Evaluation of Density Functional Theory for Lithium Ion Migration in 1T-LiTiS2

Vanessa Werth[1], Mazharul M. Islam[2], Kai Volgmann[1], Paul Heitjans[1], Thomas Bredow[2]

[1] *Institut für Physikalische Chemie und Elektrochemie, Universität Hannover, Callinstr. 3-3a, 30167 Hannover, Germany;* [2] *Mulliken Center for Theoretical Chemistry, Universität Bonn, Beringstr. 4-6, 53115 Bonn, Germany*

E-mail: vanessa.werth@pci.uni-hannover.de

Weak interactions and properties of solids containing transition metals are often problematic to describe with standard generalized gradient approximations (GGA). One challenge for GGA is the experimentally well studied host material 1T-TiS_2, where lithium is the most prominent intercalation material. The addition of dispersion corrections [1–3] and an on-site Coulomb repulsion term [4] to the Perdew-Burke-Enzernhof (PBE) functional is studied [5] using the plane-wave program package VASP. An overall improvement with respect to experimental data can be observed in comparison to the PBE functional. The most significant improvement is the structural description, in particular the c lattice parameter, of TiS_2 and the calculated band gap of TiS_2. Also quadrupole coupling constants and chemical shifts are closer to experimental data, if both correction terms are included. The calculated activation energy in 1T-Li_xTiS_2 for $x \approx 1$ for a Li ion migration to a tetrahedral interstitial position is 0.4 eV and close to experimental values.

[1] A Consistent and Accurate Ab Intio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu, S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. 132 (2010) 154104.
[2] Effect of the Damping Function in Dispersion Corrected Density Functional Theory, S. Grimme, S. Ehrlich, L. Goerigk, J. Comp. Chem. 32 (2011) 1456.
[3] Accurate Molecular Van der Waals Interactions from Ground-State Electron Density and Free-Atom Reference Data, A. Tkatchenko, M. Scheffler, Phys. Rev. Lett. 102 (2009) 073005.
[4] Electron-Energy-Loss Spectra and the Structural Stability of Nickel Oxide: An LSDA+U study, S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, A. P. Sutton, Phys. Rev. B 57 (1998) 1505.
[5] Density Functional Theory Evaluated for Structural and Electronic Properties of 1T-Li_xTiS_2 and Lithium Ion Migration in 1T-$Li_{0.94}TiS_2$, V. Werth, M. M. Islam, K. Volgmann, P. Heitjans, T. Bredow, Z. Phys. Chem., in press, 2017 (DOI: 10.1515/zpch-2016-0919).