



Synthesis, Structure and Electrochemistry of Lithium Vanadium Phosphate Cathode Materials

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The Li-ion battery positive electrode materials, α -LiVOPO₄, β -LiVOPO₄, and Li₃V₂(PO₄)₃ have been prepared as individual phases from a common precursor mixture by controlling the synthesis conditions. These phases result because of their distinct crystal symmetries and V oxidation states. The synthesis involves the decomposition of a precursor mixture prepared from NH₄VO₃, NH₄H₂PO₄, LiF and hexanoic acid which when heat-treated under different conditions produced the three Li_wV_xO_y(PO₄)_z products. The materials were characterized by means of elemental analysis, X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS) and Li cell data. The Li cycling performance and the accompanying structural effects on α - and β -LiVOPO₄ were also studied under normal and deep discharge conditions using XAS to probe the local vanadium environment. XANES and EXAFS confirm reversible changes in the two structures when intercalation does not exceed 1Li/VOPO₄. Deeper discharge revealed more disruption to both structures, including an additional 0.25 Å increase to the V=O bond length. A greater range in the VO₆ symmetry of α -LiVOPO₄ resulted in a more flexible accommodating host, in agreement with its improved low voltage performance compared to β -LiVOPO₄. © 2011 The Electrochemical Society. [DOI: 10.1149/2.003112jes] All rights reserved.

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Transition metal phosphate positive electrode materials now compete with layered and 3-D structured transition metal oxides and their derivatives for a share in the lithium-ion battery market. The phosphate group provides a thermally stable, high voltage electrode material attributed to the inductive effect of the PO₄ moiety, with these qualities exemplified by LiFePO₄.¹ Electrical transport limitations originating from low ionic and electronic conductivities have plagued such phosphate frameworks. Poor Li-ion cell charge/discharge performance ascribed to these problems, especially at high rates, have been alleviated with nanophase materials² and metal ion doping³ with the result that high power LiFePO₄ cells are now a practical reality. However, certain metal phosphates such as α -LiVOPO₄ and β -LiVOPO₄ have improved features such as a high theoretical specific capacity of 166 mAh/g at discharge voltages approximately 500 mV higher than that of LiFePO₄, which translates into a theoretical specific energy of 650 Wh/Kg in a Li cell. However, they yield only about 70% of their theoretical capacity at rates of C/50 to C/5.^{4,5} At a higher cycling rate (4.22C) α -LiVOPO₄ has achieved 25% of its theoretical capacity.⁶ The reason for the poor practical performance of these materials is not fully understood. Interestingly, vanadium exists in a variety of stable valence states, useful in both increasing energy density via insertion of multiple Li/equivalent and also for opening possibilities for new synthetic strategies.

Here, we first look to capitalize on this range of vanadium oxidation states and distinct phases that provide a unique synthetic opportunity to determine structural connections that exist among α -LiVOPO₄, β -LiVOPO₄, and α -Li₃V₂(PO₄)₃. This is done with an aqueous precursor-based synthesis yielding these three different active materials from the same starting material precursor mixture. This method is of interest for the following reasons; 1) it allows for product control from an *in situ* generated reducing agent, with the final structure dependent on sintering conditions (gas, flow rate, and temperature) used for the thermal decomposition of the precursor; and, 2) it yields several electrochemically active phases from one common precursor mix; and 3) it provides an explanation for how and why these different phases are formed.

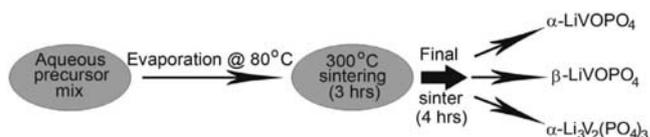
Although a large oxidation state window is an important requisite for high energy cathodes, it also requires strain tolerance of the structure in order to avoid deterioration and/or phase transformation, as in the case of V₂O₅ cycled beyond 1 Li.⁷ X-ray absorption spectroscopy

(XAS) was utilized in order to understand electrochemical/structural correlations of α - and β -LiVOPO₄ during normal discharge to 3 volts and what is considered overdischarge to 2 volts. By correlating electrochemical properties with structural dynamics we have gained new insights into the structural differences between these close analogues. XAS is also used here to elucidate the cause of deep cycling capacity fade in these phases.

Experimental

The three compounds, α -LiVOPO₄, β -LiVOPO₄, and α -Li₃V₂(PO₄)₃ were produced from a precursor mixture prepared in an aqueous process, followed by two sintering steps as seen in Scheme 1. Equivalent molar ratios of all starting materials, specifically, 0.8069 g NH₄VO₃ (Sigma Aldrich, 99.999%), 0.7934 g NH₄H₂PO₄ (Sigma Aldrich, 99.999%), 0.1789 g LiF (Sigma Aldrich, 99.99%), and 0.864 ml hexanoic Acid (CH₃(CH₂)₄COOH) (Sigma Aldrich, 99.5%) were mixed in 300 ml H₂O for 24 hrs and then evaporated at 80°C. Low solubility of LiF required long mixing times; however, only this inorganic source of lithium gave the results presented here. (see Results and Discussion) The resultant bright yellow cake was then dried, ground, pressed at 3000 psi, and sintered at 300°C for 3 hours under a constant argon flow. The final product depended on the subsequent four hour sintering which varied in temperature, gas flow rate in the tube furnace, and reducing atmosphere, consisting of either argon or 5% H₂/argon. These conditions are summarized in Table I. Flow rates were determined using flow meter calibration data (Porter Instrument Co. Inc, Hatfield, PA). Heating rates were held constant for all samples at 4°C/minute. Thermal analysis including differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) on the precursor mixture after the 80°C evaporation step was performed in the range of 25°–450°C and 25°–800°C respectively, both at a heating rate of 4°/min under 45 cc/min N₂. Inductively coupled plasma mass spectrometry (ICP-MS) measurements were contracted out to Geolabs Inc. (Braintree, MA) to determine elemental composition.

X-ray diffraction (XRD) measurements were performed using a Rigaku D-Max 2200 (Cu K α _{1,2} radiation). Unit cell constants of



Scheme 1. Overall synthetic procedure.

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