Study of the Calcium Insertion in Layered and Non-Layered Vanadium Oxide Phases from First Principles

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Multivalent metals have attracted attention as possible alternatives to lithium (Li) in future high-performance secondary batteries due to their potentially high gravimetric capacity and the possibly advantageous use of bulk metal as anode material without dendrite formation during cycling. A drawback of such elements as magnesium, zinc, or aluminium, on the other hand, is that their low-magnitude standard potentials limit the achievable full battery voltages and therefore lead to lower energy densities which, as of today, cannot compete with those achieved with Li-ion batteries. One exception to this trend is calcium (Ca). We investigated the insertion energetics of Ca at low concentrations in four promising layered and non-layered vanadium oxide phases (α and δ vanadium pentoxide (V_2O_5) polymorphs, as well as rutile- (R) and bronze-type (B) vanadium dioxide (VO_2)) using density functional theory (DFT). We found α-V_2O5 to be the most suitable material for an application as cathode, driven by a stable coordinative environment for the Ca^{2+} ions, with a voltage at the discharge onset of about 3.07 V, and 2.93 V for δ-V_2O_5, in accordance with previously reported results. Calcium insertion into vanadium dioxides is predicted to be less favorable, with a computed initial voltage of 2.57 V in VO_2(B). The low-concentration phase of rutile-type Ca_xVO_2 on the other hand is not found to be stable at all, due to severe distortions of the host lattice caused by the large Ca^{2+} ion, but phases with higher Ca concentration might be stable and form in a two-phase mechanism during cycling. The results provide insight into the possibility of employing these phases as active cathode materials of future Ca-ion batteries.

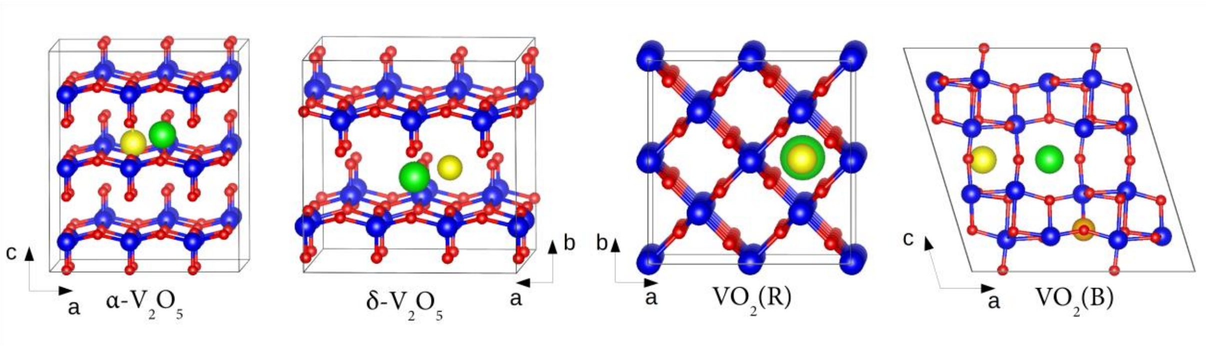

Fig. 1. Simulation cells of the four investigated phases, from left to right: α-V_2O_5, δ-V_2O_5, VO_2(R), VO_2(B). Blue spheres indicate vanadium, and red ones oxygen ions. Possible insertion sites are indicated by green and yellow spheres.