The Testing/Characterization of interfaces and Molecular Simulation in Lithium-ion batteries

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Overview

- A new test method is proposed to realize direct measurement of the **adhesion strength** of the electrode under a **combined tension/shear loading** for different stress states.
- **Li-ion diffusion** in LiFePO4 and **lastic constants in different SOCs** are studied by first-principle density function theroy(DFT) and the mechanical response till fracture of LiFePO4 crystal during the Li-ion diffusion is studied via Molecular Dynamics Simulations.

The work shows a multi-scale and comprehensive study of the mechanical properties of interfaces in lithium-ion batteries via mechanical testing ways and molecular simulation.

Introduction

Fracture of the electrode material is one of the main degradation mechanisms in Li-ion batteries, which causes the loss of electric contact as well as enhances side reactions such as solid electrolyte interface formation and dissolution due to the generation of new interfaces. The electrode fracture may occur at various size scales, including crystals, polycrystals, and aggregates. And the deformation of active particles can build a stress field in the crystalline particles, thus causing fracture at the level of aggregates such as the debonding of binder and particles. To capture the failure of the constituent materials of the electrode, we must take into account the mixture of several components with different sizes and properties and the multi-field coupling effect. It is important to understand the interfacial interactions inside the constituent materials in order to mitigate the undesirable failure.

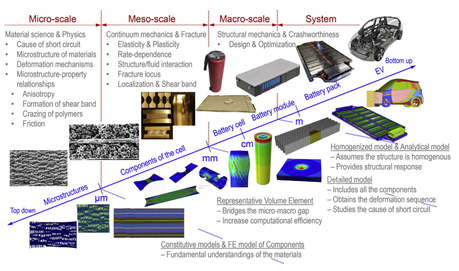


Figure 1: The study of mechanical properties of LIBs involves multiple scales and various models have been proposed to characterize the mechanical behavior of LIBs at each length scale[3].

Experiments Design

The Specimen for testing of adhesion strength of Anode/Cathode and the loading method in different directions are shown as follows:

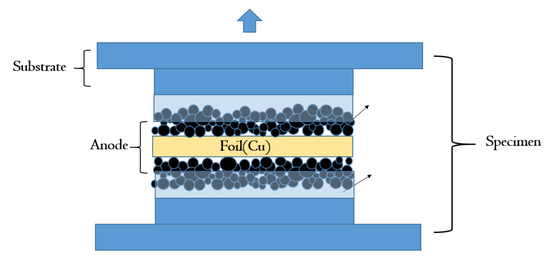


Figure 2: Specimen Preparation

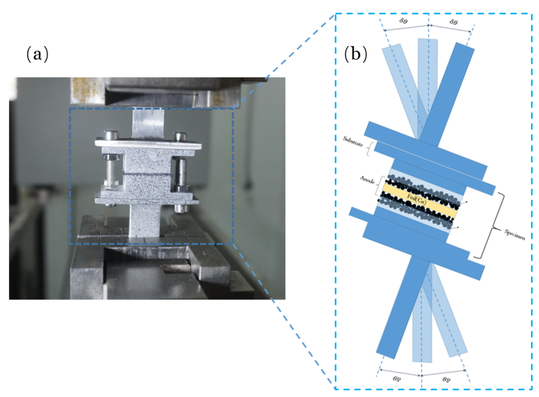


Figure 3: Combined Loading testways

Important Results

For the **cathode**, the **shear strength** of the coating-foil interface is almost **two times** of its **tensile strength**. **Young's modulus** will have a **reduction of up to 23%** during Li-ion diffusion.

Adhesion Strength Results

The testing results of adhesion strength are shown:

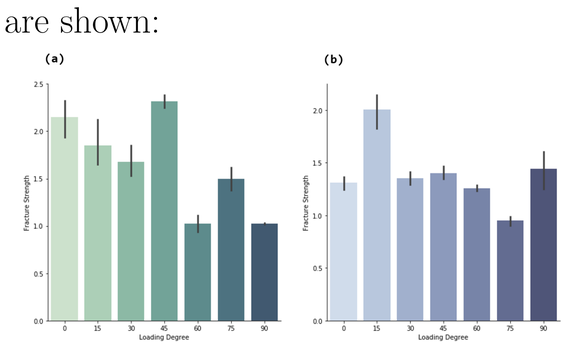
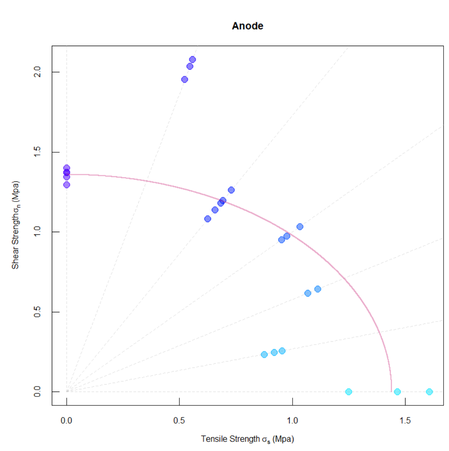


Figure 4: Loading in different directions:(a)Cathode (b)Anode

Also, cohesive zone model is adopted for the tensile and shear component of anode:



Molecular Simulation Methods

To study the change of mechanical properties of LiFePO4 during the Li-ion diffusion process(namely, in different SOCs), first principles density functional theory (DFT) calculations are adopted to calulate the energy barrier in B/C diffussion directions and the elastic constants(also the Young's modulus).

Based on the former simulation, the structures in the diffusion process can be established. So Molecular Dynamics Simulations are employed to study the stress-strain response of LiFePO4 in different SOCs under tensile and compression loading.

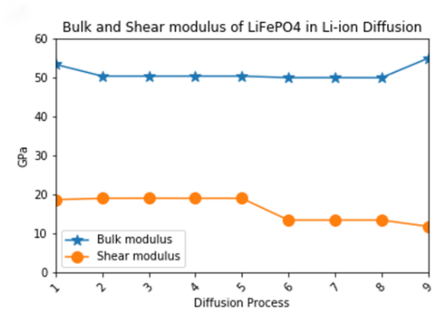
DFT calculations are conducted via Vienna ab initio simulation package[1](VASP), and the Molecular Dynamics Simulations are conducted using LAMMPS[2].

Molecular Simulation Results

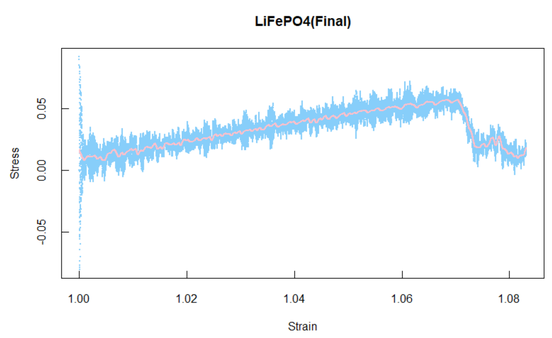
The energy barrier of Li-ion diffusion in B/C direction is shown:

Direction	Barrier(eV)	k_{HTST}
B	0.03	2.5×10^{6}
C	2.5	1.9×10^{-26}

And also the modulus changes during diffusion:



The stress-strain response of LiFePO4 crystal and its fracture is shown below:



Conclusion

1. The coating adhesion strength of anode and cathode varies between 0.9MPa and 2.4MPa and the strength of cathode is bigger than that of anode.
2. **A combined adhesion and cohesion failure mode** was observed at the failure interface, where with larger shear component, the adhesion failure became dominant.
3. The mechanical properties(for example, Young's Modulus) can produce significant changes during the Li-ion diffusion process and **the fracture** will happen even for **perfect lattices** with the strain of about 7%, which indicates that it is very necessary to consider **the influence of the strain caused by the volume change** on the mechanical integrity.

References

[1] Kresse G and FurthmÃijller J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys Rev B Condens Matter*, 54(16):11169–11186, 1996.

[2] Steve Plimpton. *Fast parallel algorithms for short-range molecular dynamics.* Academic Press Professional, Inc., 1995.

[3] Juner Zhu, Tomasz Wierzbicki, and Wei Li. A review of safety-focused mechanical modeling of commercial lithium-ion batteries. *Journal of Power Sources*, 378:153–168, 2018.

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