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

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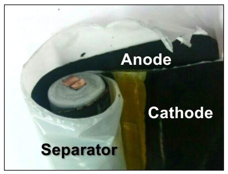
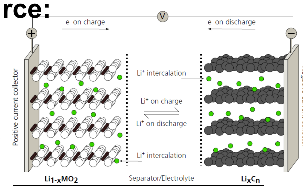
Introduction and Background

Promising Power Source: Lithium-ion Batteries





Lithium De/intercalation (LiFePO4)

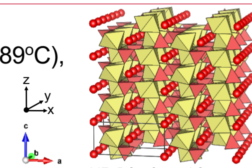
$$Fe_xPO_4 + xLi^+ + e^- \underset{charge}{\overset{discharge}{\rightleftharpoons}} Li_{1-x}FePO_4$$

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

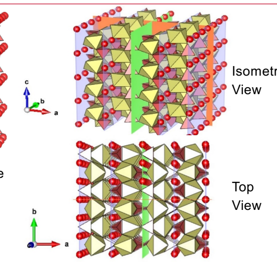
- High volumetric energy (970 WhL^{-1}), low exothermic peak temperature (289ºC), and low heat flow (-6 Wg^{-1}).
- One dimensional lithium diffusion (along y-direction, *i.e.*, b-direction)
- Li-poor phase ($FePO_4$) → Li-rich phase ($LiFePO_4$); volume expansion.

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.



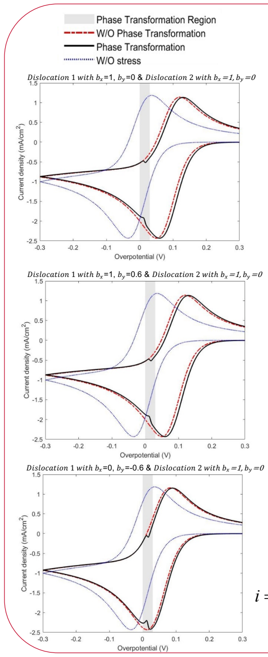
LiFePO4 Crystal Structure



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

Results

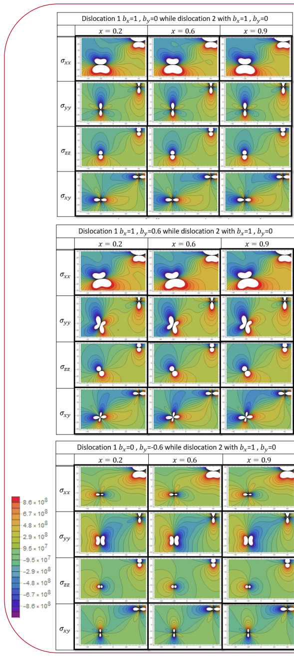
Phase Transformation On Cyclic Voltammogram



- **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

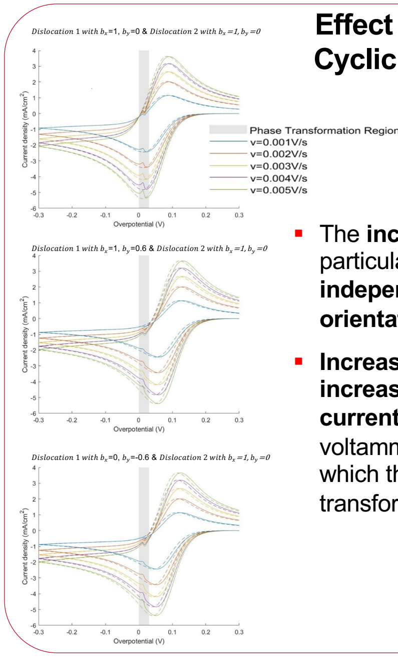


$$[C_{ij}] = (1-x)\left[C_{ij}\right]_{FeO_4} + x\left[C_{ij}\right]_{LiFeO_4}$$

FePO4		LiFePO4	
C_{11}	137.4 GPa	C_{11}	164.3 GPa
C_{22}	146.0 GPa	C_{22}	162.9 GPa
C_{33}	132.0 GPa	C_{33}	181.1 GPa
C_{44}	40.8 GPa	C_{44}	40.8 GPa
C_{55}	38.2 GPa	C_{55}	40.5 GPa
C_{66}	42.1 GPa	C_{66}	43.9 GPa
C_{12}	41.0 GPa	C_{12}	61.1 GPa
C_{13}	29.1 GPa	C_{13}	54.9 GPa
C_{23}	29.1 GPa	C_{23}	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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