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-Iron-Phosphate (LiFePO₄) as a Cathode Material:
- High volumetric energy (970 Wh/L), 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 (FePO₄) → Li-rich phase (LiFePO₄); 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.

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.

Stresses During Phase Transformation
\[ [C_a] = (1-x)[C_{a,FePO_4}] + x[C_{a,LiFePO_4}] \]

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.