



Dynamic charge-discharge phase transitions in $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathodes

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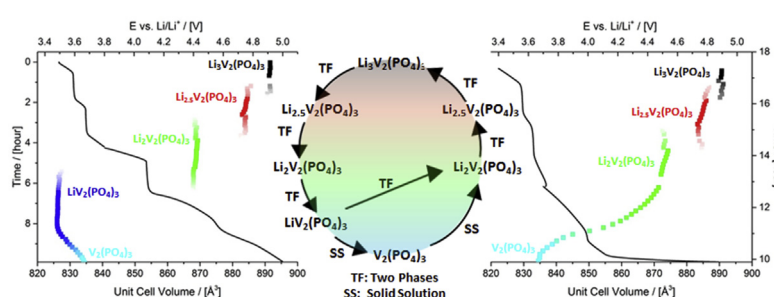
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HIGHLIGHTS

- Phase transitions in $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ probed by *operando* synchrotron X-ray diffraction.
- Two-phase behavior observed for all transitions during extraction of two Li-ions.
- Solid solution transition is discovered for extraction of the last Li-ion.
- Extended solid solution regimes observed during discharge.

GRAPHICAL ABSTRACT



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ABSTRACT

Monoclinic $\alpha\text{-Li}_3\text{V}_2(\text{PO}_4)_3$ is a promising cathode material for future Li-ion batteries due to its high theoretical capacity, good capacity retention and relatively high ionic conductivity. The material undergoes a series of complex phase transitions which depend on the number of Li-ions extracted during charge. The phase behavior has been extensively studied under (quasi-) equilibrium conditions, however insight into the phase evolution during dynamic conditions is lacking. Through *operando* synchrotron X-ray diffraction we report the complex series of structural phase transitions under dynamic battery charge-discharge conditions in $\alpha\text{-Li}_3\text{V}_2(\text{PO}_4)_3$ cathodes with extraction of both two and three Li-ions. For extraction of two Li-ions, the phase evolution follows the series of expected two-phase transitions, while for extraction of three Li-ions the dynamic phase behavior differs significantly from that observed by equilibrium studies, e.g. we reveal unexpected solid solution behavior during removal of the last Li-ion and unforeseen structural hysteresis between charge and discharge. Our results are further reinforced by electrochemical analysis. This paper joins a series of recent reports, where extended solid solution behavior in battery electrode materials is observed under *operando* conditions, and reinforces the importance of these types of measurements to provide a more realistic picture of working battery materials.

1. Introduction

Rechargeable Li-ion batteries are today one of the most promising technologies for energy storage, and are expected to play a key role in especially automotive applications. However, in order to meet the demands of future applications, significant improvements to the present technology are required such as enhanced rate capability, longer cycle life and lower production costs [1]. These characteristics are to a large

extent governed by the nature of the electrode materials and the processes occurring therein during battery charge and discharge, i.e. the thermodynamics and kinetics of the oxidation/reduction and the accompanying phase transformation [2]. Thus, to truly develop novel superior batteries one must understand the details of these underlying processes.

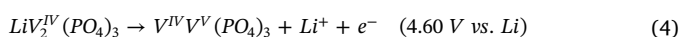
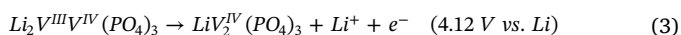
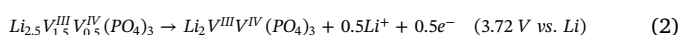
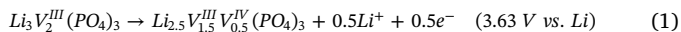
The development of intercalation-type batteries has produced a wide selection of cathode materials, each with distinct advantages and

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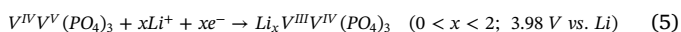
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disadvantages. Since the first commercialized cobalt-based oxides, especially phosphate-based intercalation materials have attracted much attention following the work of Goodenough and co-workers [3]. Among these, monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, often denoted $\alpha\text{-Li}_3\text{V}_2(\text{PO}_4)_3$, shows promise due to its high theoretical capacity (197 mAh g^{-1}), good capacity retention and relatively high ionic conductivity [4–6]. Like other phosphate-based cathode materials, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ has a high operating voltage due to the inductive effect of the phosphate groups [7], but on the down side a low intrinsic electronic conductivity. To enhance the latter, the materials are therefore often coated with carbon.

It has been shown, that under equilibrium (or pseudo-equilibrium) conditions $\alpha\text{-Li}_3\text{V}_2(\text{PO}_4)_3$ undergoes a series of four consecutive phase-transitions during battery charge (see reactions equations (1)–(4)), visible by four plateaus in a galvanostatic potential profile [8,9].



The listed potentials in Equations (1)–(4) are the measured values [10], which are very close to the equilibrium potential for extraction of the first two Li-ions (Equations (1)–(3)), while the overpotential for extraction of the last Li-ion is significantly higher (Equation (4)) [8,11–13]. On subsequent discharge, the potential profile of the material will depend on the number of Li-ions extracted during charging [8]. Following extraction of two Li-ions (Equations (1)–(3)), the pathway of the delithiation is reversible, and lithiation goes through the reverse reactions, exhibiting the same number of plateaus in the galvanostatic potential profile. In contrast, when all three Li-ions are extracted during charge, the subsequent discharge is characterized by sloping potentials until the insertion of two Li-ions is complete. This behavior points towards Li-disorder and solid solution reaction during insertion of two Li-ions according to Equation (5). Insertion of the third Li-ion is again characterized by a flat potential plateau and two-phase behavior (Equations (2) and (1)) [10]:



The hysteretic phase evolution is explained by charge-ordering on the vanadium ions [8,14]. The structure of $\alpha\text{-Li}_3\text{V}_2(\text{PO}_4)_3$ (space group $P2_1/n$) includes three crystallographic distinct Li-ions (see Fig. 1), where Li1 is 4-fold coordinated, while Li2 and Li3 are 5-fold coordinated [12,13]. When extracting the first Li-ion, Li3 is preferentially removed, since it has the highest energy [15]. This gives rise to an ordering of the charge on vanadium, where columns of either V^{III} or V^{IV} form along the b -axis. The position of the Li2-ion changes slightly, while the Li1-positions remain fixed. Due to repulsion between V^{IV} and Li, Li1 is preferentially extracted secondly. If lithium is now reinserted, it will

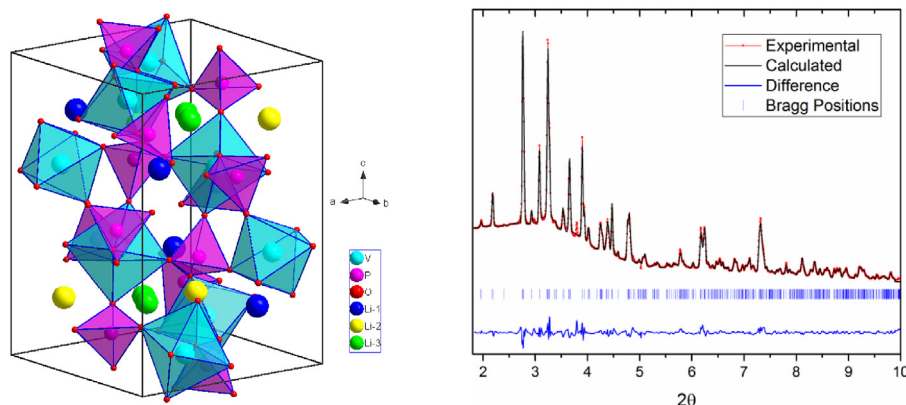


Fig. 1. Crystal structure and powder X-ray diffraction data of monoclinic $\alpha\text{-Li}_3\text{V}_2(\text{PO}_4)_3$. Left: The structure of monoclinic $\alpha\text{-Li}_3\text{V}_2(\text{PO}_4)_3$ (Space group $P2_1/n$, $a = 8.611$ (5) Å, $b = 8.598$ (4) Å, $c = 12.044$ (7) Å and $\gamma = 90.605$ (49)° (lattice parameters from refinement of diffractogram to the right)). PO_4 -tetrahedra in purple, VO_6 -octahedra in light blue, Li1 in blue, Li2 in yellow and Li3 in green. Right: Rietveld refinement profile of *ex situ* synchrotron powder X-ray diffraction data of as-prepared $\alpha\text{-Li}_3\text{V}_2(\text{PO}_4)_3$ (from this work, $\lambda = 0.2071$ Å, P02.1, PetraIII). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

first enter back into the Li1 position and subsequently into the Li3-position as the site energy of the Li3-site is higher. This ensures that the lithiation is the reverse of the delithiation. If on the other hand all three Li-ions are extracted, V^{IV} and V^{V} are formed and are randomly distributed in the structure. Since there is no order left to guide the lithiation, Li-ions will be randomly inserted on both the Li1- and Li2-sites. This disorder results in the solid solution behavior observed during discharge. When the Li1- and Li2-sites are fully occupied, only the Li3-site is vacant, and the two-phase behavior reemerges.

Thus, the phase behavior of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ is quite well understood under equilibrium (or pseudo-equilibrium) conditions based on studies of the individual chemically prepared stable phases as well as indirectly from electrochemical observations. However, to this point the described phase transformation mechanisms have not been observed and well analyzed directly from experimental data. Furthermore, very little is known about the structural phase evolution of this material occurring during battery operation, i.e. under dynamic working conditions. Measurement of the structure under equilibrium conditions might not reveal important features of the structural evolution of a cathode material under realistic conditions, since a battery in operation inherently is not at equilibrium. The importance of performing *operando* measurements in order to properly understand the structural phase transformation mechanism has recently been highlighted by several discoveries of unexpected transition pathways involving widely extended Li-regimes of metastable solid solutions in LiFePO_4 [16] and $\text{LiMn}_{1-y}\text{Fe}_y\text{PO}_4$ [17,18], and formation of a nanocrystalline solid solution in the $\text{NaFePO}_4\text{-FePO}_4$ system [19], which alleviates misfit strain between the two end-members. For $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, investigation have so far mainly relied on non-*operando* diffraction measurements, either *ex situ* following chemical oxidation of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ [8], or pseudo *in situ*, i.e. an *ex situ* measurement when equilibrium has been obtained following a current pulse [12]. A single *operando* synchrotron radiation powder X-ray diffraction investigation on $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ has been published [20]. Unfortunately, this study only presents a single measurement, where all Li-ions are extracted and the discharge data is not analyzed in detail, i.e. changes in unit cell dimensions are not extracted. Furthermore, in the charge state, the cathode in this study contains a mix of $\text{Li}_2\text{V}_2(\text{PO}_4)_3$, $\text{LiV}_2(\text{PO}_4)_3$ and $\text{V}_2(\text{PO}_4)_3$, i.e. single phase $\text{V}_2(\text{PO}_4)_3$ is not reached.

Here, we use *operando* synchrotron powder X-ray diffraction (SR-PXD) and Rietveld analysis combined with standard material- and electrochemical-characterization techniques to investigate the structural phase evolution of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathodes during dynamic battery charge and discharge. We elucidate how the phase transition mechanism dependent on the degree of Li-extraction and surprisingly we discover that contrary to previous equilibrium studies the extraction of the final Li-ion does not proceed via a two-phase reaction mechanism.

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