Electrochemical calcium ion intercalation into Na$_x$V$_2$(PO$_4$)$_3$, as a cathode material for calcium batteries

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Calcium-ion batteries (CIBs) is one of the candidate for the next generation battery systems due to their many benefits in terms of energy density and low cost—calcium has a similar redox potential with lithium (Li = -3.04 V, Ca = -2.87 V vs SHE), and the capacity can be doubled by the divalency of the ion compared with monovalent lithium ion. However, there are only a few materials known as a reversible intercalation host of calcium ions. So far, some of known examples are Prussian blue analogues and CaCo$_2$O$_4$.$^{1,2}$

Herein, we report a remarkable new host material, NaV$_2$(PO$_4$)$_3$ (R-3c, a = 8.73 Å c = 21.81 Å) as a cathode material for CIBs, which was prepared by electrochemical Na ion extraction from Na$_3$V$_2$(PO$_4$)$_3$. It has the NASICON-type structure with an open three-dimensional framework enabling a facile diffusion of calcium ions. Prior to attempting electrochemical calcium intercalation, we have found that the calcium ion can be chemically inserted into the NaV$_2$(PO$_4$)$_3$ structure by soaking the electrode in a calcium ion solution with a reducing agent. The calcium ion insertion was clearly evidenced by elemental analysis and structure refinement. The inserted calcium ion position in the structure was located by the electron density mapping using the techniques of structure determination from powder X-ray diffraction (XRD) data. In addition, two-phase calcium intercalation reaction of Ca$_x$NaV$_2$(PO$_4$)$_3$ was confirmed with in-situ XRD. The electrochemical performance of reversible calcium ion intercalation into NaV$_2$(PO$_4$)$_3$ with calcium organic electrolyte was also confirmed as well as chemical intercalation, demonstrating the potential for NaV$_2$(PO$_4$)$_3$ as a calcium-ion battery cathode.

References: