

Rutile VO₂: Cathode or Anode for Na Ion Batteries? – an Ab Initio Study

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Vanadium oxides can and have been used as active electrode materials for different types of metal ion batteries (Li, Na, Mg, Ca, Al, etc.) [1]. Typically, vanadia are explored as cathode materials. The phase space is rich, and despite many existing experimental and computational studies [1-5] there are many phase – active cation combinations that remain unexplored. Specifically, computational studies of those combination can provide a preview into their limits of performance as well as mechanistic insight. One such system is sodiation of rutile vanadium dioxide.

We investigate ab initio, using Density Functional Theory, the sodiation mechanism of rutile (R) VO₂ as a possible electrode material for Na-ion batteries. While the predicted specific capacities are appreciable, the computed voltages are small compared to current state-of-the-art sodium-ion battery cathodes, which we can relate to the large space demand of sodium ions in the compact rutile structure and the resulting severe lattice deformations compared to other working metals. Due to the same reason large anisotropic unit cell volume changes are predicted during cycling. We find a change of the preferred reaction mechanism during discharge, with a switching between insertion- and conversion-type reaction at higher degrees of sodiation. While computed voltages on the order of 1 V vs Na/Na⁺ are too low for use as cathode, this phase may be of interest as an anode which helps avoid reductive decomposition of common electrolytes.

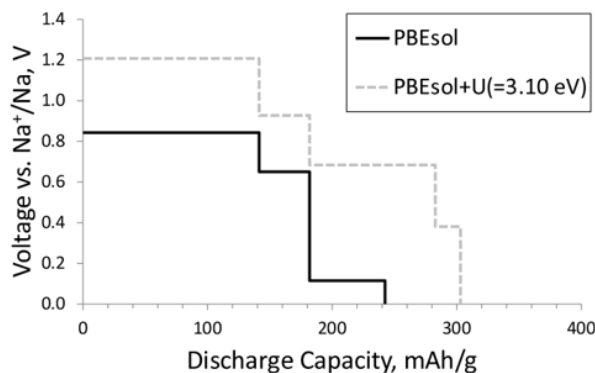


Figure 1. Voltage-capacity curve of the Na-VO₂(R) system. The curve with an additional Hubbard correction (not recommended due to the metallic nature of the phase) on the PBEsol exchange-correlation functional is plotted as dotted grey line.

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