

# Improved Calculation of Li and Na Intercalation Properties in TiO<sub>2</sub> Polymorphs using the Screened Exchange Functional

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There are numerous examples of density functional theory (DFT) and potential-based calculations of Li and Na intercalation in a wide variety of host materials, however, these methods are not without their shortcomings. While potential-based calculations are useful for very large or low symmetry systems, they are not appropriate for bulk systems with complex electronic or magnetic structures and their quality is fully dependant on the quality of the model used. Standard DFT calculations in such works nearly always use the local density approximation (LDA) or generalized gradient approximation (GGA), which have both been shown to underestimate intercalation energetics [1] and fail in reproducing several other structural and electronic properties of the host materials. They are also well-known for their severe band-gap underestimation and inaccuracies in the calculation of defect transition levels. While some of these errors can be reduced using post-DFT methods like the inclusion of the Hubbard  $U$  parameter, it is not clear whether they are sufficiently accurate in predicting defect levels [2].

To correct for the problems associated with local-density methods, we use the screened exchange (sX) functional for the calculation of Li and Na defect formation energies, charge transitions and electronic structures in various TiO<sub>2</sub> polymorphs (anatase, rutile and TiO<sub>2</sub>(B)). The sX functional has the major advantage of replacing all LDA exchange with a Thomas-Fermi screened Coulombic exchange potential [2]. The local exchange and correlation functionals underlying the LDA and GGA cause spurious self-interaction which increases the energy of occupied states and decreases the energy of unoccupied states, whereas the exchange potential is self-interaction free. This results in more accurate defect formation energies and charge transition levels. The sX functional has successfully been applied to several cathode and anode materials [3-5].

By comparing our results to those calculated using GGA (both in this work and the literature), we report improved agreement with experiment in terms of local and electronic structure of the TiO<sub>2</sub> polymorphs and intercalation energetics. For rutile, sX and GGA calculated energetics are similar, while for anatase, sX shows a significant improvement on the GGA underestimated values. In agreement with the literature, all polymorphs are shown to readily incorporate Li, while for Na, the situation is more complicated with negative intercalation energies calculated for anatase and TiO<sub>2</sub>(B), but not for rutile.

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