

Phase transformations during battery operation in vanadium phosphate cathode materials

Daniel Risikov Sørensen^a, Dorthe Bomholdt Ravnsbæk^a

^a *Department of Physics, Chemistry and Pharmacy, University of Southern Denmark, Campusvej 55, 5230 Odense M, Denmark.*

E-mail: drs@sdu.dk

Phosphate based cathode materials has seen great success following the demonstration of LiFePO₄ as a functioning Li-ion battery cathode material [1], especially due to its very low cost and high safety compared with the previously used oxide based materials. However, despite the inductive effect of the phosphate group, LiFePO₄ has a relatively low discharge potential compared with materials based on other transition metals, such as vanadium, cobalt and nickel. The capacity is also low due to the limited number of oxidation states for iron, yielding only a single Li-ion per formula unit.

Cathode materials based on vanadium phosphate has a number of advantages over LiFePO₄ due to higher discharge potential and broader range of oxidation states, giving a higher energy density, but maintaining the thermal stability provided by the phosphate group. A very interesting candidate in this category is Li₃V₂(PO₄)₃ as it has the highest gravimetric capacity among the known phosphates (197 mAh g⁻¹) [2]. The materials displays a complex series of phase transformations during charge and discharge, and interestingly, these transformations are very dependent on the number of Li-ions extracted during charging [3]. Another interesting vanadium phosphate compound is LiVPO₄F, which has received significant attention due to its very stable anion framework, which also helps deliver a high discharge capacity [4]. It also exhibits complex phase transformations during operation.

In recent years, new methods have been developed to investigate the dynamic structural behavior of battery materials during operation using synchrotron X-ray diffraction. Traditionally, structural information has been obtained mainly by ex-situ diffraction studies, but these methods fail to probe the dynamic behavior, as an operating battery is inherently not at equilibrium. In this study, we investigate the dynamic structural behavior of Li₃V₂(PO₄)₃ as a function of extracted Li-ions and LiVPO₄F prepared by different synthetic routes, using in-situ synchrotron diffraction. In both cases, new structural details were uncovered, showing e.g. a remarkable phase transition dependence on the synthetic route for LiVPO₄F, and an extended solid solution regime for Li₃V₂(PO₄)₃. The detailed structural information of the phase transformations in these materials clear demonstrate the strength of in-situ diffraction methods.

References:

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