Li Diffusion in Various Polymorphs of $LiTiS_2$: Insights from Theory

Mazharul M Islam, Thomas Bredow

Universität Bonn, Mulliken Center for Theoretical Chemistry, Institut für Physikalische and Theoretische Chemie, Beringstr. 4, D-53115 Bonn, Germany

Corresponding author: Mazharul M Islam, E-Mail: rana-islam@thch.uni-bonn.de

The layered transition metal dichalcogenides (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 (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 TiS_2 layers electrochemically or chemically by treatment with n-butyl lithium. Two most widely known $LiTiS_2$ polymorphs are hexagonal 1T-$LiTiS_2$ and cubic c-$LiTiS_2$. Apart from these, the 3R-$LiTiS_2$ exhibits a higher average voltage against lithium compared to 1T-$LiTiS_2$ 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 (Li_xTiS_2) are investigated theoretically with periodic quantum chemical methods. The calculated energetic shows that 3R-$LiTiS_2$ 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-$LiTiS_2$ 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 Li_xTiS_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, Li^+ ion migrates along the crystallographic a (or b) direction either in a direct pathway through Li point defect or via vacant tetrahedral site. Li^+ diffuses along the c direction via Ti point defect and Ti Frenkel defect. In c-Li_xTiS_2, 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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