

# Li Diffusion in Various Polymorphs of $\text{LiTiS}_2$ : Insights from Theory

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The layered transition metal dichalcogenides ( $\text{MX}_2$ , M= Transition elements and X = S, Se, Te) have attracted considerable interest for batteries due to their structural and electronic properties of low dimensional character. Of them, titanium disulphide ( $\text{TiS}_2$ ) is one of the most suitable materials for energy storage electrode due to its semimetal nature. Lithium ions can be easily inserted into the van-der-Waals gap between the  $\text{TiS}_2$  layers electrochemically or chemically by treatment with n-butyl lithium. Two most widely known  $\text{LiTiS}_2$  polymorphs are hexagonal 1T- $\text{LiTiS}_2$  and cubic c- $\text{LiTiS}_2$ . Apart from these, the 3R- $\text{LiTiS}_2$  exhibits a higher average voltage against lithium compared to 1T- $\text{LiTiS}_2$  and therefore has attracted a considerable attention in recent years.

In the present contribution, the stoichiometric and defect properties in 1T, c and 3R polymorphs of lithium titanium disulphide ( $\text{Li}_x\text{TiS}_2$ ) are investigated theoretically with periodic quantum chemical methods. The calculated energetic shows that 3R- $\text{LiTiS}_2$  is less stable than the most common 1T phase (by 4 kJ/mol), and is more stable (by 5 kJ/mol) than the known phase c- $\text{LiTiS}_2$  thus confirming the importance of this phase for further investigations [1]. Li preferentially occupies the octahedral site rather than the tetrahedral site. The dispersion-uncorrected pure DFT approach gives better agreement with experiment for the structural parameters than the dispersion-corrected DFT-D approaches.

Comparison of calculated formation energies of a Li point defect, a Ti point defect and a Ti Frenkel defect show that Li point defect is the most preferable defect [2]. Various pathways for Li diffusion in  $\text{Li}_x\text{TiS}_2$  (for  $x = 0.63, 0.75, 0.88$  and  $1.0$ ) are investigated using the climbing-image Nudged-Elastic-Band (cNEB) approach. In both 1T and 3R polymorphs,  $\text{Li}^+$  ion migrates along the crystallographic a (or b) direction either in a direct pathway through Li point defect or via vacant tetrahedral site.  $\text{Li}^+$  diffuses along the c direction via Ti point defect and Ti Frenkel defect. In c- $\text{Li}_x\text{TiS}_2$ ,  $\text{Li}^+$  ion migrates along the crystallographic a (or b or c) direction and ab (or bc) plane through Li point defect. The calculated activation energies are in well accordance with experiment.

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## References

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