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

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Outline

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Part 1

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Research Background

Fig 1： Lithium ion battery fires：
(a) Chevrolet Volt (b) BYD e6 (c) Boeing 787 (d) Tesla Model X

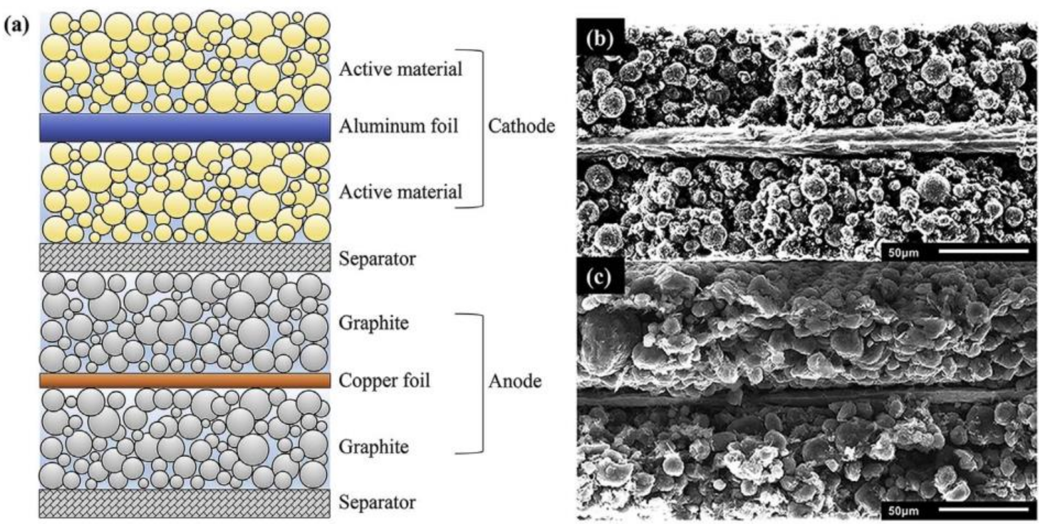

Fig 2：
(a) Repetitive structure of lithium ion battery
(b) SEM images

Juner Zhu, Tomasz Wierzbicki, and Wei Li. A review of safety-focused mechanical modeling of commercial lithium-ion batteries. Journal of Power Sources, 378:153168, 2018.

Research Overview

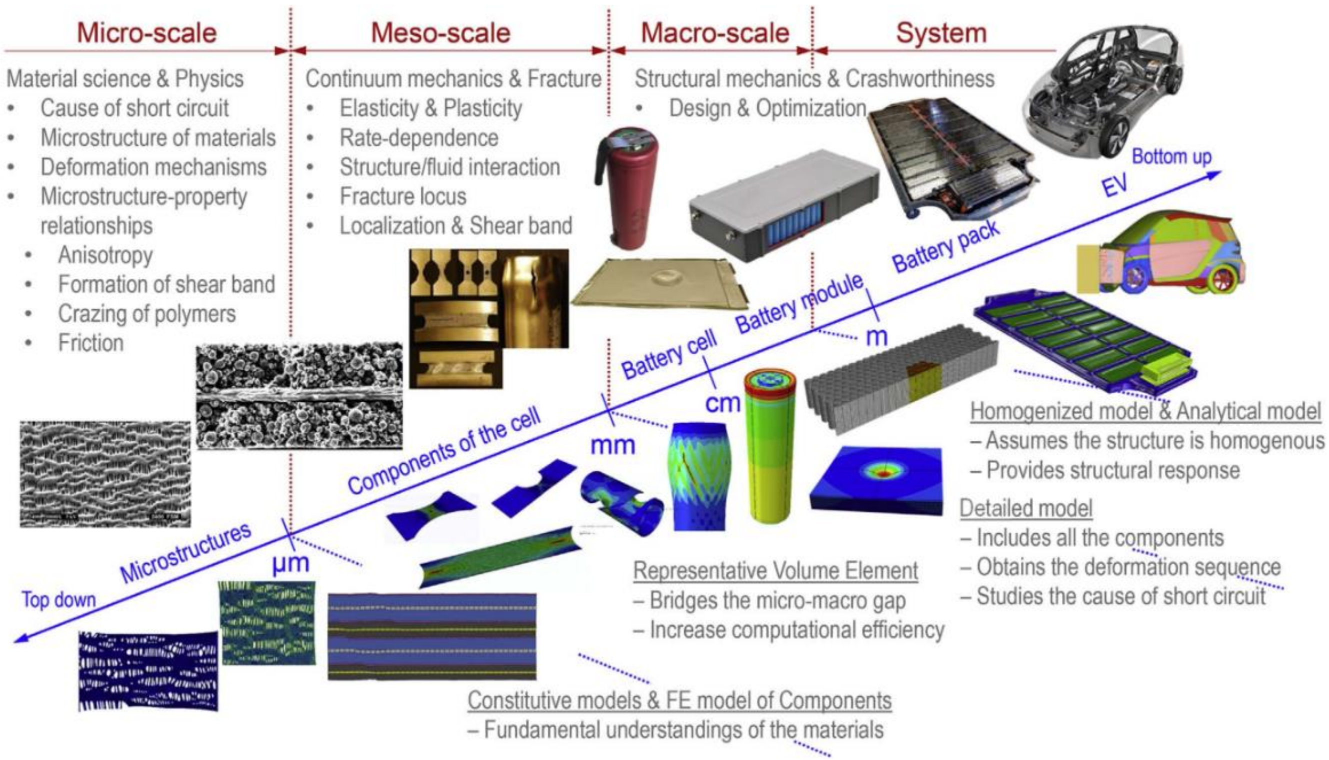

Fig 3: Research on mechanical properties of lithium-ion batteries involves multiple scales and dimensions

Juner Zhu, Tomasz Wierzbicki, and Wei Li. A review of safety-focused mechanical modeling of commercial lithium-ion batteries. Journal of Power Sources, 378:153168, 2018.

- On the macroscopic scale, mechanical tests of the adhesion strength of the electrode under combined tension/shear loadings were studied.
- On the microscopic scale, molecular simulation of the changes in the elastic properties and even the fracture properties of LiFePO4 during lithium ion intercalation and de-intercalation was carried out.

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Testing method： different failure modes

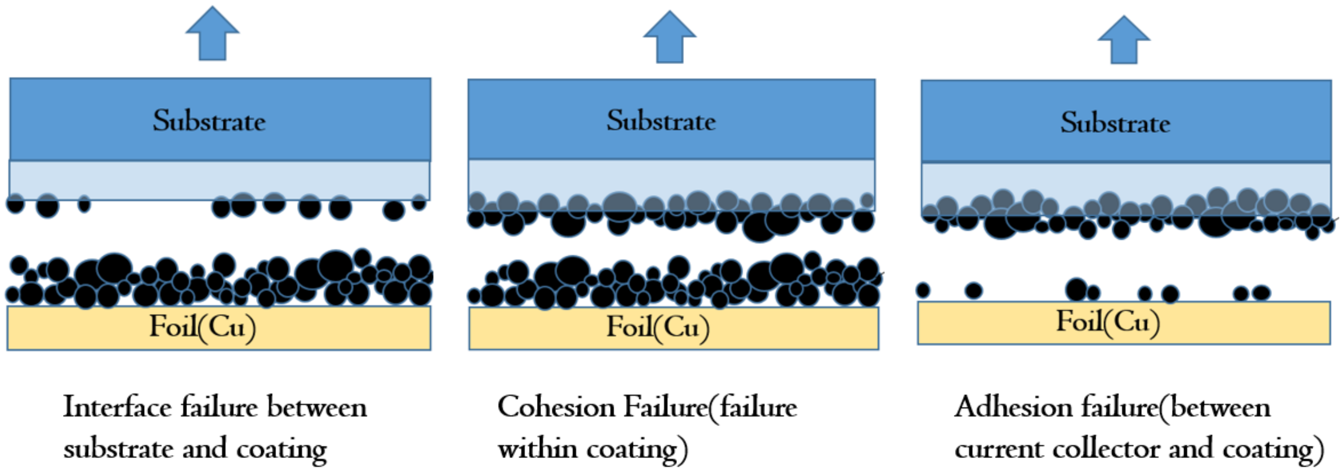


Fig 4： Three possible fracture modes

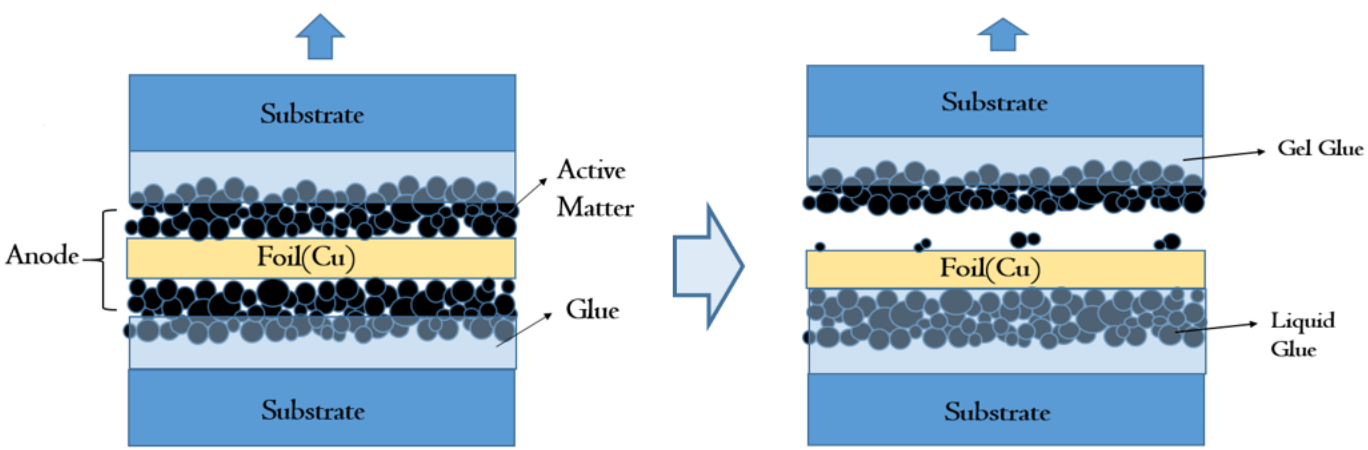
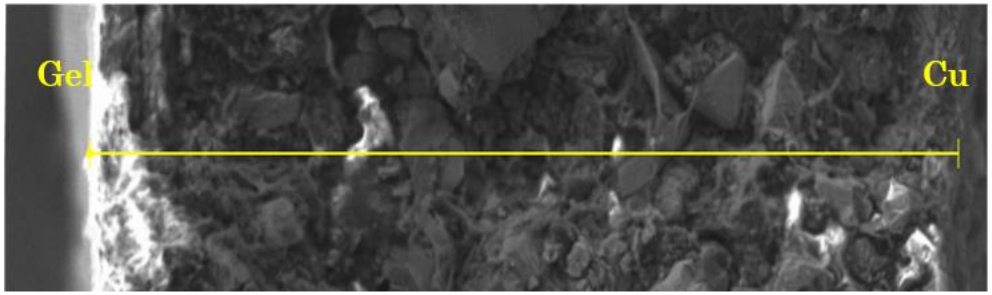


Fig 5： Gel is used to ensure the third failure mode

Testing method : EDS



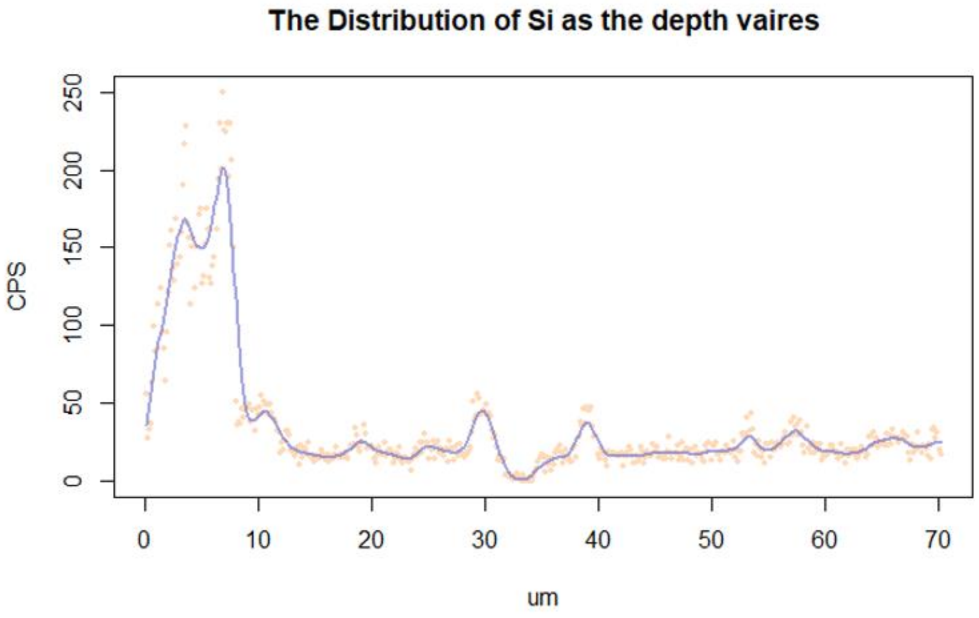


Fig 6: EDS Line Scan Results of Silicon(Only contained in Gel)

The key to the experiment is to ensure that the gel does not affect the fracture.

EDS results show that the glue on the gel side will not affect the test results

Combined tension/shear loading fixings

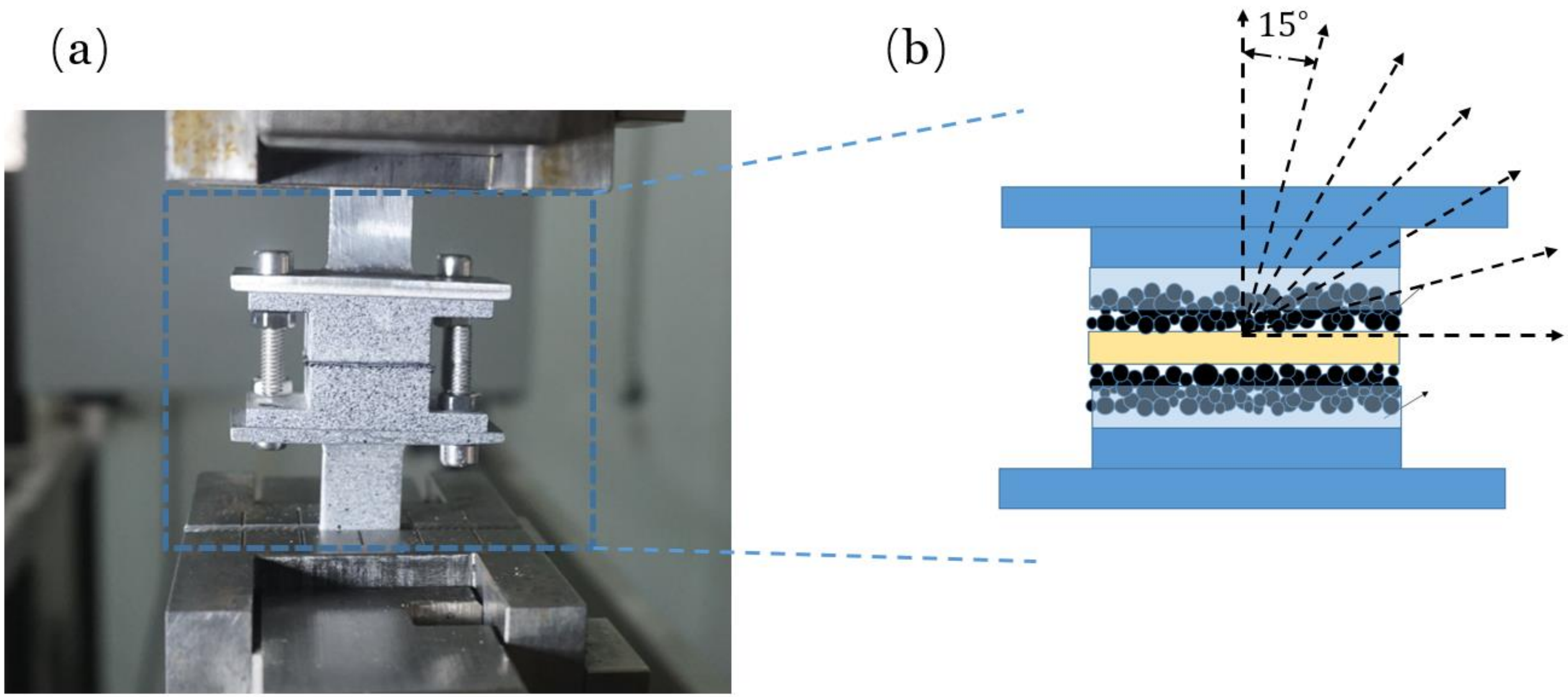
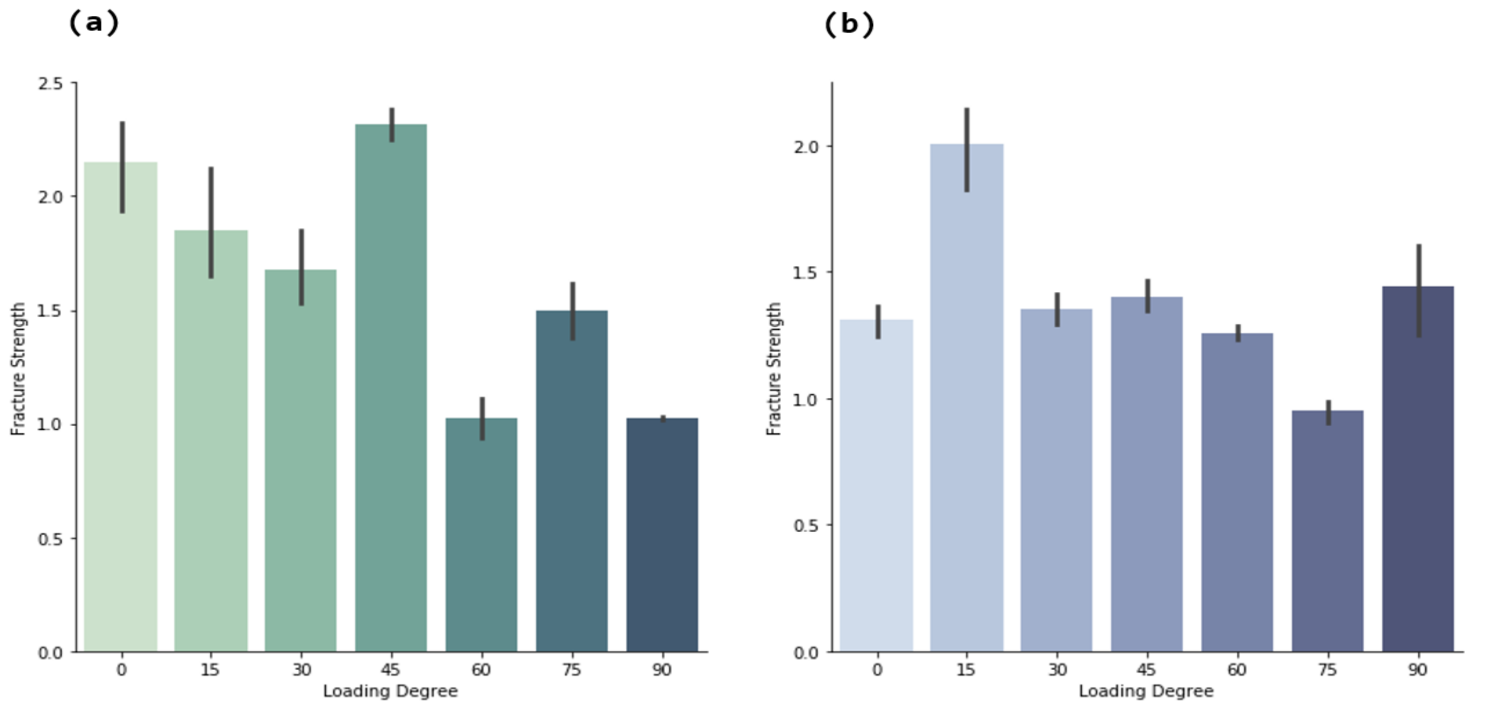


Fig 7:　Combined tension/shear loading fixings

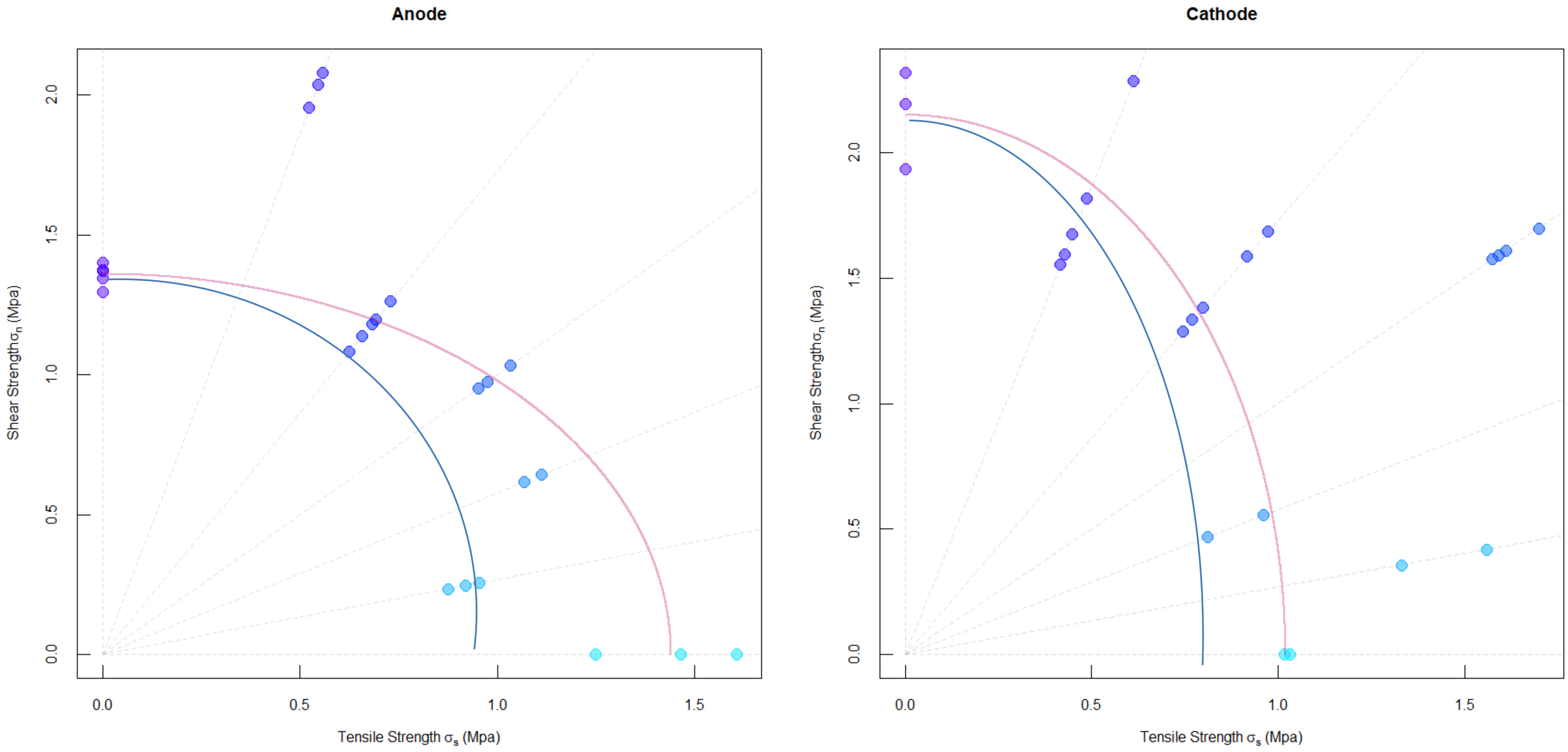
Loading angle changes every 15 degrees to achieve mixed tensile-shear loading

Static experiment： different Loading angles



- For cathode, as the shear component decreases, the fracture strength gradually decreases, and the bond strength increases with larger shear component loading
- For the negative electrode, the coherent strength is relatively smaller than that of the positive electrode.

Results： Tensile and shear component distribution



Cohesive Zone Model：

$$\left(\frac{\sigma_n}{NFLS}\right)^2 + \left(\frac{\sigma_s}{SFLS}\right)^2 = 1$$

The blue failure line can be a relatively conservative input for material in modeling

Dynamic experiment： Cathode results

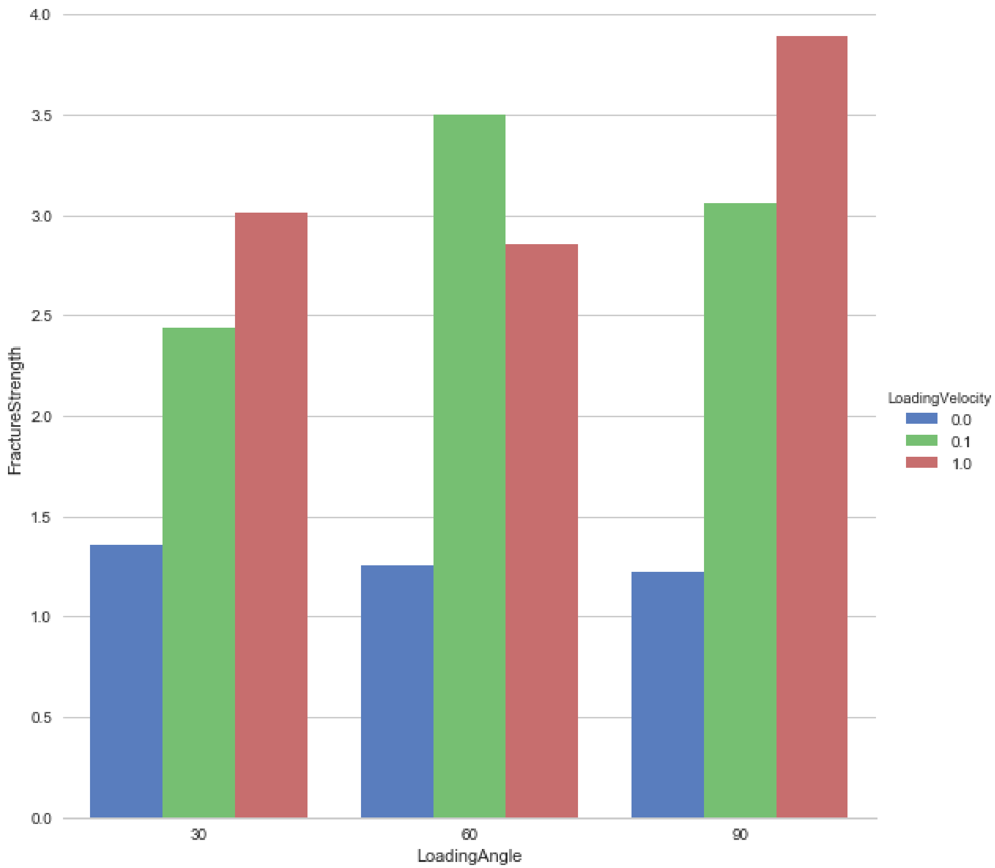


Fig 8： Three different angles of strength test results for cathode at loading speeds of 0.1m/s and 1m/s

- When the loading speed increases, the interface fracture strength increases significantly
- No significant change in breaking strength for different speed loading
- The breaking strength at different loading speeds varies with the loading angle

Analysis

Highlights: Shear strength is twice that of tensile strength for cathode

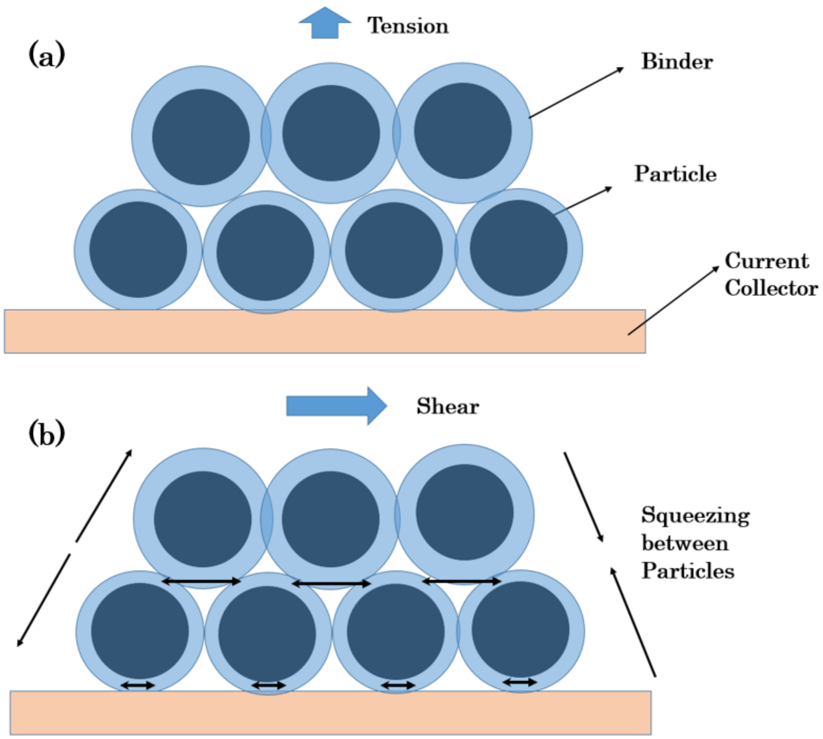
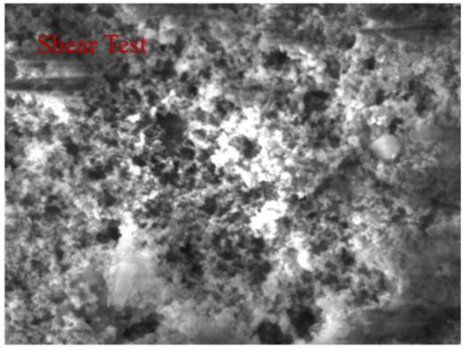
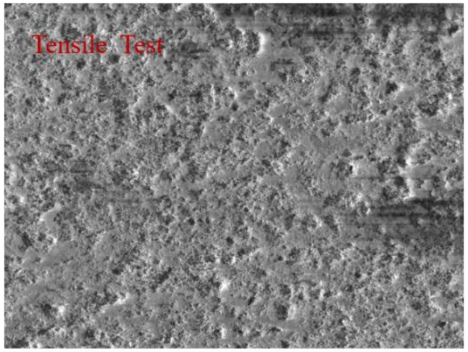


Fig 9: Distribution of binder in coating





- The thickness of the adhesive layer near the underlying particles is thinner than the other layers;
- In the shear test, a lot of active material particles are still attached to the current collector side of the fracture surface.

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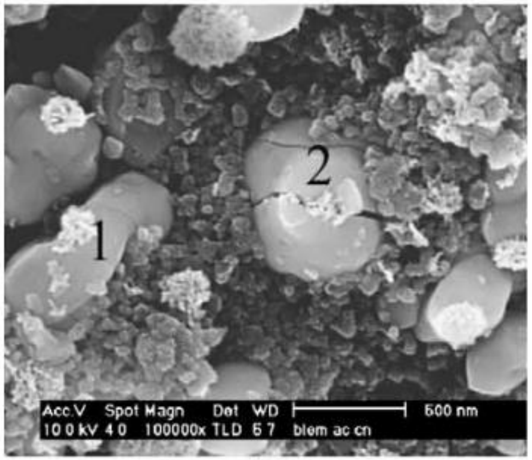
Li-ion transport mechanical effect : Background



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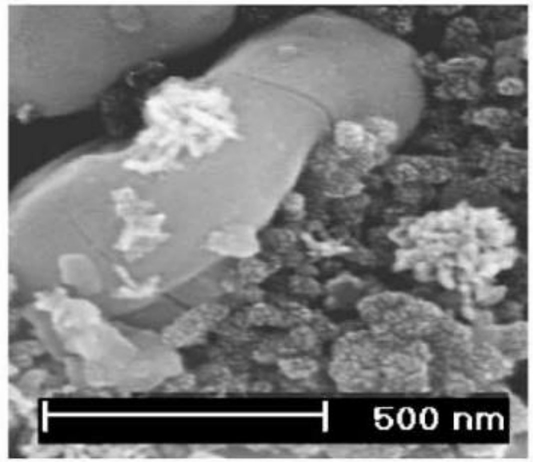

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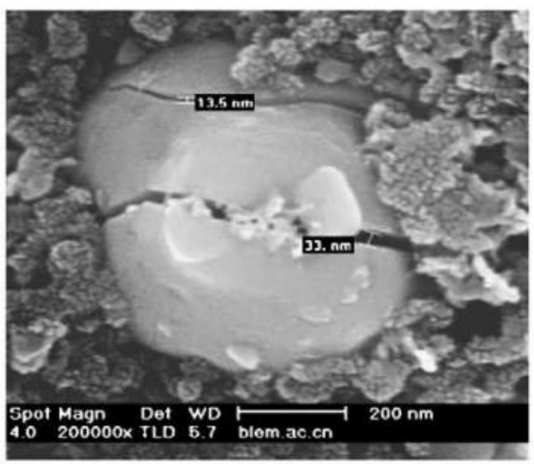


(g)

LiFePO4 particles may break during electrochemical cycling , causing：

- Internal crack propagation
- Current path blocking
- Decrease of battery capacity

Fig 10：

The fracture of LiFePO4 particles in charge and discharge process

Wang D, Wu X, Wang Z, et al. Cracking causing cyclic instability of LiFePO4, cathode material[J]. Journal of Power Sources, 2005, 140(1):125-128.

Calculation of Elastic Constants in Li-ion Migration

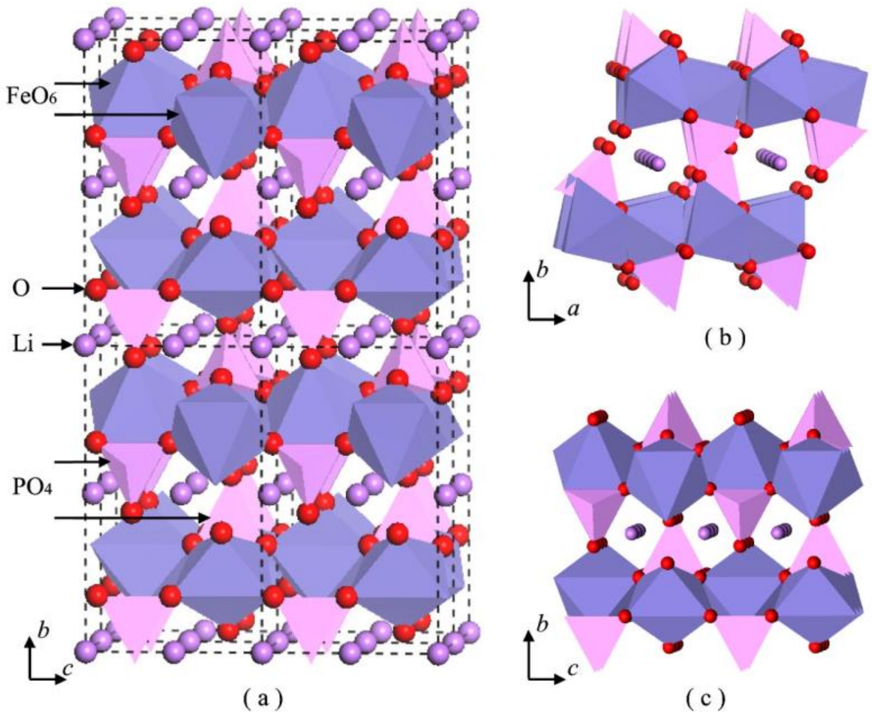


Fig 11: Anisotropic structure of LiFePO4

Wang D, Wu X, Wang Z, et al. Cracking causing cyclic instability of LiFePO4, cathode material[J]. Journal of Power Sources, 2005, 140(1):125-128.

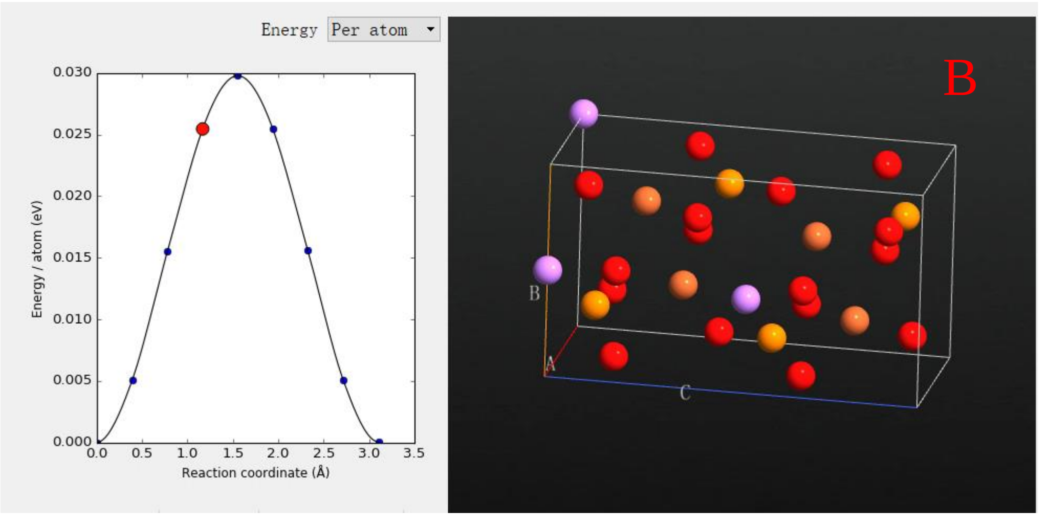
Calculation steps:

1. Remove lithium ions in a certain direction
2. Determine the configurations during the migration process
3. Calculate the energy change in the migration process to get the energy barrier
4. Apply DFT Method to Determine Elastic Constants During Migration

Calculation Tools:

Density functional method(DFT)
VASP First-principle Calculation Package

Main migration direction of Li-ions



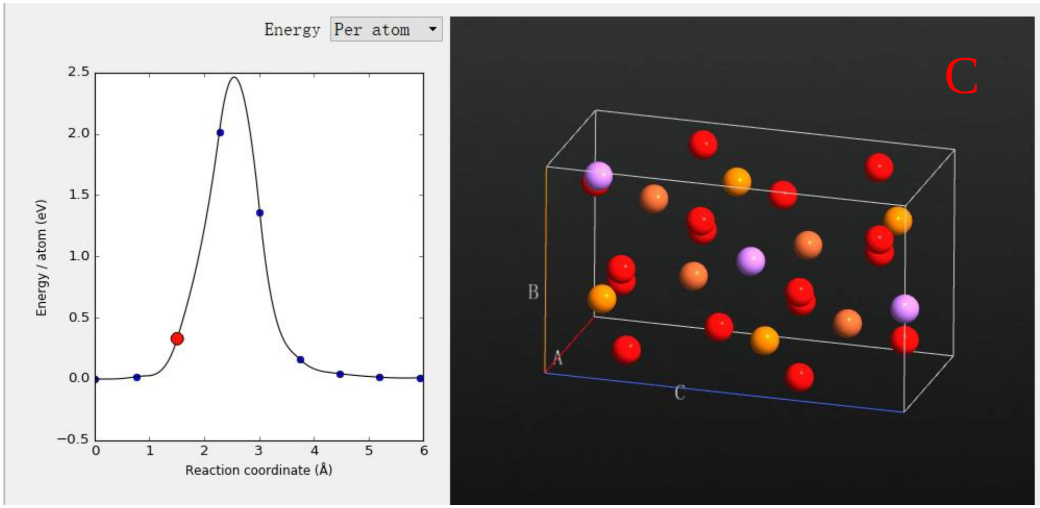


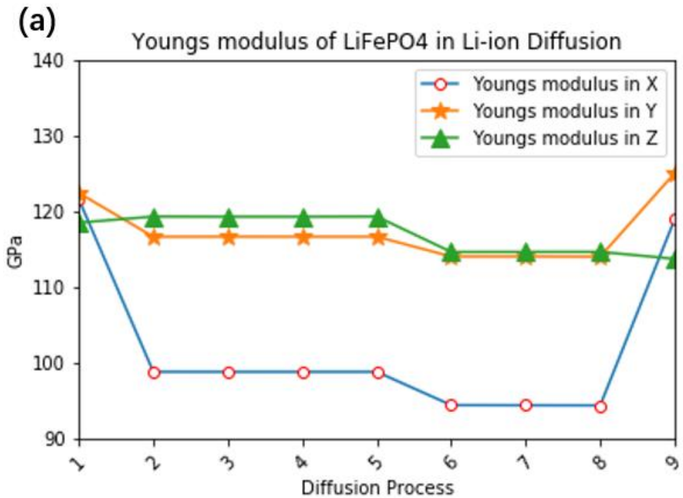
Fig 12： Energy changes in the migration

Direction	Barrier(eV)	k_{HTST}
B	0.03	2.5×10^{6}
C	2.5	10^{-300}

Tab 1： Barrier and reaction rate

The diffusion of lithium ions in the B direction is much easier than the diffusion in the C direction due to the small potential barrier

Results: Elastic constants and elastic modulus



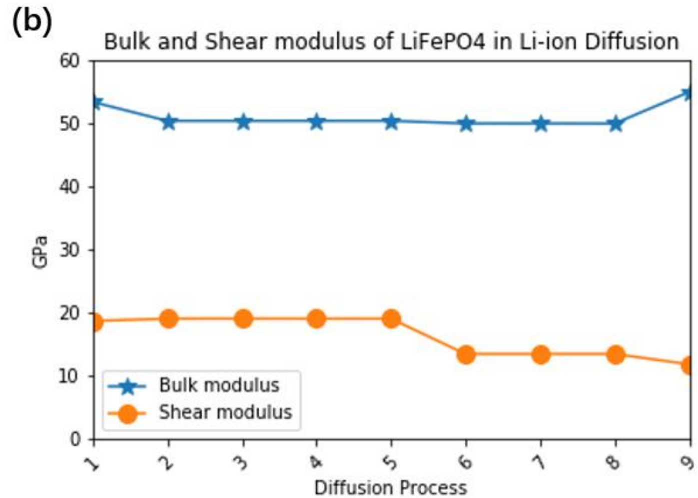
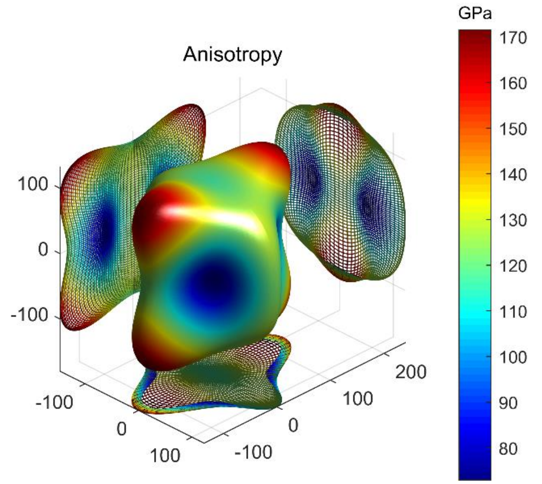


Fig 13: Modulus Change in Li-ion Migration



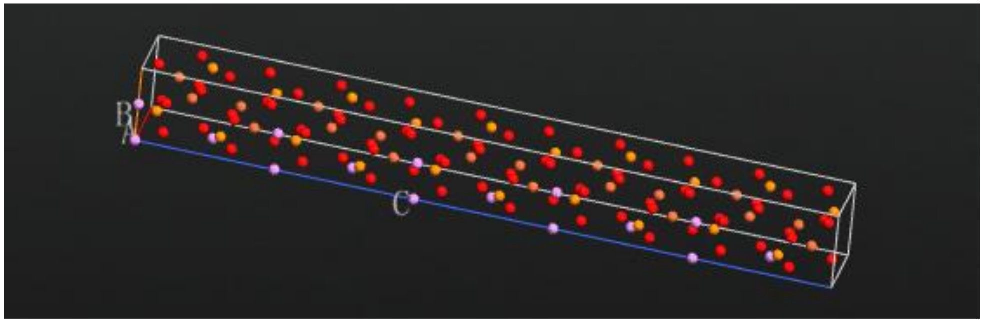
During the migration process:

- Modulus has a decreasing trend ;

  The weakening of bond formation at the time of diffusion

- Modulus will have a reduction of up to 23%

Tensile Fracture Simulation



原子对	$D_{ij}(eV)$	$a_{ij}(\AA^{-2})$	$r_0(\AA)$	$C_{ij}(eV\AA^{12})$
Li-O	0.001114	3.429506	2.681360	1.0
Fe(II)-O	0.078171	1.822638	2.658163	2.0
Fe(III)-O	0.418981	1.620376	2.382183	2.0
P-O	0.831326	2.585833	1.800790	1.0
O-O	0.042395	1.379316	3.618701	22.0

Tab 2: Potential energy model parameters

Steps:

1. Periodic boundary conditions, 300K hot bath
2. determine the stress and strain at each time

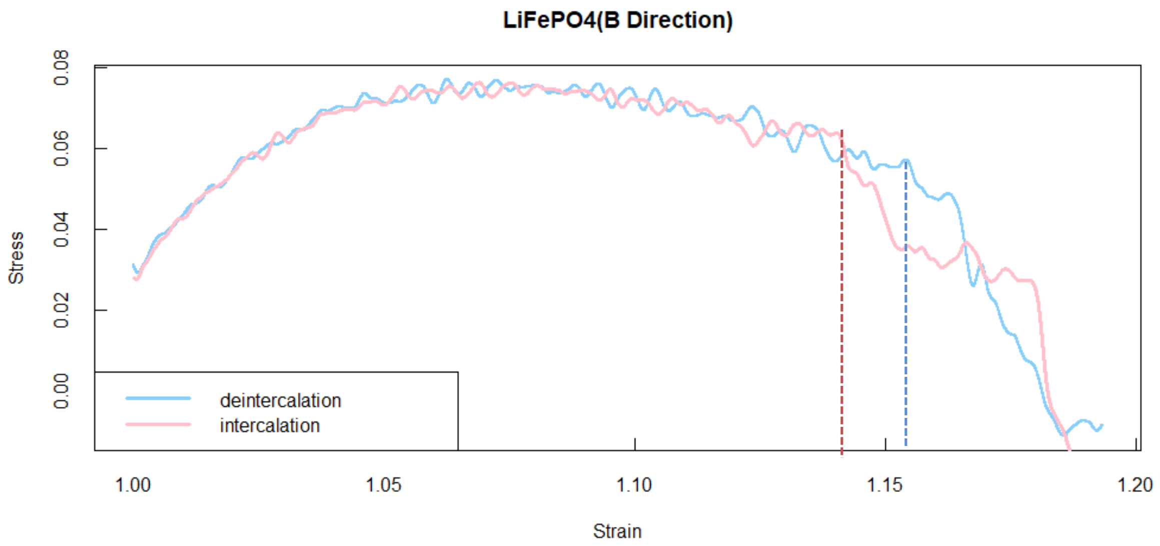
Tools:

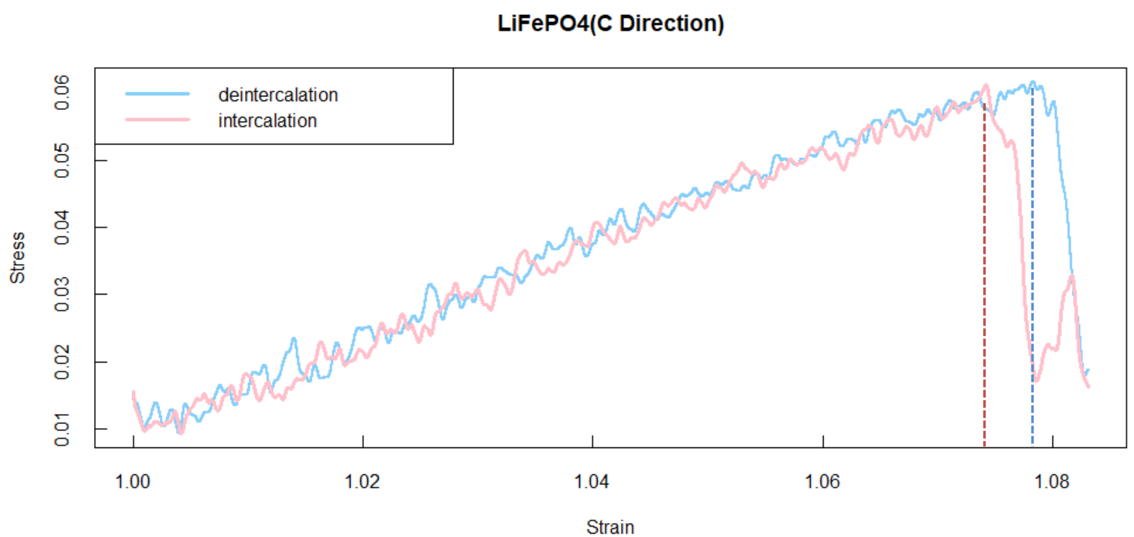
Molecular dynamics(LAMMPS software package)

$$U(r) = \frac{z_i z_j e^2}{r} + D_{ij}\left[\{1 - e^{-a_{ij}(r-r_0)}\}^2 - 1\right] + \frac{C_{ij}}{r^{12}}$$

$$\sigma(\mathbf{r}) = \frac{1}{\Omega}\sum_i\left[-m_i\dot{\mathbf{u}}_\mathbf{i}\otimes\dot{\mathbf{u}}_\mathbf{i} + \frac{1}{2}\sum_{j\neq i}\mathbf{r_{ij}}\otimes\mathbf{f_{ij}}\right]$$

Results





- Li-ion intercalation and de-intercalation can affect the mechanical response of crystals
- Li-ion intercalation reduces the fracture strain of the crystal
- The crystals have different fracture mechanics responses before and after the migration.

Outline

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Part 4

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Conclusion： Strength test

- In static experiments, the strength of the positive electrode is relatively stronger than that of the negative electrode.
- For the cathode, the shear strength of the coating-foil interface is almost twice of its tensile strength
- Under dynamic loading, the fracture strengths of the anode and cathode interfaces are significantly increased, but the strain rate effect is not obvious

Conclusion : Molecular simulation

- Lithium ion migration has a strong directionality
- The mechanical properties of the crystal during the migration of lithium ions have a significant change, the Young's modulus can be reduced by up to 23%
- Li-ion intercalation reduces the fracture strain of the crystal, indicating that the active particles of the positive electrode are more likely to break due to mechanical load during discharge.

Thank you for listening!

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Automobile Crash Laboratory, Tsinghua University