

## Hydrothermal Synthesis and Electrochemical Behavior of Oxide Cathodes for Lithium Batteries

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Many solid state ionic devices are limited by the cathode material. Thus the oxide cathode for lithium batteries has not increased in energy density in the last 20 years. Such oxides must show rapid reaction to give high current densities or equilibration within a reasonable time period. In the case of lithium batteries this dictates an open crystalline lattice that can accommodate lithium ions. The oxide of choice should meet the following criteria:

1. Reacts with 1 lithium per transition metal in a totally reversible manner over many cycles.
2. Maintains its structural integrity during reaction.
3. Reacts rapidly,  $\geq 5 \text{ ma/cm}^2$ .
4. Is low cost, environmentally harmless and preferably is a good electronic conductor.

No present oxide meets all these criteria. We have been investigating, in a systematic manner, the synthesis of a range of manganese and vanadium oxides to ascertain the role of structure on electrochemical behavior and to see if a rational approach to the synthesis of inorganic solids can be accomplished. The latter in the long term will allow for the synthesis of materials with the desired properties. We have used a mild environmentally friendly approach to synthesize these materials: hydrothermal synthesis as used on the large scale for zeolite manufacture.

Manganese dioxides are particularly attractive for the cathode of reversible lithium batteries because of their low cost and environmental inertness. Their layered structures, that are similar to  $\text{Li}_x\text{TiS}_2$  and  $\text{Li}_x\text{CoO}_2$ , have the potential of reacting with up to one lithium per manganese. This is double the capacity of the spinel  $\text{LiMn}_2\text{O}_4$  which is now available as an alternative to the costly cobalt oxide. However, the layered oxides have a tendency to convert to a spinel-like form on cycling, and indeed at high rates the conversion occurs on the first charge [1]. This is true for both hydrothermal [1] and high temperature synthesized materials [2]. These structures only differ in the distribution of the manganese and lithium ions in the essentially cubic close-packed oxygen lattice [3].

These layered structures can be stabilized by either modification of the crystalline structure (geometric factor), or by modification of the electronic structure (electronic factor). The latter can be accomplished by partial substitution of part of the manganese by ions such as cobalt, iron, nickel or chromium amongst others. These modify the electronic structure leading to enhanced electronic conductivity [4], and to a probable breakdown of the magnetic ordering of the manganese ions. This results in enhanced cyclability and capacity in both hydrothermal and high temperature materials [5]. The layer structure of the oxides can be stabilized by pillaring the layers, thus removing the driving force for manganese migration into the lithium containing layers. We have

accomplished this through placing vanadium oxide species between the  $\text{MnO}_2$  sheets [6]. During this study we also found several new manganese vanadium oxides. One of these uses manganese ions to stabilize the double sheet  $\text{V}_4\text{O}_{10}$  structure of vanadium oxide [7]. This new material resists conversion to the  $\omega\text{-V}_2\text{O}_5$  form on cycling. The synthesis, characterization and electrochemical behavior of these new materials will be discussed. When the aqueous medium in the hydrothermal reaction is replaced by a predominantly water free medium, different structures are formed. Thus, in glacial acetic acid the oxide  $\text{H}_2\text{V}_3\text{O}_8$  is formed. This material whose structure is intermediate between that of a typical layer and a tunnel compound, cycles lithium well with almost one Li per vanadium above 2 volts [8].

The lithium iron phosphates have been of much interest recently because of their low cost and the work of the Armand group [9] to overcome their high resistivity with carbonaceous surface coatings. This class of cathode material is very readily synthesized by mild hydrothermal synthesis, as shown in Figure 1 for a  $\text{LiFePO}_4$  material made by us in less than 3 hours.

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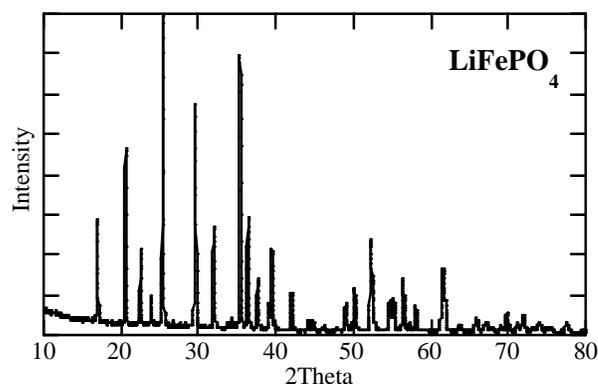


Fig. 1. X-ray diffraction pattern of hydrothermally synthesized  $\text{LiFePO}_4$ ; total reaction time  $\leq 3$  hours.

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