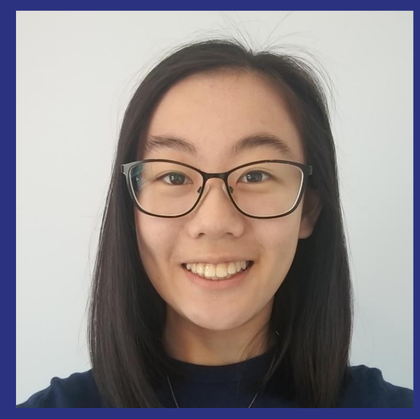
Modelling anode material Lithium Titanate $Li_4Ti_5O_{12}$

Molecular dynamics investigation of structure of lithium titanate



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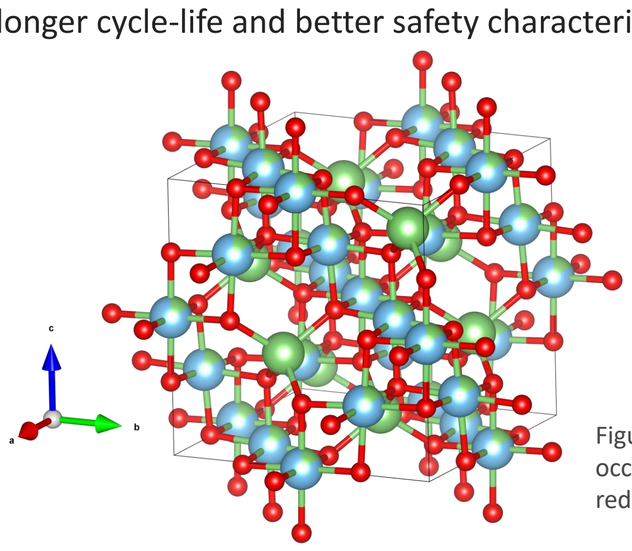
Abstract

Lithium titanate ($Li_4Ti_5O_{12}$ or LTO) is a promising alternative to carbon-based anodes for electric vehicles (EVs) and portable electronic devices. LTO has a longer cycle-life and better safety characteristics.[1] [2]



LTO has a spinel-like structure, consisting of oxygen atoms with a cubic closed packed arrangement, lithium ions occupying 1/8 of the tetrahedral sites and lithium and titanium ions share half of the octahedral interstitial sites.[2]

Figure 1[3]: structure of LTO showing partial occupancies at octahedral sites, 5/6 Ti and 1/6 Li; red: oxygen, blue: titanium, green: lithium

In this computational project, the structure of LTO was modelled by testing a series of configurations of Li and Ti ions in octahedral interstitial sites using density functional theory (DFT) calculations. It was found that structures with more spaced-out Li ions have a lower free energy.

- The energetics of proton-lithium (H-Li) exchange was investigated, and its solution energy was found to be favourable. The most favourable exchange was when an octahedral Li ion was exchanged out by a H.

Motivation

Energetics of the H-Li exchange was investigated for two main purposes:

- Hydrogen gassing in operating LTO cells is a known safety issue.[4] This is related to H-Li exchange.
- A key aim for recycling of LTO is Li recovery. H-Li exchange can potentially selectively leach out the Li and the lithium can be recovered through precipitation.

Methods

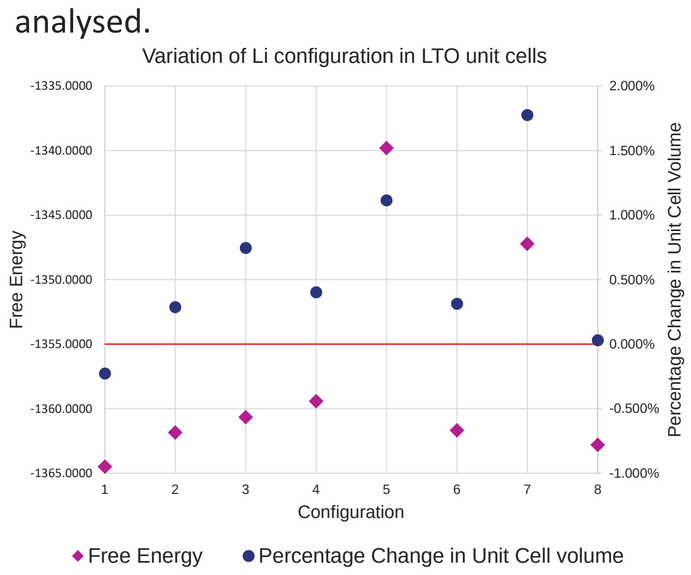
- VESTA[5] for production and visualization of structures
- VASP[6] [7] [8] for density functional theory calculations
- Input parameters were set as ENCUT = 500, EDIFF = 1E-4 and EDIFFG was not used
- A 2 x 2 x 1 k-point grid was used in all calculations

Section 1 - Input Parameters

- Unit cell of LTO used in research was $Li_{24}Li_8Ti_{40}O_{96}$
  - A cubic unit cell of $Li_8Ti_{16}O_{32}$ with lattice parameter $8.35957\ \text{Å}$ was repeated 3 times along the c-axis to ensure there would be no half occupation of atoms when Li is substituted into the octahedral interstitial sites.
  - 8 Ti ions were then changed into Li ions, the configurations of these 8 Lithium ions were varied (see Section 2).
- K-point grids of 1 x 1 x 1, 2 x 2 x 1, 3 x 3 x 1, 4 x 4 x 1 was tested on an initial structure (Configuration 1) of LTO to optimize between accuracy of free energy calculated and the time taken to do the calculation. 2 x 2 x 1 k-point grid was the most efficient and used in all subsequent VASP calculations on the LTO cells.

Section 2 - Varying Lithium Configuration in LTO Unit Cell

- A total of 8 different unit cells were made. This was done to investigate the clustering effect of octahedral Li ions and to optimise the initial structure of LTO for the proton-exchange calculation
- 8 Ti ions from $Li_{24}Ti_{48}O_{96}$ were selected to be changed into Li ions in octahedral sites. Their free energies and unit cell deformation were analysed.



- For the optimisation, the free energy is aimed to be as low as possible while the percentage change is aimed to be as close to 0% (red line) as possible.
- Configuration 1 and 8 (C1 and C8) were chosen for the lowest free energy and least change in unit cell volume respectively.

Figure 2 (above): Graph of free energies and percentage change in unit cell volumes for 8 configurations of LTO unit cells

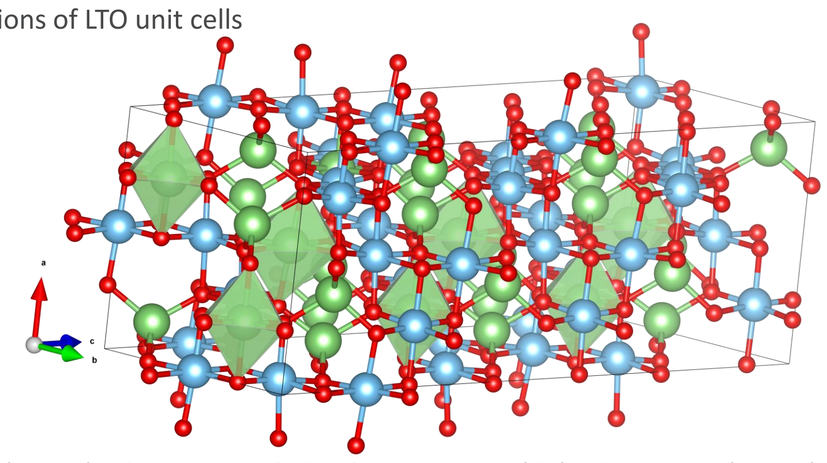
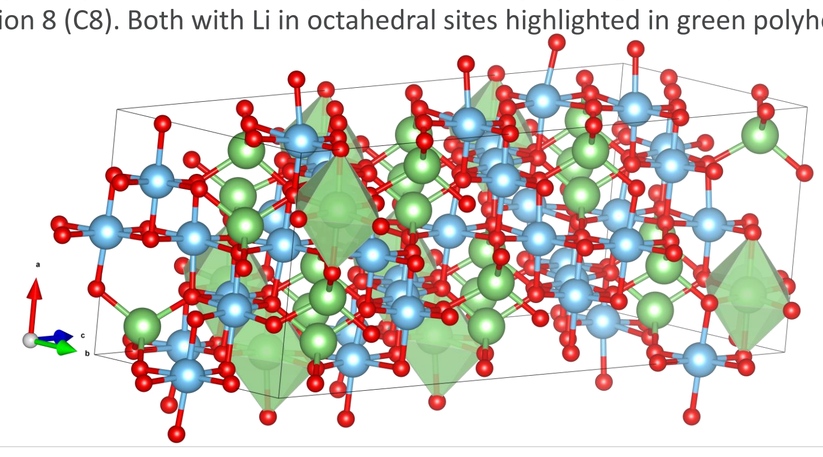


Figure 3 (above): Structure of Configuration 1 (C1); Figure 4 (below): Structure of Configuration 8 (C8). Both with Li in octahedral sites highlighted in green polyhedra.



Section 3 - Proton-Lithium Exchange

- The reaction investigated for proton-lithium exchange for one hydrogen atom is $Li_{32}Ti_{40}O_{96} + H_2O \rightarrow Li_{31}HTi_{40}O_{96} + LiOH$ (Eqn 1).
- Hydrogen atoms were substituted for the Li ions in tetrahedral and octahedral site in 2 separate structures.

Conclusions

- The two structures selected for further investigation have the two lowest free energies. Clustering of Li ions was shown not to be favourable as the structure with the highest free energy (Configuration 7) were made by changing the 8 closest Ti ions into Li ions. Both configuration 1 and 8 were made by changing Ti ions that are as far apart as possible into Li ions and they gave the lowest free energies.
- The H-Li exchange energies of Eqn 1 were found to be in the range of 0.0-0.3 eV, which is low. This suggests that the reaction is feasible.

Structure and Type of Li Substituted	H-Li Exchange Energy (Eqn 1) (eV)
C1 - substituted tetrahedral Li	0.304
C1 - substituted octahedral Li	0.122
C8 - substituted tetrahedral Li	0.126
C8 - substituted octahedral Li	0.072

Impact / Next steps

- The reaction of $Li_{32}Ti_{40}O_{96} + H_2O \rightarrow Li_{30}H_2Ti_{40}O_{96} + Li_2O$ could be studied.
- This would investigate the clustering effect of hydrogen atoms within a substituted LTO cell. Relevant structures have been made.
- Further study could also determine whether $LiOH$ or Li_2O is a more favourable product in the reaction between LTO and water.

Intern bio

Veronica is reading Materials Science at the University of Oxford. She is entering her 2nd year and will be studying towards an MEng with a research project in her fourth year. She is exploring various fields and is open to opportunities within academia or industry, particularly interested in electric vehicles and clean energy.

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