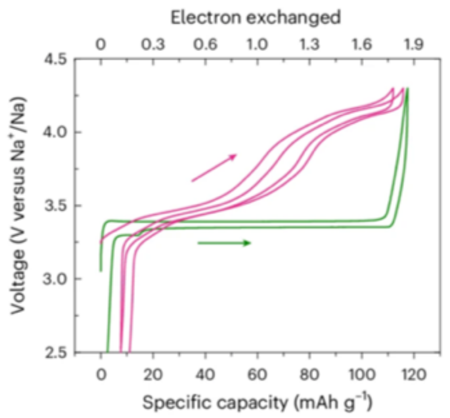

Obtaining $V_2(PO_4)_3$ by sodium extraction from single-phase $Na_xV_2(PO_4)_3$ (1 < x < 3) positive electrode materials

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Abstract

We report on single-phase $Na_xV_2(PO_4)_3$ compositions (1.5 ≲ x ≲ 2.5) of the Na super ionic conductor type, obtained from a straightforward synthesis route. Typically, chemically prepared c-Na2V2(PO4)3, obtained by annealing an equimolar mixture of $Na_3V_2(PO_4)_3$ and $NaV_2(PO_4)_3$, exhibits a specific sodium-ion distribution (occupancy of the Na(1) site of only 0.66(4)), whereas that of the electrochemically obtained e-$Na_2V_2(PO_4)_3$ (from $Na_3V_2(PO_4)_3$) is close to 1. Unlike conventional $Na_3V_2(PO_4)_3$, when used as positive electrode materials in Na-ion batteries, the NaxV2(PO4)3 compositions lead to unusual single-phase Na+ extraction/insertion mechanisms with continuous voltage changes upon Na+ extraction/insertion. We demonstrate that the average equilibrium operating voltage observed upon Na+ deintercalation from single-phase $Na_2V_2(PO_4)_3$ is increased up to an average value of ~3.70 V versus Na^+/Na (thanks to the activation of the V4+/V5+ redox couple) compared to 3.37 V versus Na^+/Na in conventional $Na_3V_2(PO_4)_3$, thus leading to an increase in the theoretical energy density from 396.3 Wh kg_{-1} to 458.1 Wh kg_{-1}. Electrochemical and chemical Na^+ deintercalation from c-$Na_2V_2(PO_4)_3$ enables complete Na-ion extraction, increasing energy density.