A Reversible 3.88 V single plateau in sodium-ion battery by iso-energetic structural rearrangement : experiment and theory.

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Utilizing the advantages of unlimited resource, low material cost, and easy worldwide accessibility, sodium ion batteries (SIBs) have received increasing attention, especially targeting grid-scale energy storage systems (ESSs)[1-3]. However, electrochemical performance of current SIBs is still inferior to that of well-matured lithium ion batteries (LIBs)[4,5], requiring substantial further improvements for SIBs to be practically used in diverse real applications. One important such effort is to find SIB cathode materials that hold high redox voltages (high energy) and operate based on fast diffusion of Na ions (high power), comparable to the Li-counterpart. Indeed, various crystal structures containing different transition metals (TMs) have been actively investigated quite lately[2,4], yet still show critical drawbacks in their electrochemical operations: low and poorly defined potentials and limited cycle life.

Herein, we report vanadium-based ortho-diphosphate, $Na_7V_4(P_2O_7)_4PO_4$, that significantly reduces all of the latter barriers. $Na_7V_4(P_2O_7)_4PO_4$ exhibits the highest single-valued voltage plateau to date at 3.88 V vs. Na/Na^+ and substantial capacity retention over 500 cycles. Ab initio calculations reveal that the remarkable single plateau and cycle life are originated from a unique structural rearrangement that keeps the energy levels of $Na_7V_4(P_2O_7)_4PO_4$ nearly constant throughout the entire charge-discharge with very little energy penalty. A simple energetic consideration also suggests that the presence of stable intermediate phases is beneficial for cell kinetics via smaller volume changes and associated low overpotentials, and this trend can be a general principle in the future design of battery materials.

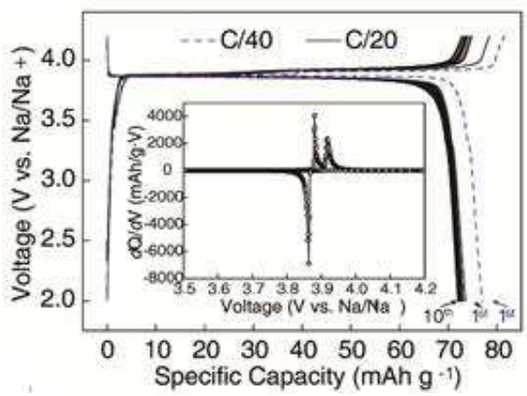

Figure 1. Galvanostatic profiles of $Na_7V_4(P_2O_7)_4PO_4$ measured at C/20 and C/40 in the first cycles. The profiles at C/20 in the cycle range of 2~10 are also presented. (Inset) The differential capacity curve (dQ/dV) obtained from the galvanostatic profile measured at C/20

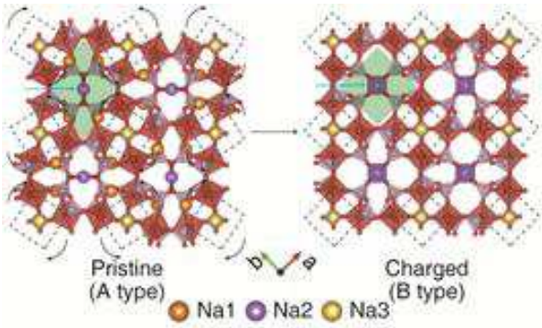

Figure 2. The crystal structures of the pristine and charged phases indicative of a crystal structure rearrangement during phase transformation between both phases.

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