

Lithium, Sodium and Magnesium Insertion in Brookite TiO_2 : a Comparative Computational Study

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Phases of titania have been actively explored as active electrode materials for Li, Na, and Mg ion batteries. Rationalization of performance and rational selection of optimal titania phases for a specific type of battery is assisted by ab initio simulations. Previously, we compared Li, Na, and Mg interaction with anatase, rutile, B and amorphous TiO_2 [1]. Here, we provide ab initio modeling results on the energetics and mechanism of Li, Na, and Mg interactions with the brookite phase. Recently the brookite phase has been gaining attention; specifically, structural similarity of this phase and amorphous titanium dioxide was reported [2]. Given that amorphization has been shown to enhance voltages [1], which can potentially make titania interesting as a cathode, a comparative study including brookite is useful. The computed low-concentration insertion energies and the corresponding voltages, however, suggest poor electrochemical performance of brookite in comparison to e.g. ‘layered’ titania phases such as B- TiO_2 . We argue that this behavior could be explained by local electronic structure leading to higher voltages in amorphous compounds, since the lattice strains induced by intercalation in brookite are not sufficient to explain the poor binding energies with the inserted Li, Na, and Mg. We also observe that, similarly to the previously reported magnetic ordering in e.g. potassium- or sodium-inserted V_2O_5 , each electron donated by the intercalant is delocalized over a nearly linear Ti-O-Ti fragment close to the insertion site, mediated by antiferromagnetic interaction of the two *d*-type states with an oxygen *p*-state in between (Fig. 1).

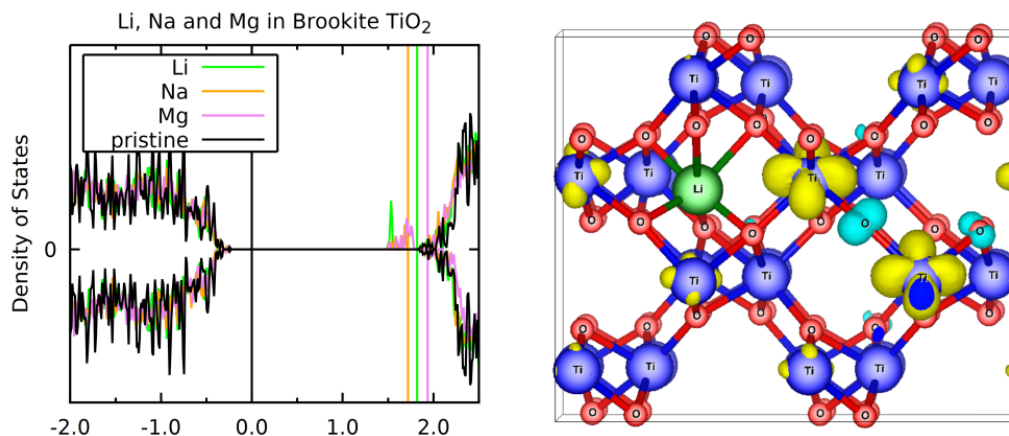


Fig. 1. Densities of states of brookite TiO_2 and Li-, Na-, and Mg-intercalated brookite (left) and the simulation cell showing the inserted Li atom (green) and density localization over a Ti-O-Ti rung (right).

[1] F. Legrain, O. I. Malyi, S. Manzhos, J. Power Sources, 278, 197 (2015).

[2] J. Mavračić et al., J. Phys. Chem. Lett. 9, 2985 (2018).