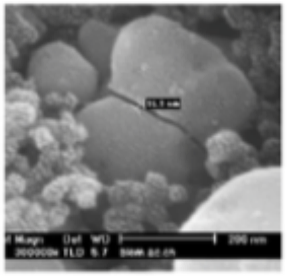


Volume change during Li-insertion

- **Capacity loss is observed at high C-rates.**
- **Particle fractures and crack growth are observed after cycling.**



B. Kang et al., 2009



Wang et al., 2005

Objective:
Investigate how C-rate might affect diffusion-induced- stresses inside materials?

Method

- Apply the thermal stress analysis approach.

Heat Flux $q = -k\dfrac{\partial T}{\partial y}$

Mass Flux $J = -D\dfrac{\partial \phi}{\partial y}$

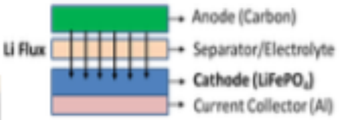
Four cases are studied: 1C, 2C, 6C, 10C

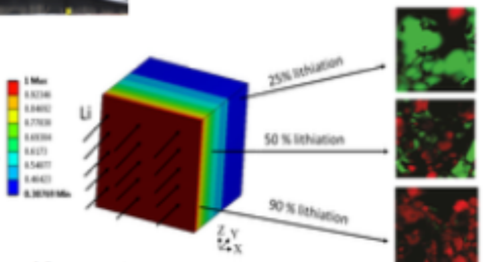
- Finite element model by ANSYS.
- Concentration dependent material property

$$[C(x)] = x[C]^{LiFePO_4} + (1-x)[C]^{FePO_4}$$

- Concentration dependent diffusivity

$$[D(x)] = x[D]^{LiFePO_4} + (1-x)[D]^{FePO_4}$$



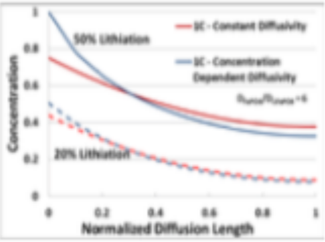


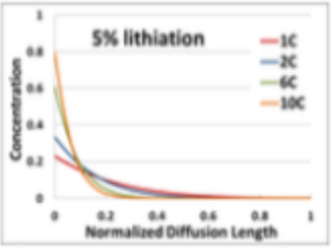
10 μm cube

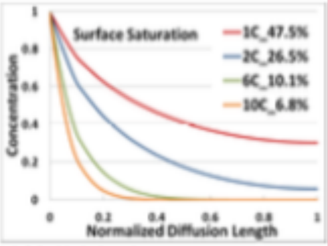
G. Brunetti et al., 2011

Results

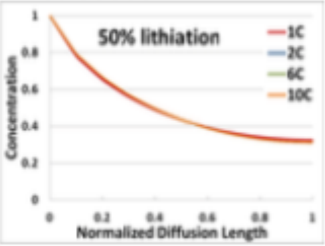
- **Concentration dependent diffusivity cannot be neglected.**
- **Higher C-rate → Higher concentration gradient.**
- **Surface concentration saturation occurs faster at higher C-rates.**

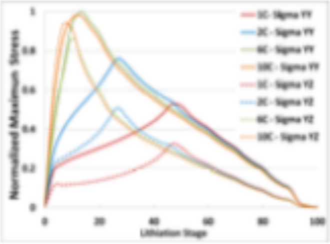


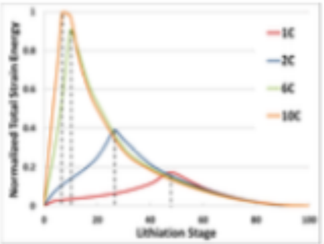




- **Concentration profiles become the same after 50% lithiation stage.**
- **Higher C-rate → Higher concentration gradient → Higher strain energy.**
- **Higher C-rate → Higher concentration gradient → Higher internal stresses.**







Conclusions

- **The concentration dependent diffusivity need to be incorporated in the simulation model since it will affect concentration profiles.**
- **Higher C-rates (more Li-ions pumped into the material in less time) will result in higher concentration gradients inside materials, leading to higher strain energies and internal stresses. Thus the tendency for the particle fracture is higher at high C-rates.**
- **The results of the current study suggest that lowering the concentration gradient could help reduce internal stresses inside battery materials and therefore reduces the capacity loss of the lithium-ion battery.**

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A Fatigue Analysis for Lithium-ion Batteries

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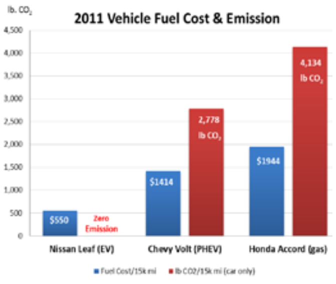
Introduction and Background

Energy Storage Need

- Batteries provide the vital storage link between energy generation and consumption around the world.
- Energy demand is increasing, thus new generation facilities are being built and require large scale batteries to store energy for future transmission or backup power.
- Oil prices and CO_2 emissions are also increasing, driving the need for transportation alternatives (EV and PHEV).

World oil consumption and price projected to rise at a relatively constant rate [1].



EV, PHEV, and Gas vehicle comparison for Operation Cost & CO_2 Emission per 15k miles driven.

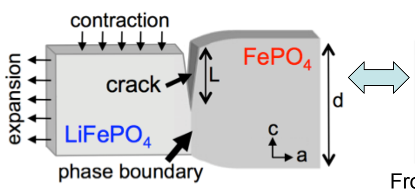
Applications

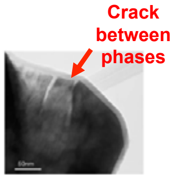
Objective

As it is known batteries experience capacity loss (power loss) over time as the electrode materials degrade, this research investigates the effects of cycling induced stresses and fatigue on $LiFePO_4$ cathode (positive electrode) particles to elucidate an understanding for crack propagation and fracture.

Simulation Method and Results for $LiFePO_4$

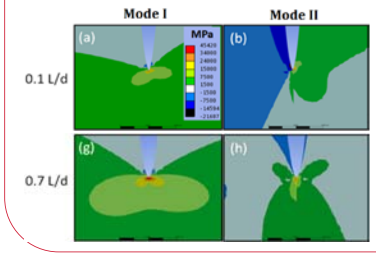
Simulation Set-Up for 2-Phase interface





From Literature [2]

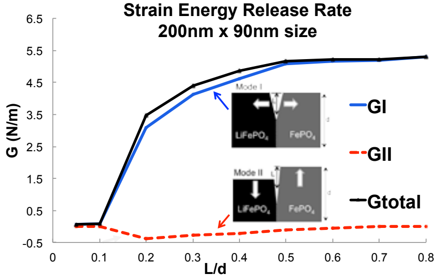
Mode Dependent Stresses



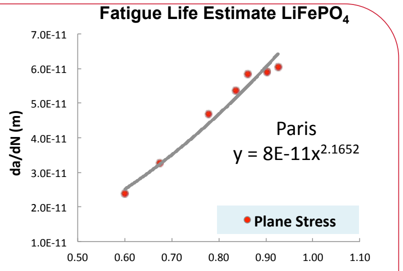
Mode I dominance increases as the crack grows.

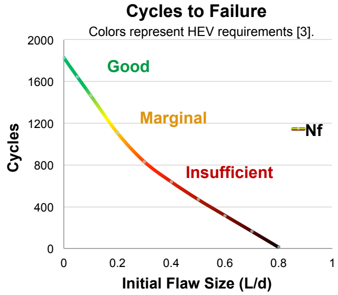
Fracture and Fatigue Analysis

- Choose $LiFePO_4$ due to long cycle life (~2000 cycles), wide op. temps. (-20 to 60°C) and superior thermal stability (safe, incombustible cells).
- Varying sized particles with varied initial crack sizes (nm scale) are analyzed via fracture mechanics.
- Plane Stress, plate-like particles are used with loading according to misfit strains (observed during lithium insertion, $FePO_4 \rightarrow LiFePO_4$).
- Mode dependent stresses , Strain Energy Release Rates (G), and Stress Intensity Factors (K) are calculated using ANSYS software.



- G is the crack driving force.
- An Energy Approach is applied to calculate da/dN and create a fatigue life estimate fit to the Paris law.
- If G > 2Υ, propagation may occur. Υ=particle surface energy on the crack faces
- Cycles to failure (Nf) can be calculated iteratively based on initial crack size.





Conclusion

- Crack propagation and fracture is highly dependent on mode (I or II), misfit %, and particle size.
- Smaller particles show reduced G (crack driving force). Max is always near L/d=0.5.
- Fatigue cycle life estimate of 1800 cycles is fairly consistent with manuf. reported value (2000).
- Understanding what happens at the nm-scale provides insight into what bulk-scale modifications could be made to improve the performance and life of batteries.

Bibliography

[1] Data for this figure compile from: U.S. Energy Information Administration (EIA), 2011.
[2] Gabrisch et al, *Electrochemical and Solid State Letters, 11*(3), A25-A29, 2008.
[3] United States Council for Automative Research LLC (USCAR), "U.S. Advanced Battery Consortium: Energy Storage System Goals", 2012.

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A Diffusion Model in a Two-Phase Interfacial Zone for Nanoscale Lithium-ion Battery Materials

Cheng-Kai ChiuHuang and Hsiao-Ying Shadow Huang
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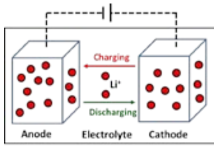
Introduction and Background

The Needs for Lithium-ion Batteries :
e.g. Energy storage units for electronic products and transportation (EVs/PHEVs).

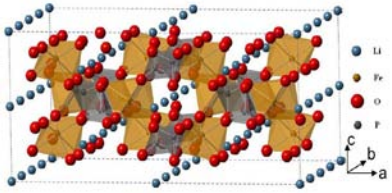


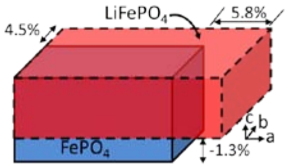
Motivations:

- Capacity loss during high charging/discharging rate.
- Experimentally observed particle fracture.
- A need for anisotropic diffusion model for $LiFePO_4$.

Characteristics of Lithium-Iron-Phosphate ($LiFePO_4$):

- One dimensional lithium diffusion (along b-axis).
- Two phase system, Li-rich phase ($LiFePO_4$) and Li-poor phase ($FePO_4$).
- Anisotropic volume change.



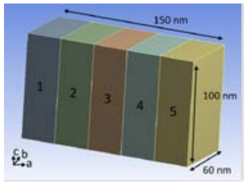


Methods and Results

Phase Boundary Movement

- Phase boundary is experimentally observed aligned with bc plane.
- Phase boundary moves along the a-direction, while lithium diffusion is along the b-direction.
- An interfacial zone with a finite thickness exists between $FePO_4$ and $LiFePO_4$ phase.

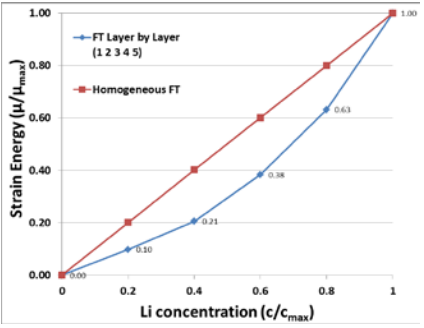
- Strain energy affected phase transformation path (Simulation approach: Anisotropic thermal expansion)

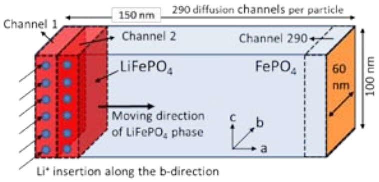


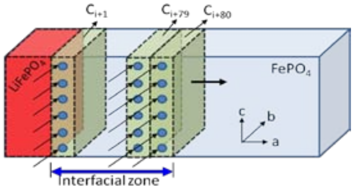
An Anisotropic Diffusion Model

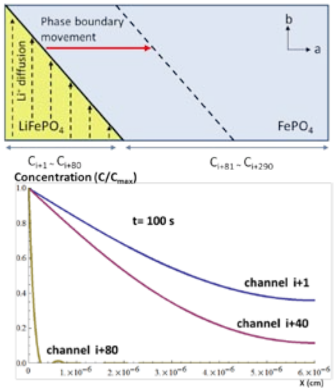
- Accumulated strain energy indicates that the phase boundary movement along the a-axis is favored.
- Based on the simulation and avialable experimental data, we assume the diffusion mainly happens in the interfacial zone.
- A single particle could be considered as a combination of many diffusion channels.
- The lithium-ion concentration profile in each channel within the interfacial zone could be calculated by 1D Fick's law.

$$\frac{\partial c_i(x,t)}{\partial t} = D_i \frac{\partial^2 c_i(x,t)}{\partial x^2}$$









Discussions and Conclusion

- Mechanical stress evolution is related to the lithium diffusion and phase transformation path in the particle.
- The interfacial zone is formed due the strain energy and lithium diffusion mainly happens in this area.
- During discharging, the diffusion channels are fully filled progressively while the interfacial zone sweeps through the particle along the a-direction.
- This anisotropic diffusion model helps explain the diffusion process in a single $LiFePO_4$ particle and contributes to a better prediction of the stress development.

A Dislocation Based Stress Development in Lithium-ion Batteries

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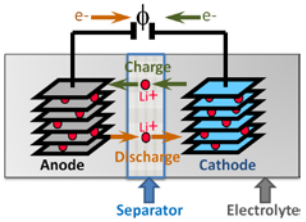
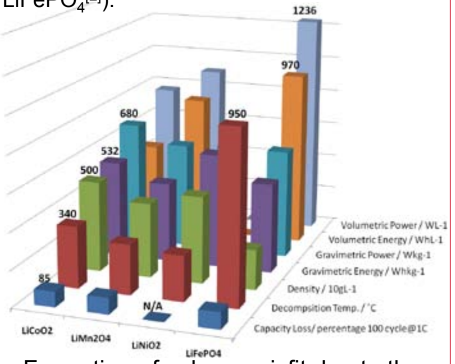
Introduction

The Needs for Li-ion Batteries

- Energy storage is becoming a vital link between energy supply and demand.
- Portable electronic devices require batteries with high volumetric energy density. Electric drive transportations require batteries with high gravimetric energy density.
- Li-ion battery has both high volumetric & gravimetric energy densities[1].



- Battery Components: Electrolyte, Separator, Anode, Cathode ($LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$, $LiFePO_4$[2]).

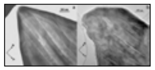


- Formation of volume misfit due to the coherent interface[3]. Dislocations are induced during (dis)charging.

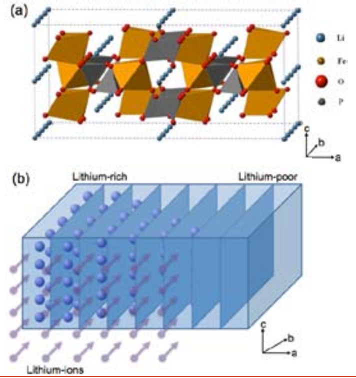
Method & Results

Lithium Ion Diffusion and Dislocation Formation

$LiFePO_4$ as a modeling system.
Cracks along c-axis is observed[4].

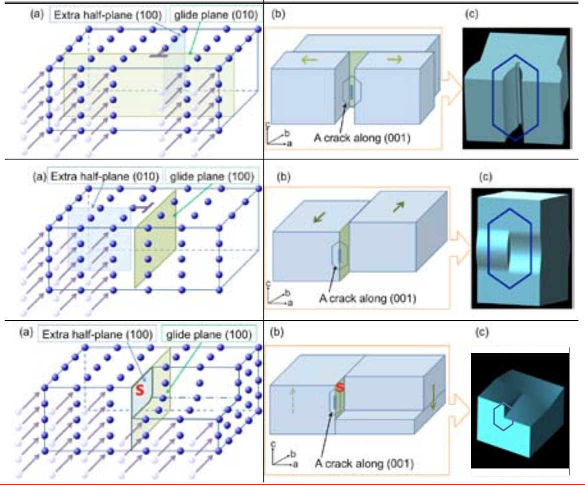


Lithium-ion diffuse in the b-direction.



(I) Kinetics of the dislocation formation due to Li-diffusion

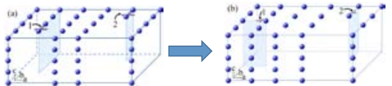
(II) Mode I/II/III fractures caused by the accumulated dislocations



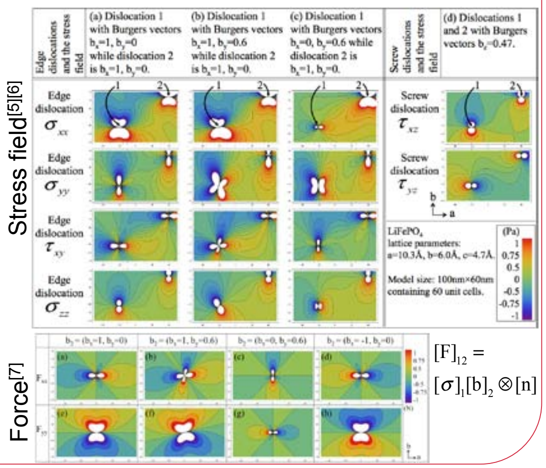
Stress Field for Multiple Edge and Screw Dislocation

Multiple dislocations present in particles

Dislocation 1 rotation



- Stress variations for arbitrary dislocation directions are investigated.
- Dislocation 2 remains its Burger's vector as (b_x=1, b_y=0), while the dislocation1 rotates from 0˚ to 90˚
- Superposition method issued to obtain the stress field of multiple dislocations in anisotropic $LiFePO_4$ material.
- The stress fields manifesting between dislocations are numerically calculated via Mathematica.



$$[F]_{12} = [\sigma]_1[b]_2 \otimes [n]$$

Conclusion

- We reported three different lithium intercalation-induced dislocation mechanisms explaining experimental observed cracks.
- It is observed that mechanical stresses between two edge dislocations could be minimized when they are orthogonal to each other.
- The force field might be one key factor that push and attract lithium ion in the crystal and results in the capacity fade.
- The results provide links between stress fields and the observed structural failure in lithium-ion batteries.

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Strain Accommodation During Phase Transformations in Lithium-Iron-Phosphate Battery Materials

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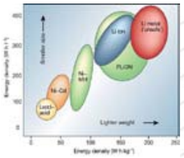
Introduction

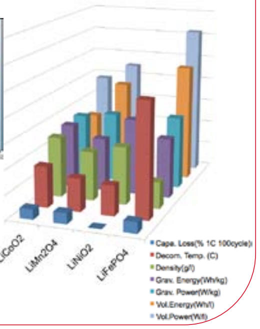
The Needs for Energy Storage

- Energy storage is becoming a vital link between energy supply and demand.
- Portable electronic devices require rechargeable batteries with high volumetric energy density.
- Electric drive transportations require rechargeable batteries with high gravimetric energy density.



Various Cathode Materials

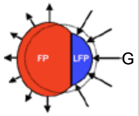
- Lithium-ion battery has both high volumetric and gravimetric energy densities.
- Among various cathode materials, $LiFePO_4$ promises safety, high power, high rate,[1] and long life.



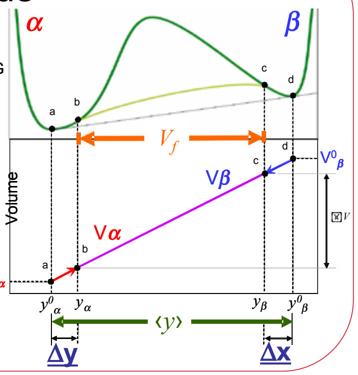
Results

Coherent Interface in Crystalline Solids

- Residual stresses occur due to different molar volumes of $FePO_4$ and $LiFePO_4$, $V_{molar}^{FP} < V_{molar}^{LFP}$
- $FePO_4$ phase is under tension and $LiFePO_4$ is under compression.[3]



Elastic strain energy plays a role in phase stability for nanoscaled $LiFePO_4$ particles.

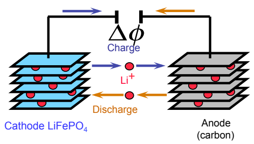


Elasto-Electrochemical Coupling

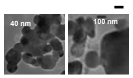
- Electrochemical driving force induces volume misfit due to the coherent interface:[4] $F\Delta\phi = \Delta\mu_{Li} + \frac{V^I}{C}\frac{du_{elastic}}{V_f}$

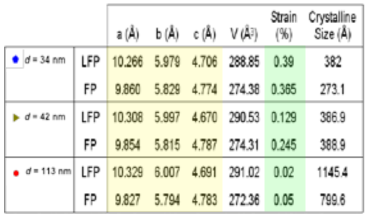
Background and Method

Nano-Scaled $LiFePO_4$ Cathode Materials

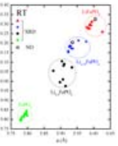


- Allowance for easy phase transformation of $LiFePO_4$ = increased rate capacity of rechargeable batteries
- Miscibility gap (or solid solution) can be calculated through x-ray diffraction data via Vegard's law.
- Size-dependent miscibility gap was observed: nanoscale provides easier phase transformation pathways for $LiFePO_4$.[2]
- The miscibility gap contracts systematically with decreasing particle size and increasing temperature.



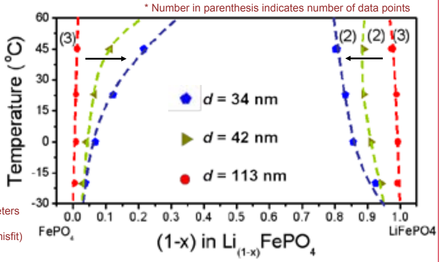


		a (Å)	b (Å)	c (Å)	V (Å³)	Strain (%)	Crystalline Size (Å)
● d = 34 nm	LFP	10.266	5.979	4.706	288.85	0.39	382
	FP	9.860	5.829	4.774	274.38	0.365	273.1
▶ d = 42 nm	LFP	10.308	5.997	4.670	290.53	0.129	386.9
	FP	9.854	5.815	4.787	274.31	0.245	388.9
● d = 113 nm	LFP	10.329	6.007	4.691	291.02	0.02	1145.4
	FP	9.827	5.794	4.783	272.36	0.05	799.6



- Yellow panels provides lattice parameters to calculate the miscibility gap.
- Green panels shows strain (volume misfit) increases with decreasing particle sizes.

* Number in parenthesis indicates number of data points



Dramatic changes in miscibility gap must be associated with changes in free energy functions

Conclusion

- New equilibrium compositions reduce elastic misfit energy.
- Miscibility gap contraction is contributed by strain accommodations in $LiFePO_4$.
- Nanoscaled $LiFePO_4$ particles provide shorter phase transformation paths and increase the rate capacity of rechargeable batteries.

Acknowledgment

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