Unraveling the nature of anomalously fast energy storage in T-Nb_2O_5

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Niobium Oxides

- Niobium(V) oxides exist in a variety of forms.

T-Nb_2O_5

Unique Properties!

B-Nb_2O_5

M-Nb_2O_5

H-Nb_2O_5

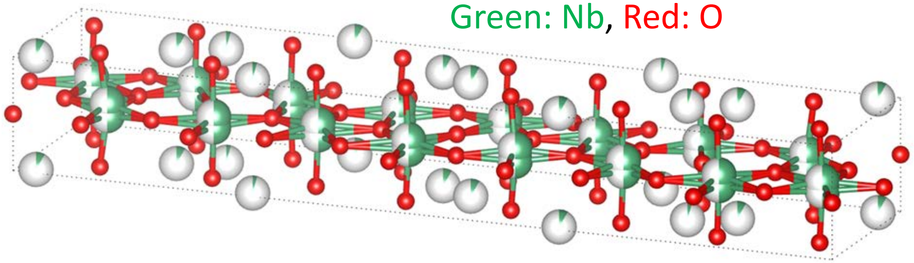
Low Temperature phase

Intermediate Temperature Phase

High temperature Phase

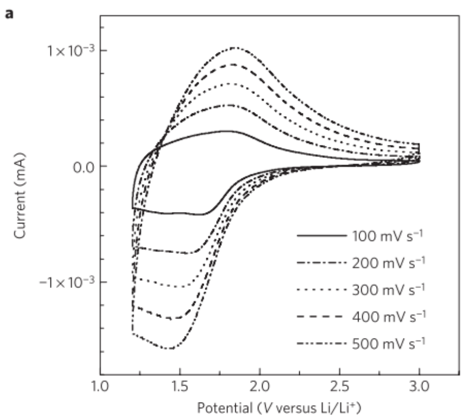
Unique properties of T-Nb_2O_5

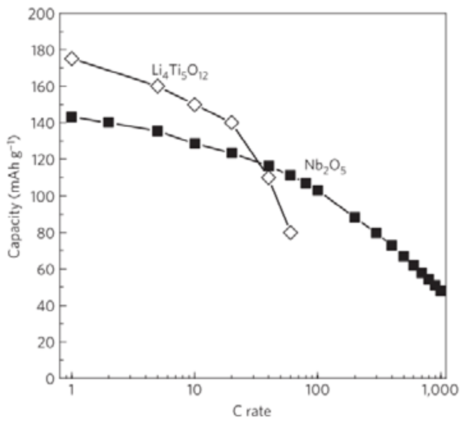
Structure of T-Nb_2O_5 :



Unit cell: orthorhombic structure
Space group: Pbam.
Stoichiometry: $Nb_{16.8}O_{42}$

When applied as Li ion battery electrodes:





Nat. Mater. **2013**, *12*, 518.

T-Nb_2O_5 presents the unparalleled rate capability.

A unique battery allows super fast charge-discharge.

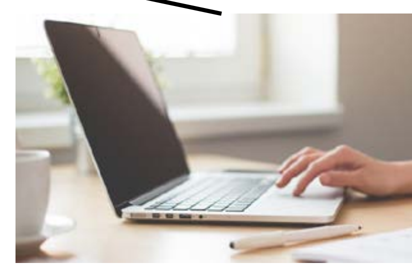
Li ion batteries, why fast charge important

Internal combustion engine cars vs Electrical cars

A few minutes

A few hours

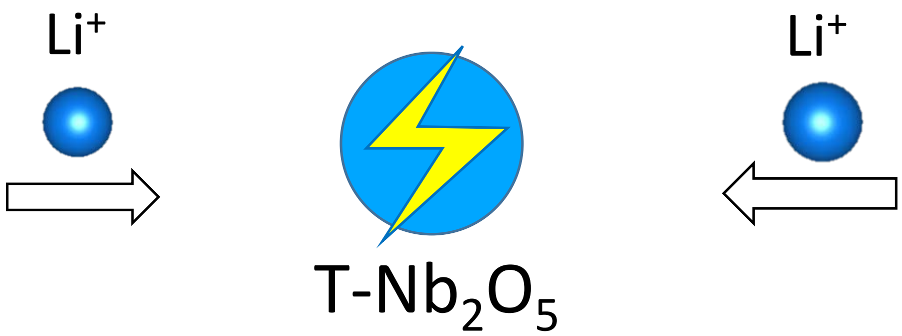
If super fast charge is realized, everything is plug-and-go



Objectives of the study

In a scientific perspective, the fast charging behavior of T-Nb_2O_5 brings important questions.

1. How Li ions are stored?



2. Why so fast?

3. How does it compare with other battery materials?

Approach

- How to reveal the structural info of T-Nb_2O_5?
  - Raman spectroscopy

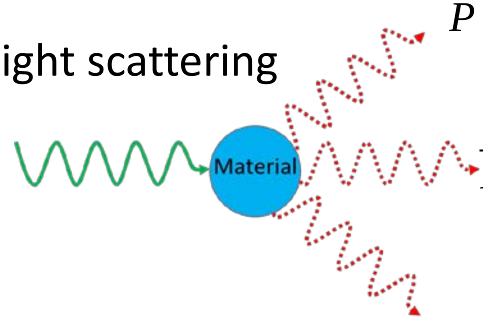
Vibration energy level

$$Mode\ Q_i:\ E_i(n_i) = (n_i + \frac{1}{2})\hbar\omega_i$$

Crystal

Inelastic light scattering

$$\vec{E} = \vec{E}_0 e^{i\omega t}$$



$$\vec{P} = \alpha\vec{E}$$

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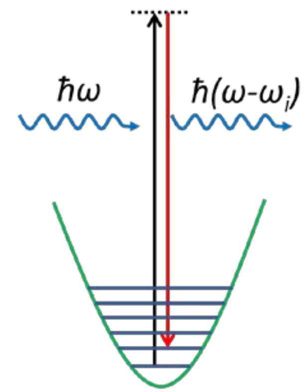


Excitation of vibration energy levels

$$Q_1 \ldots\ldots Q_N,\ \left(\frac{\partial\alpha}{\partial Q_i}\right)_0 \neq 0$$

$$\omega_i$$

$$\alpha_i' = \left(\frac{\partial\alpha}{\partial Q_i}\right)_0$$

$$I(\omega) \propto \frac{\Gamma_L}{(\omega-\omega_i)+\Gamma_L{}^2}$$

Number of Raman bands

Positions of Raman bands

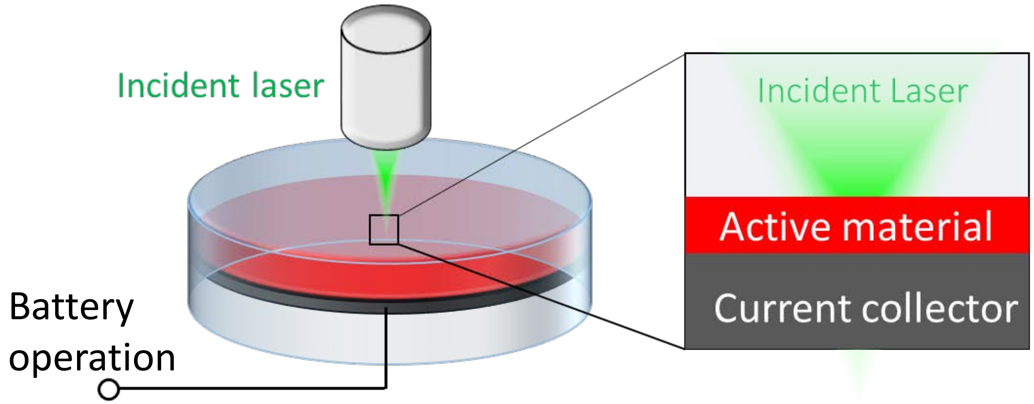
Intensities of Raman bands

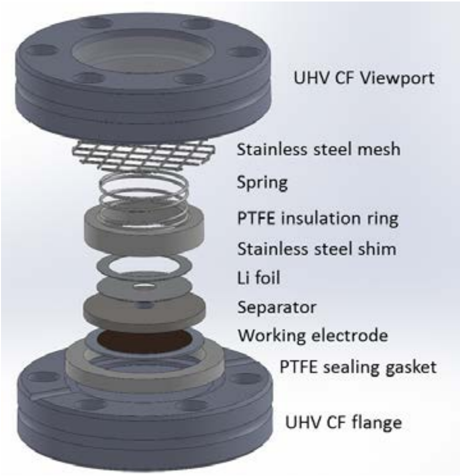
Profiles of Raman bands

Properties of scattered light -> **Properties of the material**

Operando Raman

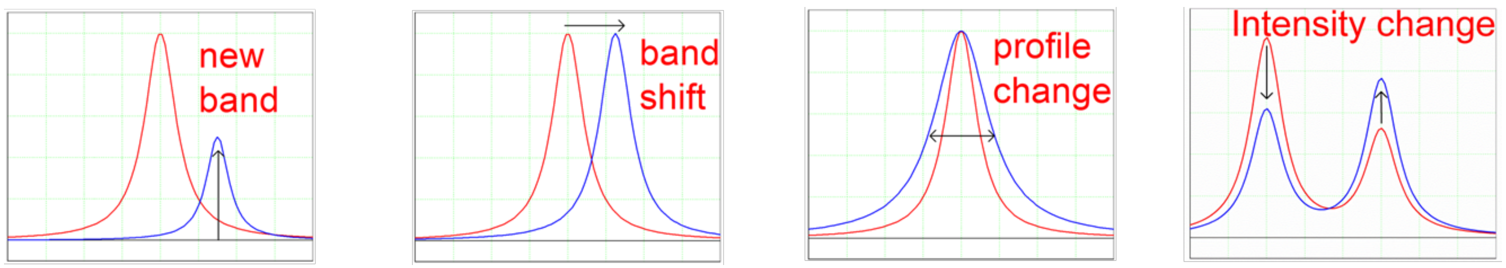
Raman spectroscopy + **Battery operation**





Operando Raman spectroscopic evolution

$$I(\omega,n) = f(E,I,Q,t,....)$$

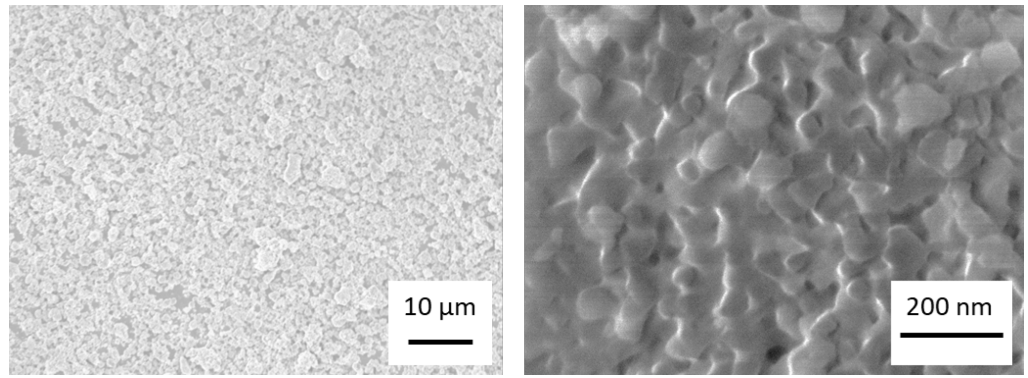


Reveal the structural change of T-Nb_2O_5 during charge-discharge

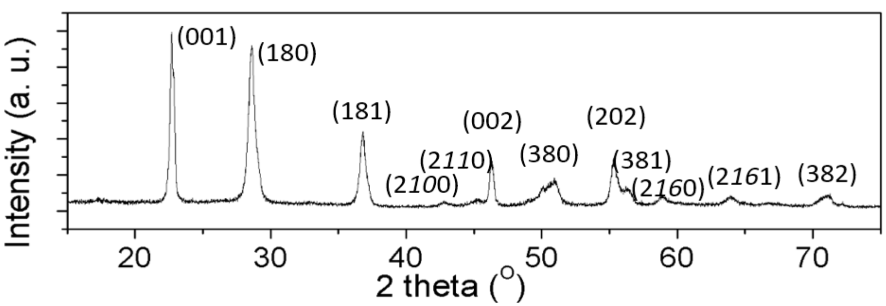
Sample preparations

- T-Nb_2O_5 battery electrodes fabricated by a sol-gel method.

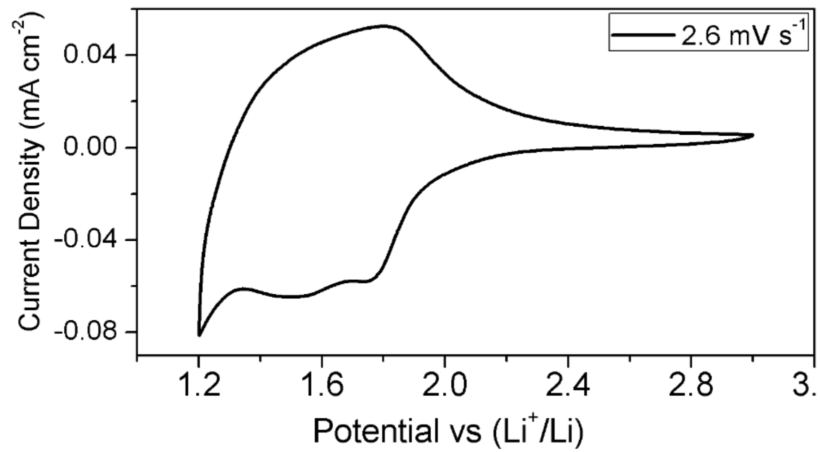
- SEM images of T-Nb_2O_5 electrodes
- No binder and carbon additives.



X-ray diffraction pattern matches the standard of T-Nb_2O_5.



Battery behavior of the prepared T-Nb_2O_5 electrodes.



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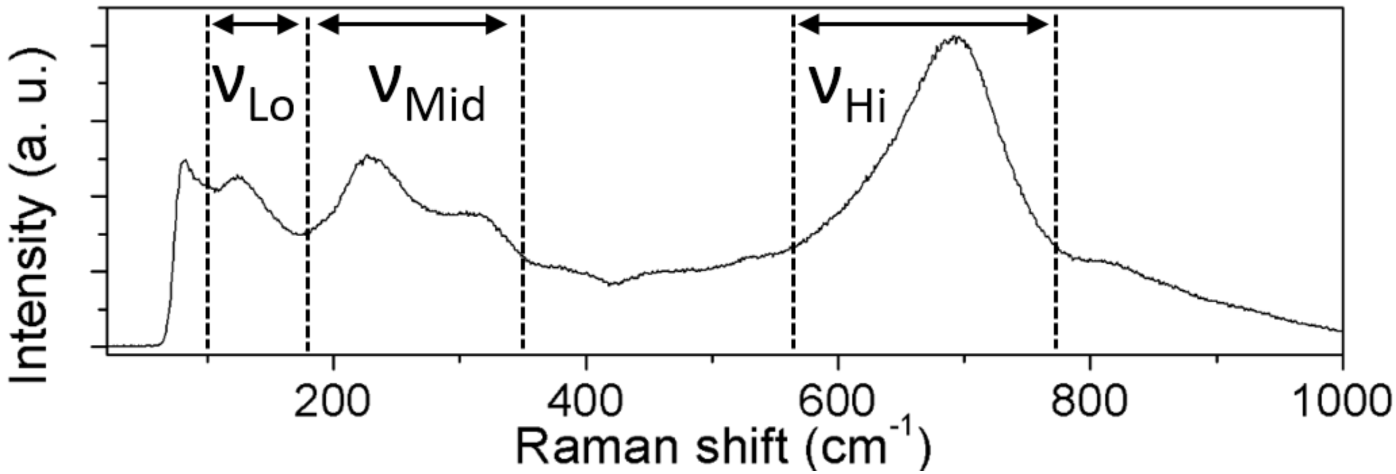
Raman spectrum of T-Nb_2O_5 electrodes

- Experimentally stacked Raman bands



Three band groups: ν_{Lo}, ν_{Mid}, ν_{Hi}.

Reason for band stacking: highly complicated cell structure. (more than 50 atoms in one unit cell)

⇩

Properties of band groups -> properties of T-Nb_2O_5

⇩

The basis for *operando* Raman

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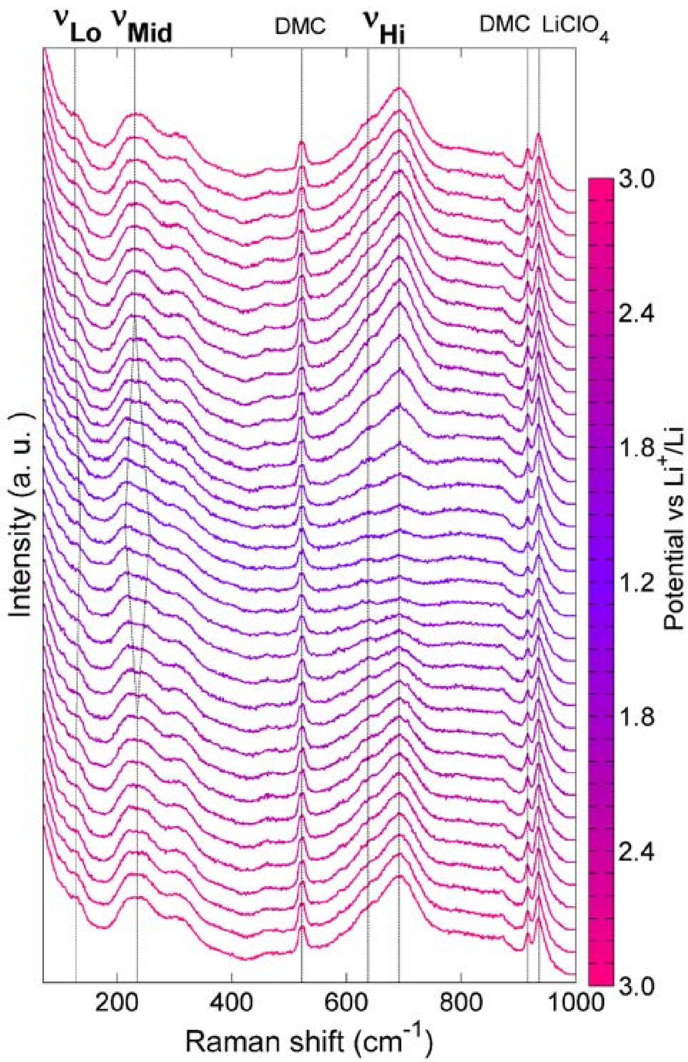
Operando Raman evolution



Reversible evolution

Hi potential -> Lo potential

- **ν_{Hi}**: intensity decrease
- **ν_{Mid}**: band splitting
- **ν_{Lo}**: band blue shift.
- All electrolyte bands remain static.

Lo potential -> Hi potential

- **ν_{Hi}**: intensity increase
- **ν_{Mid}**: band merging
- **ν_{Lo}**: band red shift.
- All electrolyte bands remain static.

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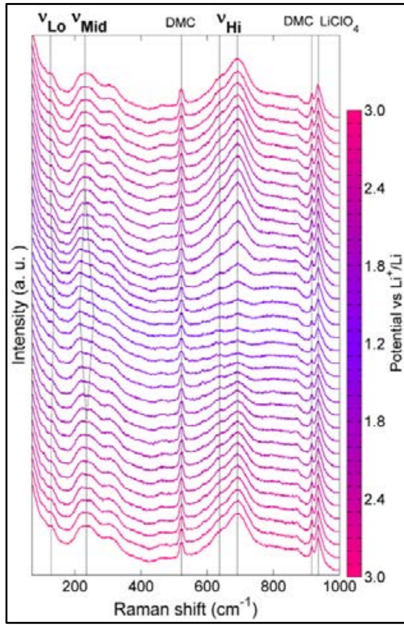
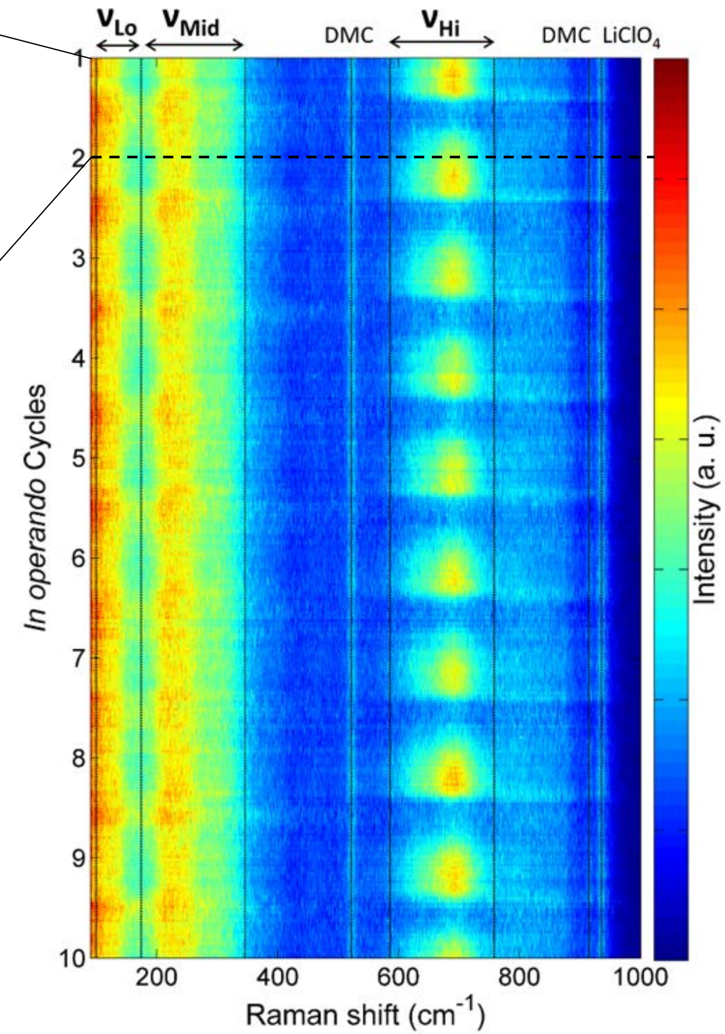
Operando Raman evolution



Operando Raman measurement is extended to multiple battery cycles.



- Spectral evolution is highly reversible in consecutive cycles
- Suggest the structural stability of T-Nb_2O_5 with battery cycling.

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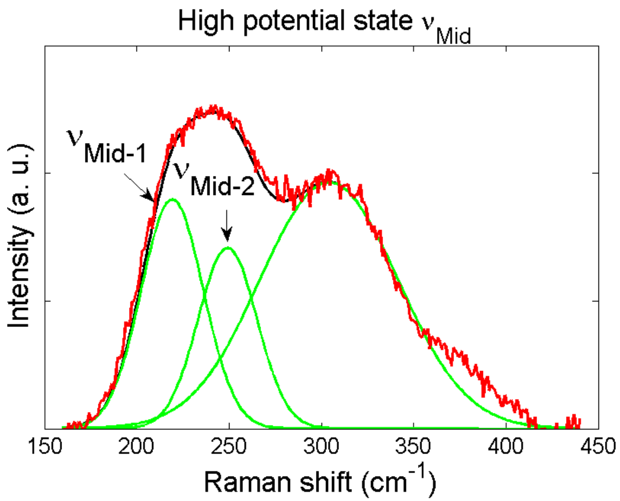
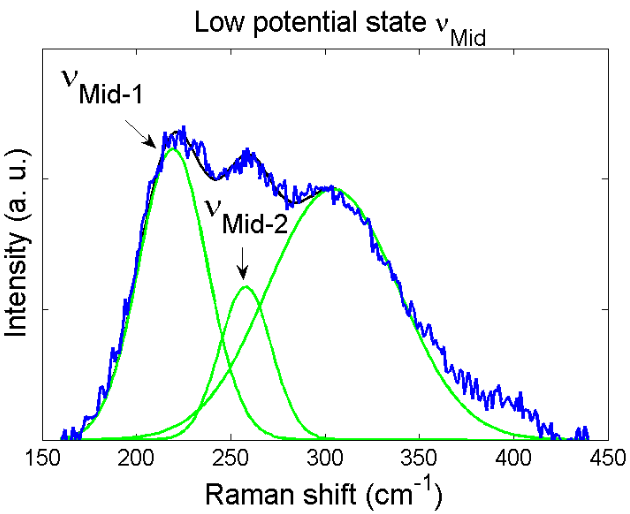
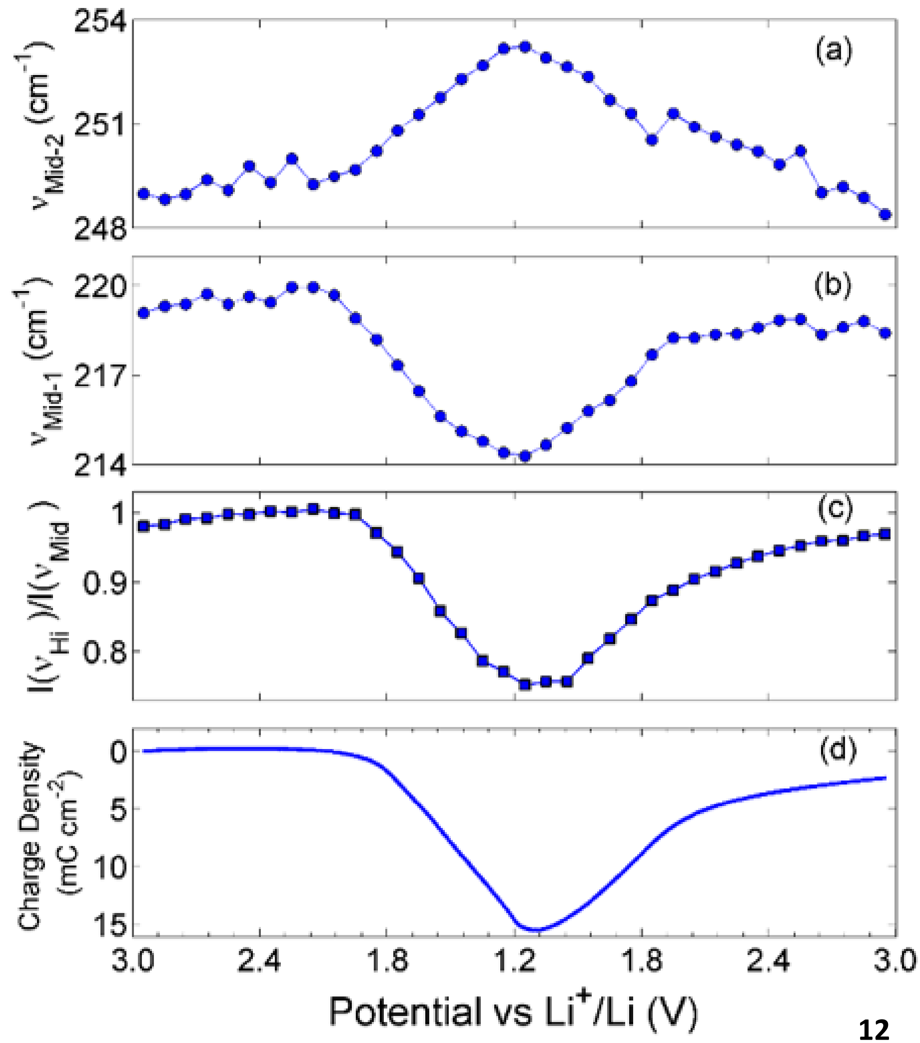
Spectroscopic info <-> Battery info

Splitting and Merging of ν_{Mid} quantified





Correlation with charge storage



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How to find the mechanism

Reason for the spectral evolution:

Li ion storage in T-Nb_2O_5 ⇦ Make a hypothetical model

⇩ ⇩ DFT calculation

Changes T-Nb_2O_5 structure

⇩ ⇩ DFT calculation

Changes properties of vibrational modes

⇩ ⇩ DFT calculation

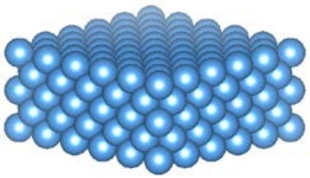
Changes the evolution of the **three band groups**

⇧ Verification

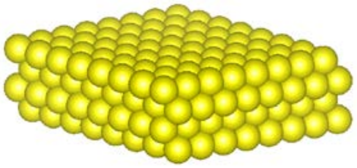
How Li ions are stored in T-Nb_2O_5

The first step of hypothesizing the Li ion storage mechanism:
analyze the **structural uniqueness of T-Nb_2O_5**

Typical close-packed structures:



ABCABC packing

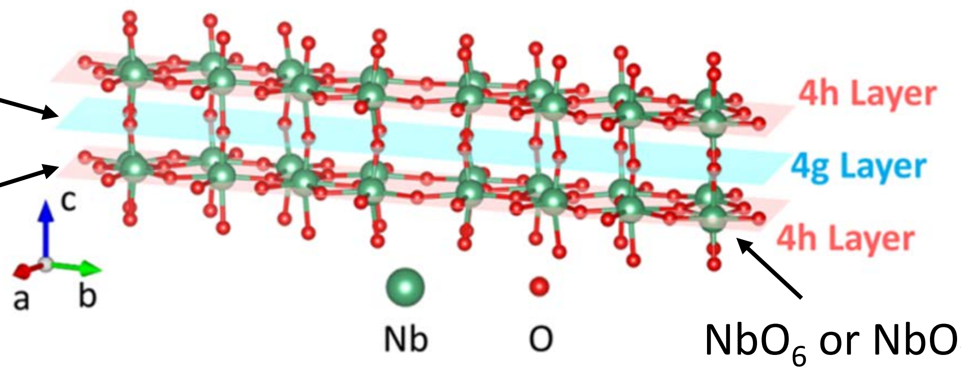


ABABAB packing

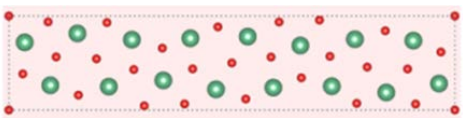
T-Nb_2O_5 is not a close-packed structure:
Alternating dense-loose-dense layer arrangement

4g sites (x,y,0) :
loose 4g Layer

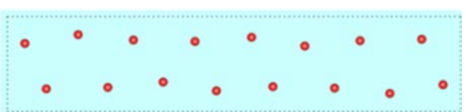
4h sites (x,y,1/2) :
dense 4h Layer



NbO_6 or NbO_7 units



4h Layer



4g Layer

- The hypothesis: 4g layer could be the most favorable “host” for Li ions.

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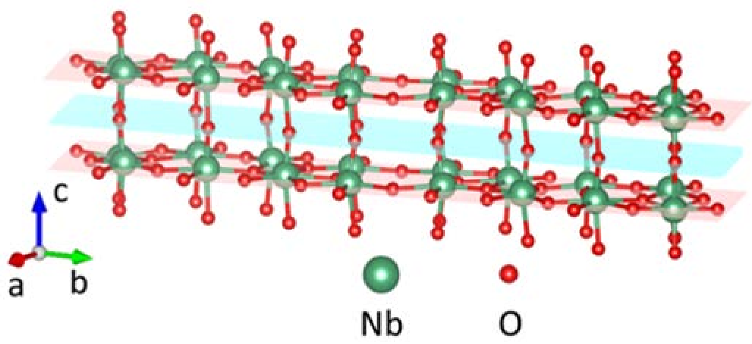
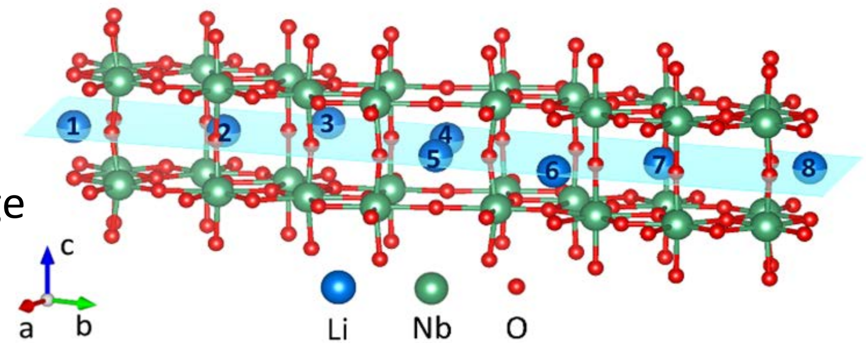
How Li ions are stored in T-Nb_2O_5

- As expected, DFT calculation proved that storing Li ions within the 4g layer is most thermodynamically stable.



Li ion storage



Absorption energies of Li

Label number	1	2	3	4	5	6	7	8
Adsorption energy (eV)	-3.45	-3.25	-3.53	-3.50	-3.45	-3.23	-3.47	-3.46

- All Li ions locate at the 4g sites exclusively.

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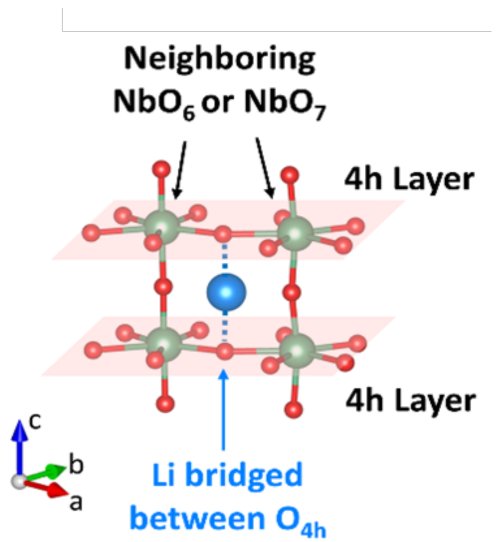
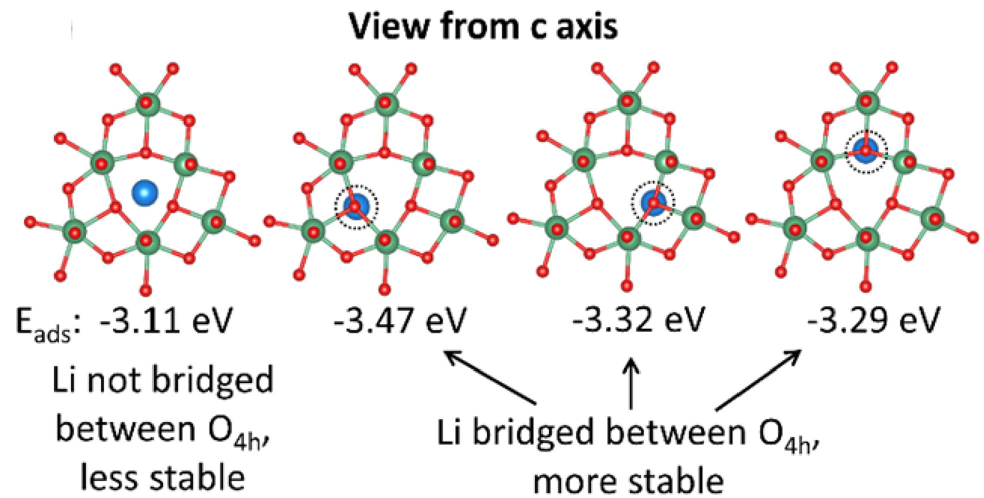
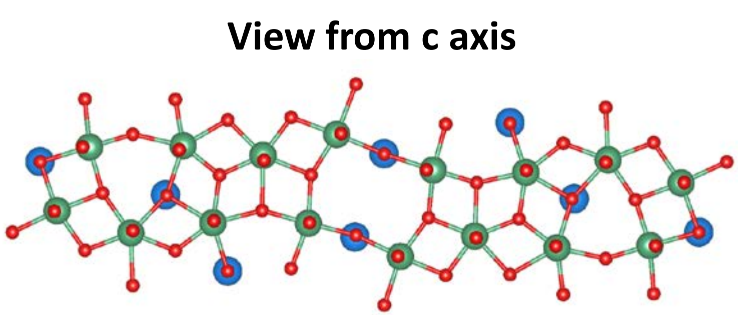
How Li ions are stored in T-Nb_2O_5

- Moreover, DFT calculation showed that T-Nb_2O_5 allows special coordination for stored Li.
  - All Li ions are “bridged” between oxygens.







- All Li ions form bridging coordination with oxygen.

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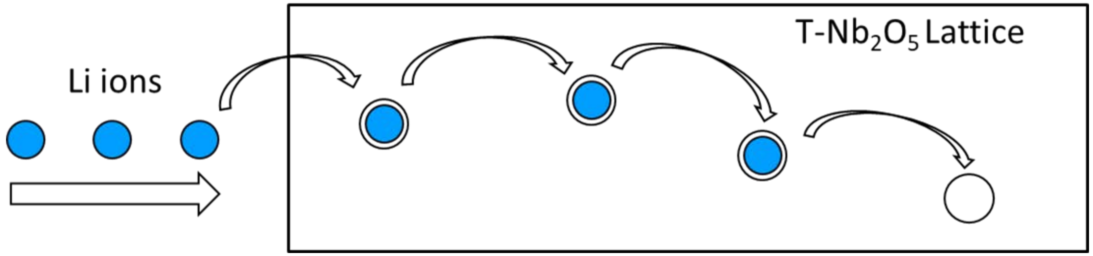
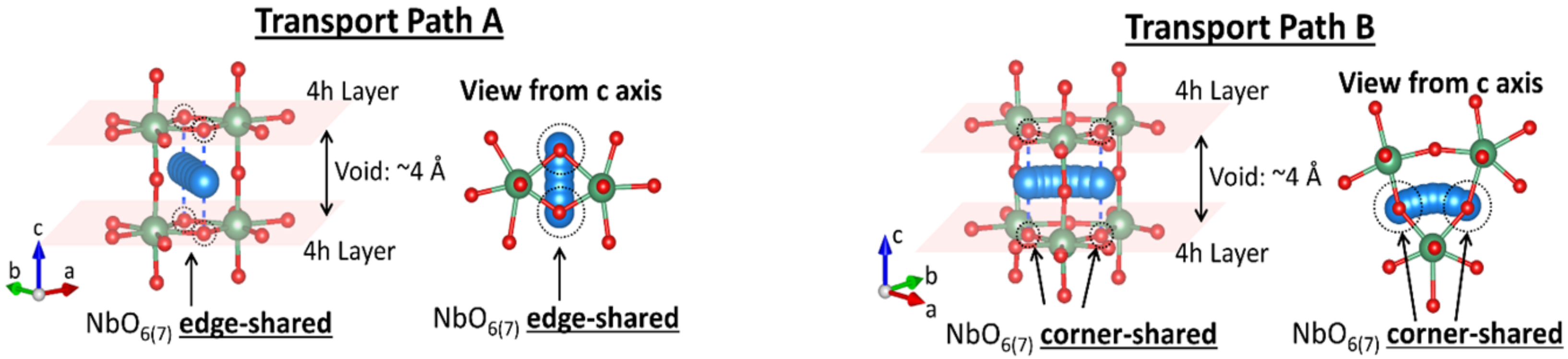
Why Li ion storage is fast in T-Nb_2O_5

- Relying on DFT calculation, Li ion storage behavior is understood
  - Li form bridging coordination with oxygen at the 4g layer.
- Next question: why the Li ion storage is fast?
  - Analyze transport paths of Li.



For T-Nb_2O_5, transport paths can be simply summarized as two types: Path A and Path B.



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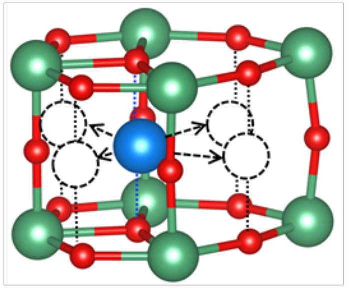
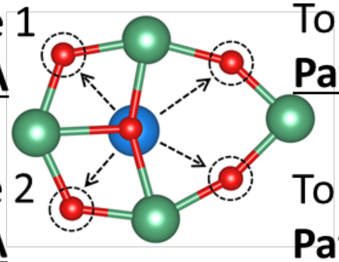
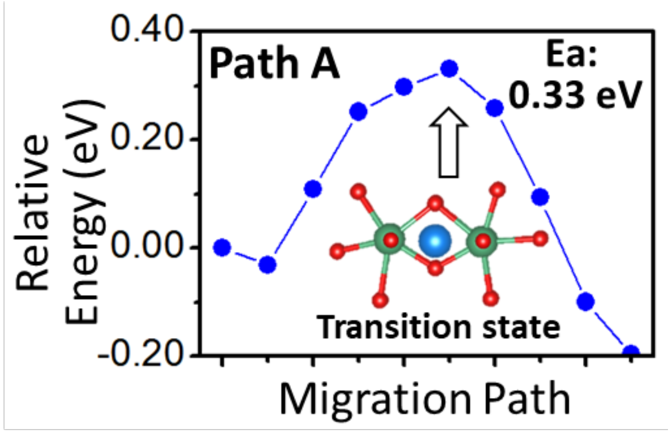
Why Li ion storage is fast in T-Nb_2O_5

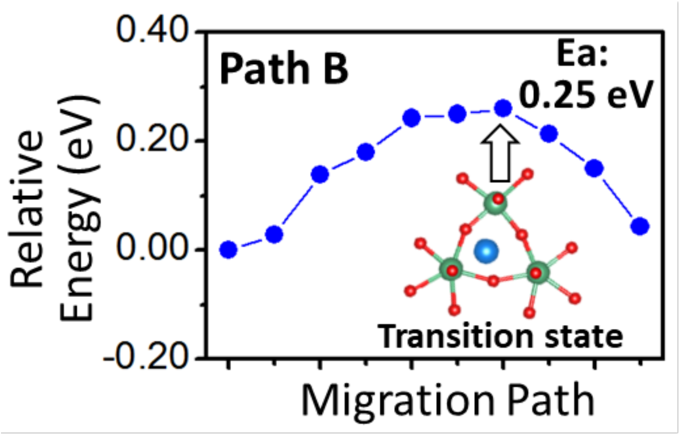
- Based on the two transport paths, each Li ion can migrate to four nearby bridging site, either via path A and path B.





- Very low energy barrier for either paths -> easy transport between Li sites
- Non-bridging sites correspond to the transition states





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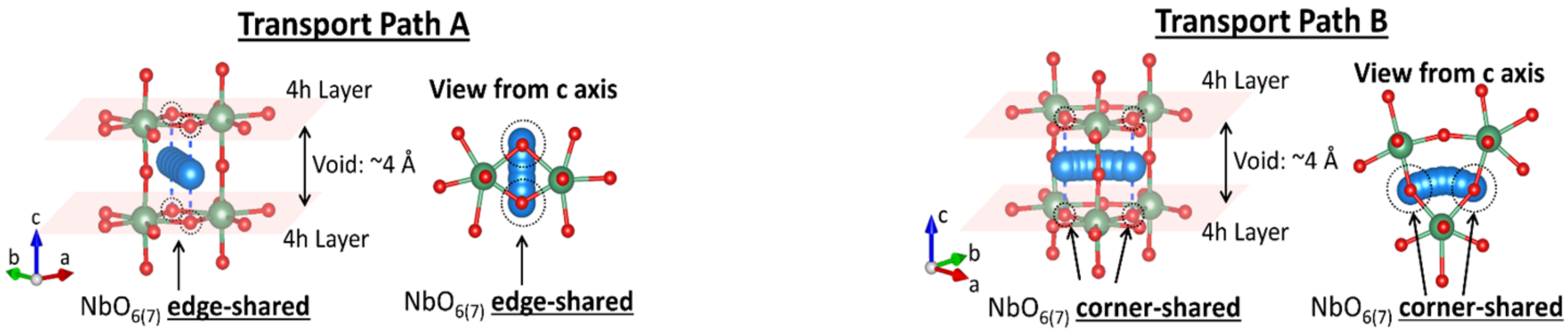
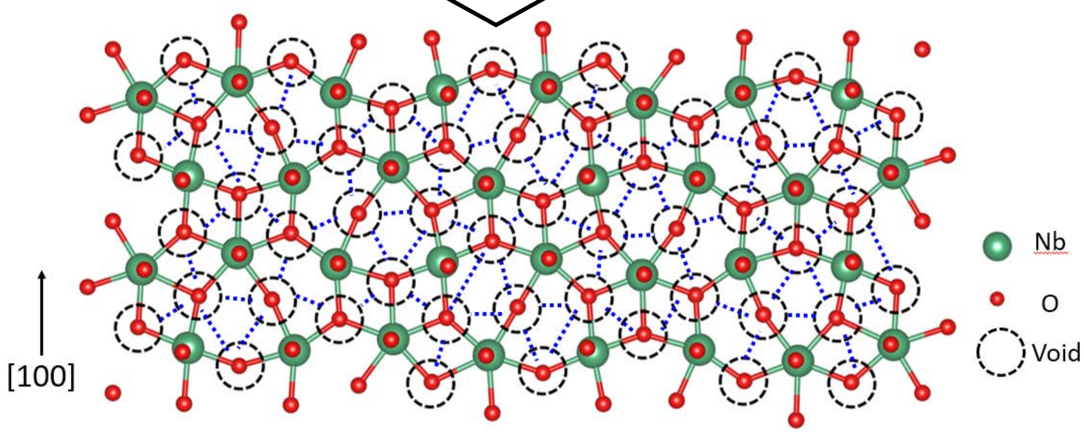
Why Li ion storage is fast in T-Nb_2O_5



- Elementary transport paths expand through the entire T-Nb_2O_5 lattice.



- A pseudo 2D Li transport network with fast kinetics:
- Answered the question: why Li ion storage in T-Nb_2O_5 is fast.

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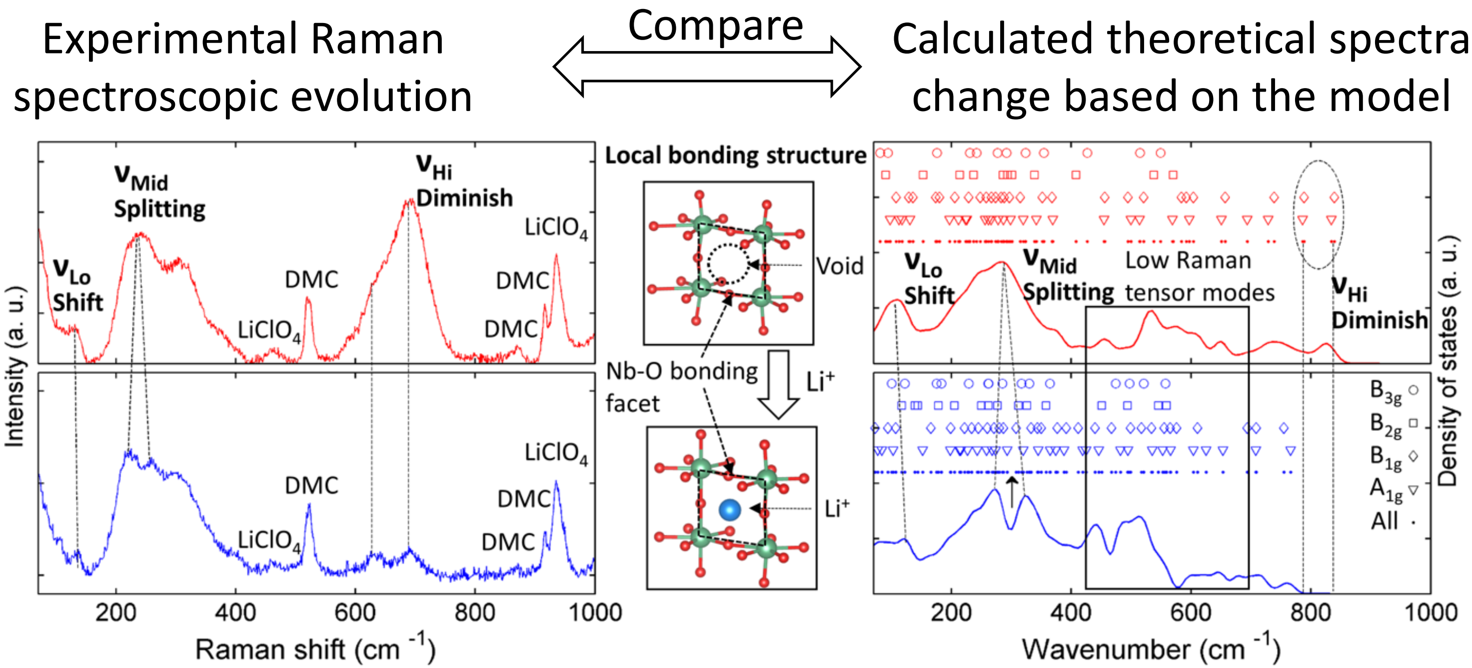
Verification of the model

- The model, which describes the Li ion storage and transport in $T\text{-}Nb_2O_5$, was proposed.
  - How to verify this model?



Experimental results and theoretical calculation are highly consistent:

υ_{Hi} Diminish, υ_{Mid} Splitting, υ_{Lo} Shift.

The proposed model is verified.

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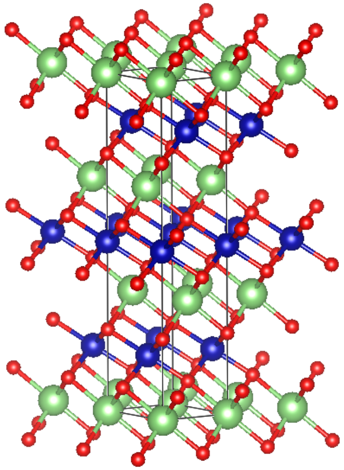
The last question

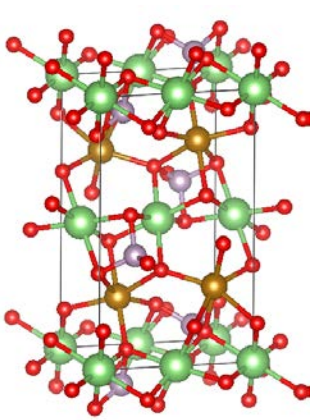
- How does T-Nb_2O_5 compare with other battery materials?

Layered



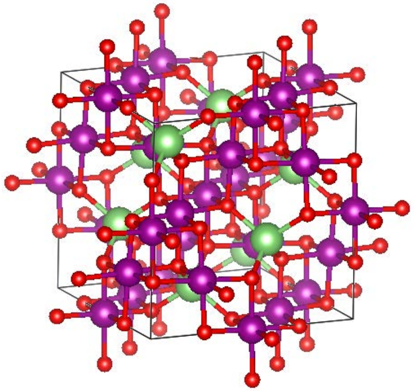
Example: $LiCoO_2$

Poly-anion



Example: $LiFePO_4$

Spinel

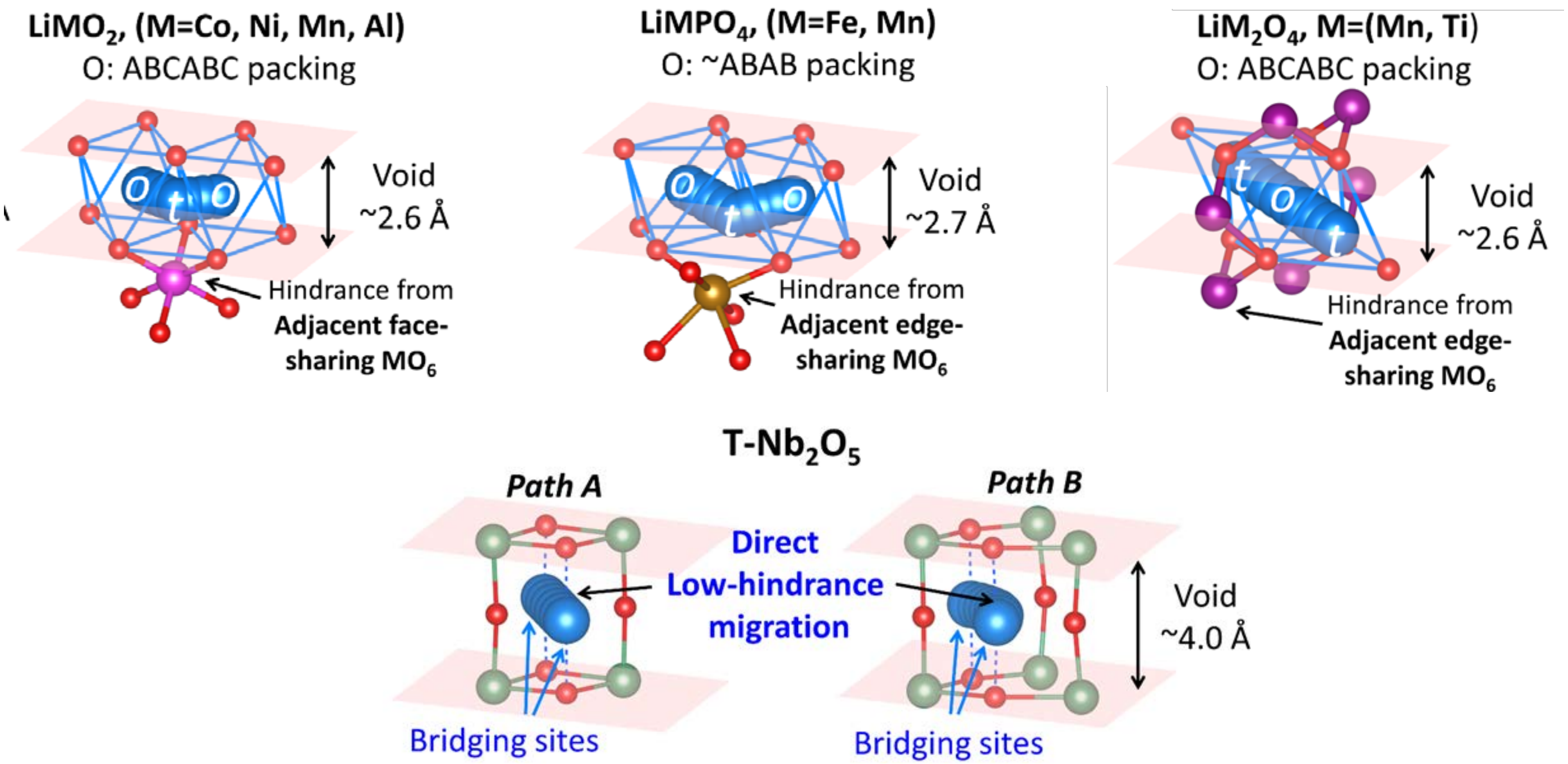


Example: $LiMn_2O_4$

These materials are most commonly found in the Li ion battery industry.

How does T-Nb_2O_5 compare with other battery materials?

Layered | Poly-anion | Spinel



Comparing to other battery materials, Li ion transport behavior in T-Nb_2O_5 is unique.

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Summary

Structure of T-Nb_2O_5

Experimentally → *Operando* Raman spectroscopy

Theoretically → Model of Li ion storage → Model of Li ion transport

Operando Raman spectroscopy → Evolution of key band groups

Model of Li ion storage → Theoretical vibration spectra change

Model of Li ion transport → Identify key reasons for fast Li ion storage

Evolution of key band groups ⟺ (comparison) Theoretical vibration spectra change

→ Unraveled the nature of fast energy storage in T-Nb_2O_5

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College of Engineering

Georgia Tech Chemistry and Biochemistry
College of Sciences

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