

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, Berlingstr. 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.

Acknowledgments: We are grateful to the Deutsche Forschungsgemeinschaft (DFG) for the funding of the DFG-Forschergruppe 1277 molife "Mobilität von Li-Ionen in Festkörpern".

References

- [1] S. Nakhal, M. Lerch, J. Koopman, M. M. Islam, T. Bredow, *ZAAC* **639** (2013) 2822.
- [2] M. M. Islam and T. Bredow, *Z. Phys. Chem.* **226** (2012) 449.

