

# Performance of $\text{LiFePO}_4$ as lithium battery cathode and comparison with manganese and vanadium oxides

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## Abstract

$\text{LiFePO}_4$  was synthesized by a high temperature method and high purity was confirmed by both powder X-ray diffraction and thermal analysis. It can deliver 136 Ah/kg, 80% of theoretical capacity at 1 mA/cm<sup>2</sup> at high cathode load levels at room temperature; 100% capacity can be obtained by raising the temperature to 60 °C or reducing the discharge rate to 0.1 mA/cm<sup>2</sup>. The method of carbon addition/coating was not found to be critical, carbon black being as efficient as in situ formed carbon coatings. These materials suffer from a low volumetric energy density, which will seriously impact their possible application. Stabilized layered structures of manganese substituted nickel oxides, such as  $\text{LiMn}_{0.4}\text{Co}_{0.2}\text{Ni}_{0.4}\text{O}_2$ , show a behavior typical of a single phase intercalation reaction, and a reversible capacity of around 180 Ah/kg with an upper voltage cut-off of 4.3 V. Stabilized  $\delta$ -structures of vanadium pentoxide show capacities approaching 300 Ah/kg, but with a median discharge potential of 2.6 V.

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## 1. Introduction

The energy density of lithium batteries has not increased in the last 20 years, and the capacity in Ah/kg has actually decreased. Thus, much effort is being directed at finding new electrode materials that have higher capacities, lower costs, and are environmentally benign. The cathode is particularly critical in determining the capacity of the lithium battery, as it is the heaviest component, and has the greatest potential for improvement. Present commercial systems such as  $\text{Li}_x\text{CoO}_2$  react with little more than 0.6Li, whereas an ideal system such as the original  $\text{Li}_x\text{TiS}_2$  reacted reversibly with 1Li per formula unit.

Many of the most effective cathode materials have been oxides with layered structures similar to the sulfides. However, their greater ionicity reduces the diffusivity of lithium ions and generally reduces their electronic conductivity so that conductive diluents must be added. These oxides, such as  $\text{Li}_x\text{NiO}$  and even  $\text{Li}_x\text{CoO}_2$ , also have high oxygen partial pressures at low lithium contents,  $\text{Li}_x\text{MO}_2$ , so that there are serious safety issues on overcharge. Since the commercialization of  $\text{LiCoO}_2$  by SONY [1] 10 years ago, alternative

cathode materials have been explored to replace the expensive and oxidatively unstable  $\text{LiCoO}_2$ .

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 [2]. This is true for both hydrothermal [2] and high temperature synthesized materials [3]. These structures only differ in the distribution of the manganese and lithium ions in the essentially cubic close-packed oxygen lattice [4].

These layered structures can be stabilized by either modification of the crystalline structure (geometric stabilization), or by modification of the electronic structure (electronic stabilization). The former can be accomplished by placing pillaring groups between the  $\text{MnO}_2$  sheets, thus removing the driving force for manganese migration into the lithium containing layers [5]. The latter can be accomplished by partial substitution of part of the manganese by ions such as cobalt, iron, nickel or chromium. These modify

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the electronic structure leading to enhanced electronic conductivity [6], cyclability and capacity in both hydrothermal and high temperature materials [7]. Recently compounds such as  $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$  [8,9] have received much attention.

The lithium iron phosphates [10] have been of much interest recently because of their low cost and many research groups have tried to improve the performance of this material [11–16]. The overcoming of their high resistivity with carbonaceous surface coatings [17] has removed one major hurdle to their use. There are a large number of different iron phosphate phases, and a number are electrochemically active but the temperature of synthesis is critical [18]. The highest capacities can be obtained in layered  $\delta$ -type phases of vanadium oxides, where capacities approaching 300 Ah/kg are found. The synthesis, characterization and electrochemical behavior of several of these compounds is discussed below with particular emphasis being placed on determining whether  $\text{LiFeO}_4$  is a viable candidate for the next generation of cathodes for Li-ion batteries relative to stabilized manganese dioxide and vanadium oxides.

## 2. Experimental

The  $\text{LiFePO}_4$  was synthesized from a stoichiometric mixture of reagent grade  $\text{NH}_4\text{H}_2\text{PO}_4$  (Alfa-Aesar),  $\text{CH}_3\text{COOLi}$  (Aldrich) and  $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  (Aldrich), which was ground for 10 min, then pressed into pellets and heated at 350 °C in a tube furnace with flowing helium gas for 4 h. After slowly cooling to room temperature, pellets were ground again for 10 min, pressed into pellets, heated slowly to 700 °C and held there for 10 h. Iron wire was placed upstream of the sample to assure a low oxygen partial pressure thus preventing the formation of ferric species. After cooling to room temperature, the sample was ground and ready for use. The manganese oxides were synthesized from the hydroxides, by heating pressed pellets first overnight at 450 °C; then at 800 °C for 8 h following a regrinding and pelletization. The vanadium pillared manganese oxide was synthesized as described earlier [5], as were the vanadium oxides [19].

All samples were analyzed for phase and purity before and after electrochemical testing by X-ray analysis, using a Scintag XDS2000 diffractometer with Rietveld refinement (WinCSD software) [20] and thermal gravimetric analysis, using a Perkin-Elmer TGA 7 in oxygen to 700 °C.

The electrochemical evaluation was done in bag cells where the cathode loading varied from 15 to 80 mg/cm<sup>2</sup>; the cathode typically contained 10% carbon black (City Services Co.) and 5% Teflon (Dupont). This cathode mixture after mixing in a mortar with a few drops of hexane was hot pressed into an Exmet grid, then wrapped in Celgard (Celgard 2400, Hoechst Corp.) separator. The electrolyte used was  $\text{LiPF}_6$  in a EC/DMC mixed carbonate (LP40 from EM Industries) and lithium (Aldrich) was used as the

negative electrode. Cathodes of  $\text{LiFePO}_4$  were also constructed with carbon coatings made from carbon gel [16], aqueous gelatin [21] and sugar [12,17]. The carbon gel coating was prepared by mixing carbon gel with the iron phosphate raw materials, firing at 350 °C for 4 h, followed by 7 h at 700 °C all under helium. The gelatin coating was prepared by adding 23 mg of gelatin in water to 1 g of  $\text{LiFePO}_4$  with stirring on a hot plate, followed by the addition of 90 mg of carbon black and another 10 mg of gelatin; finally the whole is heated to dryness. The sugar coating was prepared by dispersing hydrothermally prepared  $\text{LiFePO}_4$  in sugar solution, 9:1 weight ratio, and stirring on a hot plate to close to dryness, and finally firing at 700 °C for 3 h in helium. The electrochemical data was collected galvanostatically on a MacPile II system normally at ambient temperature.

## 3. Results and discussion

### 3.1. Stabilized layered lithium manganese oxides

Layered lithium manganese oxide,  $\text{Li}_x\text{MnO}_2$ , is a promising replacement for the  $\text{LiCoO}_2$  presently used in most Li-ion batteries. In principle close to one Li can be cycled per formula unit compared to around 0.5–0.6 in cobalt oxide. However, on charge the manganese ions tend to migrate into the lithium layers forming a spinel-like structure. The spinel structure only cycles 0.5Li/Mn within a single voltage plateau. Thus, there has been much effort to stabilize the  $\text{MnO}_2$  layers against spinel formation. Two approaches have been used. The first is geometric stabilization where immobile pillaring species are placed into the lithium layer to increase the size of the lattice sites so that they are unfavorable for occupancy by manganese ions. The second is geometric stabilization where the electronic structure of  $\text{Li}_x\text{MnO}_2$  is modified to be more like that of  $\text{Li}_x\text{CoO}_2$ , for example, by doping with an element to the right of cobalt in the periodic table, for example,  $\text{Mn} + \text{Ni} \equiv \text{Co}$ .

$\text{Zn}_3(\text{OH})_2(\text{V}_2\text{O}_7) \cdot 2\text{H}_2\text{O}$  was synthesized as a model pillared compound [22]. In this compound the zinc oxide layers are separated by V–O–V pillars; the water molecules are readily removed on heating leading to very open layers that should be able to incorporate a variety of ions and molecules. We thus attempted to synthesize a compound where the zinc oxide layers are replaced by manganese oxide. Such a compound was synthesized,  $(\text{VO})_y\text{MnO}_2$ , where manganese oxide layers are separated by vanadium oxide pillars, but the exact structure still has to be determined. The electrochemical data on this compound is shown in Fig. 1 for two current densities, 0.1 and 1 mA/cm<sup>2</sup>. As can be seen a single sloping discharge profile is observed in both cases in direct contrast to  $\text{Li}_x\text{MnO}_2$  itself where at the higher current densities, two plateaus are observed one at 4 V and the other at 3 V typical of the spinel structure. Thus, the concept of stabilization by pillaring is proven. However, as indicated in Fig. 1 the capacity falls dramatically on increasing the

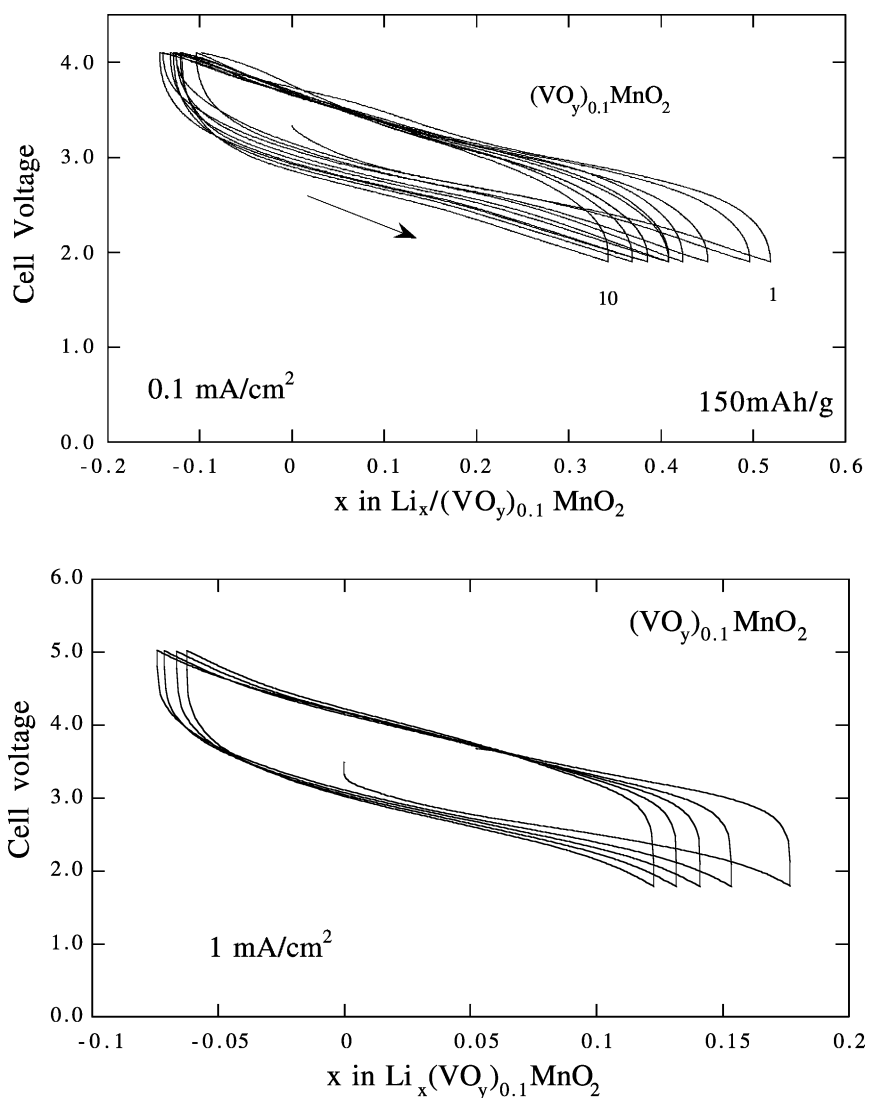


Fig. 1. Electrochemical performance of vanadium oxide pillared manganese oxide at 0.1 mA/cm<sup>2</sup> and 1 mA/cm<sup>2</sup>.

current density from 0.1 to 1 mA/cm<sup>2</sup>, even though a higher cut-off of 5 V was used on charge. The overcharge on the first cycle suggests that there are possibly some protons in the structure that are removed on the first charge. Attempts to incorporate cobalt into the manganese oxide layers whilst maintaining the pillared structure have not been successful to date.

The electronic stabilization of layered lithium manganese oxide has been studied for some years. The addition of ions such as cobalt, iron and nickel has been shown to enhance the electronic conductivity of manganese oxide by up to two orders of magnitude [6]. They in addition also significantly improve the cycling behavior in both high temperature [3] and hydrothermally synthesized [2] compounds at the 1–10% levels; however, at these substitution levels spinel formation still occurs under high charging rates (potentials well over 4 V) [2]. Even when 50% of the manganese is substituted by cobalt, spinel formation eventually occurs [23]. However, when an element to the right of cobalt is used

and the manganese level is no higher than 50%, then spinel formation is not observed. Spahr et al. [24] reported the electrochemistry of LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> in a study of the solid solution system LiNi<sub>1-y</sub>Mn<sub>y</sub>O<sub>2</sub> for 0 < y ≤ 0.5 and showed that the capacity increased with increasing manganese content, in contrast to an earlier mostly structural study [25] which reported the opposite. Ohzuku and Makimura have reported studies on LiMn<sub>0.5</sub>Ni<sub>0.5</sub>O<sub>2</sub> [9] and LiMn<sub>0.33</sub>Ni<sub>0.33</sub>Co<sub>0.33</sub>O<sub>2</sub> [8] as have Dahn and others [26,27]. We have studied a range of compositions for these highly doped compounds, and the cycling behavior of the compound LiCo<sub>0.2</sub>Mn<sub>0.4</sub>Ni<sub>0.4</sub>O<sub>2</sub> is shown in Fig. 2. The upper voltage was limited to 4.3 V to minimize electrolyte decomposition. The behavior is typical of that expected for a single phase intercalation reaction [28,29], and there was no evidence of spinel formation. This composition had lattice parameters of  $a = 2.869 \text{ \AA}$  and  $c = 14.266 \text{ \AA}$  with a volume of  $101.72 \text{ \AA}^3$  and a  $c/3a$  ratio of 1.657 compared with the ideal close-packed value of 1.732.

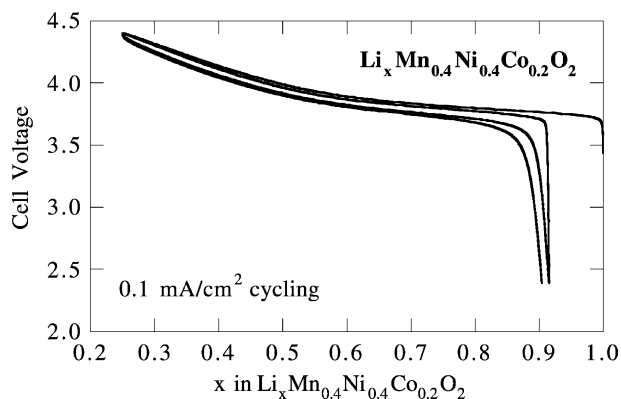


Fig. 2. Electrochemical behavior of the layered nickel manganese oxide  $\text{LiMn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$  in a lithium cell.

As studies on the Pacific Lithium compound  $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Cr}_{0.4}\text{O}_2$  indicated that the electrochemical reaction is Cr(III) to Cr(VI), we wished to determine the electrochemically active species in  $\text{LiCo}_{0.2}\text{Mn}_{0.4}\text{Ni}_{0.4}\text{O}_2$ . An XPS study [30] indicates that the manganese is mostly +4 and the nickel +2 contrary to the earlier work of Spahr et al. [24] which suggested Ni(III), surface Mn(IV) and bulk Mn(III). Our study also showed that the cobalt is +3. These results therefore suggest that the electrochemical couple is Ni(II)–Ni(IV) with the manganese stabilizing the structure. This is in agreement with a very recent proposal based on an electrochemical capacity study [27]. Thus, these materials are probably best described as manganese substituted nickel oxides. This raises the interesting question as to the nickel couple in  $\text{LiNiO}_2$  itself; are all the Ni  $\text{Ni}^{3+}$  or a mix of  $\text{Ni}^{2+}$  and  $\text{Ni}^{4+}$ ? The capacity shown in Fig. 2 corresponds to 180 Ah/kg, significantly higher than that in the commercial  $\text{LiCoO}_2$  cells, and the metal content should lead to lower costs than using pure cobalt.

### 3.2. Stabilized $\delta$ -phase vanadium oxides

Vanadium oxides have been studied [28,31] for more than 30 years as the cathode in secondary lithium batteries, and

have been the cathode of choice for polymer batteries.  $\text{V}_6\text{O}_{13}$ ,  $\text{V}_2\text{O}_5$  and  $\text{LiV}_3\text{O}_8$  have been the most studied with some emphasis on xerogel type vanadium oxides.  $\text{V}_2\text{O}_5$  itself has a tendency on over-discharge to form the disordered rock-salt compound  $\text{Li}_3\text{V}_2\text{O}_5$ . Both  $\text{V}_6\text{O}_{13}$  and the xerogel have a vanadium oxide double-sheet as an element of their structure. We therefore have investigated the  $\delta$ -structure class of vanadium oxide materials [19,32]. The compound  $[(\text{CH}_3)_4\text{N}]_y\text{Mn}_z\text{V}_4\text{O}_{10}$  had a reversible capacity exceeding 220 Ah/kg; the organic ions do not impede reaction as in the single sheet  $\text{V}_2\text{O}_5$  materials, such as  $\text{N}(\text{CH}_3)_4\text{V}_3\text{O}_7$ . If the large tetramethyl-ammonium ion could be replaced by a smaller ion such as ammonium, then the lattice size should be reduced, thereby increasing the volumetric energy density. The data for an ammonium analog is shown in Fig. 3. This graph shows that this compound has an initial capacity close to 300 Ah/kg. However, the median discharge voltage is about 2.6 V significantly lower than the manganese oxides discussed above and the lithium iron phosphate discussed below. These high capacity compounds are most likely to find application where the electrolyte has low stability, such as found for several polymers, or where capacity is critically important in a 2.5 V application. We are presently characterizing these materials, including determining their structures which tend to be complicated and not simple double-sheet vanadium oxides [33].

### 3.3. Lithium iron phosphate

Lithium iron phosphate has been studied for several years as a possible replacement cathode material for the  $\text{LiCoO}_2$  in lithium ion cells. However, a number of questions remain. These include the following.

1. Is a low cost hydrothermal process a viable approach for making  $\text{LiFePO}_4$ ?
2. What is the stability of  $\text{LiFePO}_4$ ?
  - (a) What happens on over-discharge, when  $x > 1$  in " $\text{Li}_x\text{FePO}_4$ "?

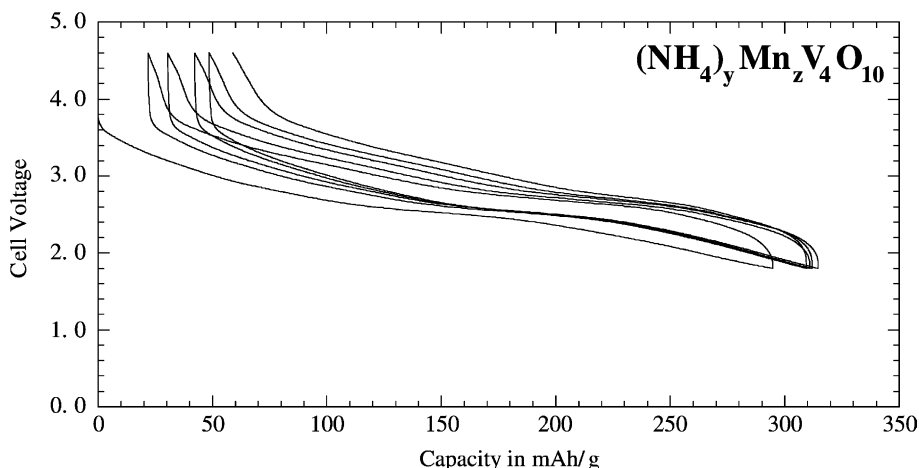


Fig. 3. Electrochemical behavior of a layered  $\delta$ -phase vanadium oxide in a lithium cell, showing the high capacity.

- (b) Which is the stable phase of  $\text{FePO}_4$ , and is the orthorhombic form kinetically stable?
3. What is the rate capability of  $\text{LiFePO}_4$ ?
- (a) How good is it at ambient temperatures at significant loadings?
4. Is a specialized conductive coating for  $\text{LiFePO}_4$  necessary?
- (a) What impact does it have on the already low volumetric energy density?
5. Are there other iron phosphate phases of interest?

Lithium iron phosphate has been successfully synthesized hydrothermally [13]. It has an X-ray pattern that appears excellent on first examination. However, an in-depth Rietveld analysis of the powder X-ray data indicates substantial electron density on the lithium site. This can be associated with about a 7% occupancy of that site by iron atoms. These iron atoms result in a much lower reactivity of this material to both lithium insertion and removal. Thus, it reacts with only 0.3 mol of butyl lithium, and on reaction with bromine no lithium is removed from the lattice [14]. On heating the material to 700 °C with carbonaceous materials the iron becomes more ordered and electrochemical activity is observed [14]. However, the capacity even when carbon coated from sugar solution is significantly lower than that obtained from materials synthesized at elevated temperatures as will be shown below. We therefore conclude that for lithium iron phosphate hydrothermal synthesis is not a viable approach. Thus all the other studies described here were made on samples prepared at elevated temperatures.

The lithium iron phosphate prepared at 700 °C was completely analyzed before use. X-ray analysis of the  $\text{LiFePO}_4$  showed it to be single phase. On heating in oxygen a weight gain of 5.0% was observed very close to the expected 5.1% for all ferrous in the sample. The sample was a dark gray color, different from the pale green color of the hydrothermally synthesized material. An X-ray Rietveld refinement indicated no extra electron density on the lithium site, indicating no iron disorder, and gave the following parameters:

$$\text{SG } Pnma, \quad a = 10.333 \text{ \AA}, \quad b = 6.011 \text{ \AA}, \\ c = 4.696 \text{ \AA}, \quad R_1 = 2.53\%, \quad R_p = 15.17\%$$

These are totally consistent with those of the Thomas group [34]. The electrical resistance of the sample, measured on a pressed pellet, was between  $10^5$  and  $10^6 \Omega\text{cm}$ . This relatively low resistance is not unexpected, because the starting materials were only reagent grade and the iron probably has 1–2% other metals in it.

As reported earlier [14],  $\text{LiFePO}_4$  reacts with 2 mol of butyl lithium, which is consistent with the formation of lithium phosphate and iron metal. The lithium iron phosphate was therefore tested under over-discharge conditions to see what impact on capacity over-discharge would have. The data is shown in Fig. 4, and clearly indicates that severe capacity loss is found. Thus, these lithium iron phosphate

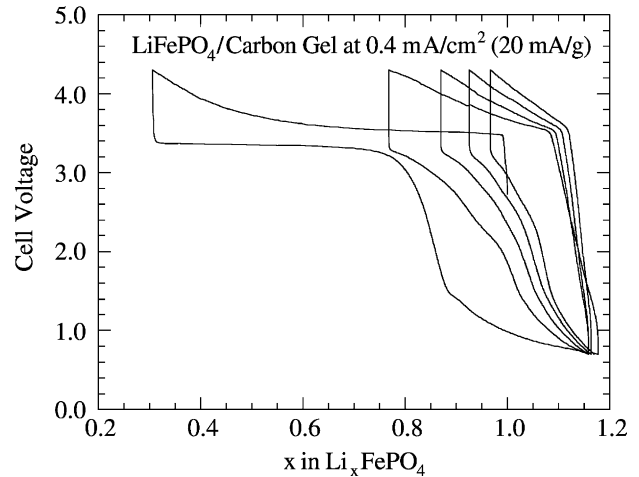


Fig. 4. Electrochemical cycling of  $\text{LiFePO}_4$  showing the impact of discharging it to 1 V. Cycling rate is  $0.4 \text{ mA/cm}^2$  and a carbon gel coating was used on the  $\text{LiFePO}_4$ .

cells will require over-discharge protection in commercial applications.

On complete lithium removal from  $\text{LiFePO}_4$ , an orthorhombic form of  $\text{FePO}_4$  is formed which is isostructural with the mineral heterosite,  $\text{Fe}_{0.65}\text{Mn}_{0.35}\text{PO}_4$ . There are at least three other crystalline forms of  $\text{FePO}_4$ , trigonal  $\text{FePO}_4$  which has a quartz-like structure with all the cations in tetrahedral coordination, and monoclinic and orthorhombic forms formed from the corresponding hydrates [35]. All these forms of  $\text{FePO}_4$  as well as amorphous  $\text{FePO}_4$  convert to the trigonal form on heating [14,18,35]. In the case of the  $\text{FePO}_4$  from  $\text{LiFePO}_4$  this transformation is slow and does not go to completion until over 500 °C. Thus, it would appear that this material will be kinetically stable in a battery environment. However, care must be taken to ensure that in any synthesis no free  $\text{FePO}_4$  is present, otherwise the trigonal form will be formed on heating. Moreover, at high temperatures the trigonal  $\text{FePO}_4$  appears to grow a glassy phase on the surface [36] that has no electrochemical activity [14].

The capacity of lithium iron phosphate was determined, and the data at 60 °C and room temperature is shown in Fig. 5 for a current density of  $1 \text{ mA/cm}^2$ . At 60 °C close to the theoretical capacity can be obtained. After the first two cycles the temperature was dropped to around 21 °C, and capacity loss can be seen at both deep charge and discharge consistent with an ionic diffusion limited process, or with loss of contact with some particles. Exactly the same behavior is seen at room temperature, if the initial current density is  $0.1 \text{ mA/cm}^2$  and it is then increased to  $1 \text{ mA/cm}^2$ . This is again indicative of a diffusion limited process, and is consistent with the Thomas model for incomplete material utilization [37].

Much of the electrochemical evaluation of  $\text{LiFePO}_4$  in lithium cells has been done at rather low cathode loading levels, 5–20  $\text{mg/cm}^2$ . For large commercial batteries, the loading is likely to be much higher to limit the cost and

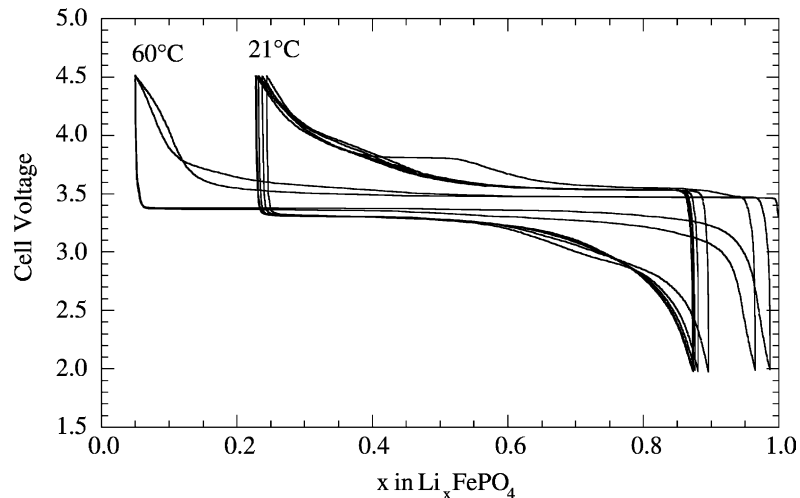


Fig. 5. Electrochemical cycling of a Li/LiFePO<sub>4</sub> cell at 60 and 21 °C both at 1 mA/cm<sup>2</sup>. The first two cycles are at 60 °C and the subsequent ones are at room temperature. A similar behavior is observed when the first two cycles were run at 0.1 mA/cm<sup>2</sup> and the subsequent ones at 1 mA/cm<sup>2</sup>.

volume of the inert components, such as current collectors. LiFePO<sub>4</sub> is unlikely to find significant use in volume limited applications, such as cell phones and lap-top computers because its volumetric energy density even at 100% utilization is inferior to the present entrenched commercial LiCoO<sub>2</sub>-based cells. Fig. 6 shows the cycling of a cell at 1 mA/cm<sup>2</sup> where the cathode loading is 55 mg/cm<sup>2</sup>. The capacity obtained is about 70% of the theoretical based on 1Li/Fe, and little capacity loss is observed on extensive cycling (about 25% over 100 cycles in non-optimized

cathodes). Fig. 7 shows the impact of varying the loading. Little change is observed in the capacity. For loadings much below 20 mg/cm<sup>2</sup>, pressed Exmet™ cathodes are not the optimum geometry, and we observe lower and sometimes irreproducible results. For these loading levels, coated foil cathodes are probably preferable. We can therefore conclude that cathode loading levels do not impact the obtained capacity in the range up to 80 mg/cm<sup>2</sup>.

A critical issue with these cathodes is the electronic conductivity of the LiFePO<sub>4</sub> itself. In the material prepared

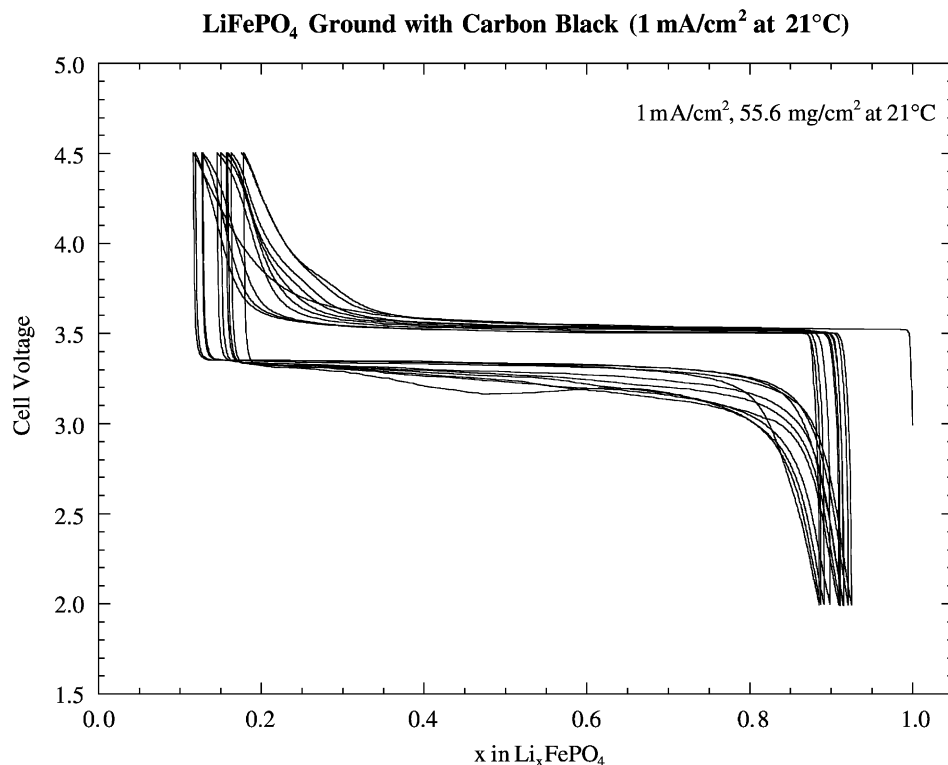


Fig. 6. Electrochemical performance of a LiFePO<sub>4</sub> cell at high loading, 55.6 mg/cm<sup>2</sup>, at 1 mA/cm<sup>2</sup> when ground with carbon black.

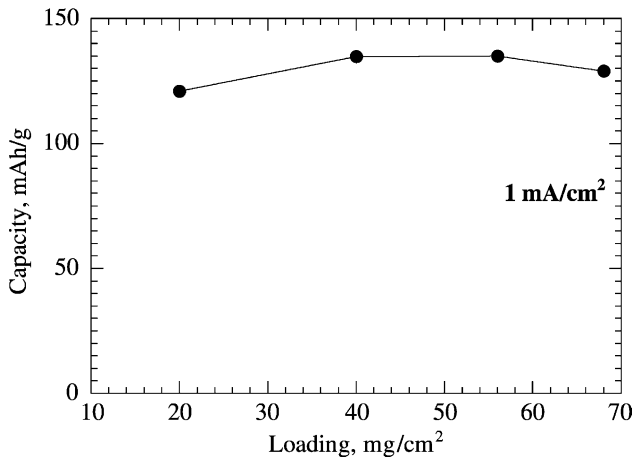


Fig. 7. Impact of cathode loading on capacity of LiFePO<sub>4</sub> cells at 1 mA/cm<sup>2</sup> at room temperature.

here from reagent grade starting compounds it is in the range of  $10^{-5}$  to  $10^{-6}$  S/cm. Padhi et al. [10] recognized this as maybe the capacity limiting step, and Ravet et al. [12] proposed an in situ formed carbon coating, for example from sugar decomposition, to solve the problem. Huang et al. [16] subsequently proposed coating the material with carbon-gel also during the synthesis step and found capacities approaching 100% at very low cathode loadings, 5 mg/cm<sup>2</sup>, and rather high carbon contents, 20%. Masquelier et al. proposed [38] extensive milling of the material with carbon and then found high capacities at elevated temperatures. To better determine the impact of the carbon addition method of the obtained capacity, we evaluated cathodes made by four different methods: grinding with carbon black, coating with sugar, the carbon gel approach, and an aqueous gelatin carbon method following the technique of Dominko et al. [21]. The results are shown as the mean capacity of the first five cycles in Fig. 8 as a function of current density. The charge and discharge currents were the same in each case.

For the carbon black results, no difference was observed for carbon loadings from 6 to 15 wt.%, except that the polarization observed was slightly higher at 6 wt.%. For carbon black loadings of 5 wt.% significantly lower capacities were observed; however, coating optimization, such as particle size, grinding time, etc. may determine the critical lower limit. The one sample coated with sugar was a hydrothermally prepared sample that was subsequently fired with sugar solution so may not be typical of all sugar coatings. This hydrothermal sample had a particle size of around 3  $\mu$ m [13], smaller than the 20  $\mu$ m reported by Yamada et al. [11] for materials prepared at high temperatures; the high temperature samples prepared here had particles sizes varying from well under 1 to over 5  $\mu$ m. Thus, we do not believe particle size plays any role in the poor performance of the hydrothermal sample. The overall results shown in Fig. 8 suggest that there is no measurable difference between the samples with carbon added by the different techniques. In fact, the data shown for 1 mA/cm<sup>2</sup> shows that the scatter from sample to sample (for example, different LiFePO<sub>4</sub> loading levels) is more critical than the carbon addition procedure. These data also indicate that 100% capacity can be achieved at 0.1 mA/cm<sup>2</sup>, and upwards of 80% at 1 mA/cm<sup>2</sup>; engineering optimization of cells should still further increase these rate and capacity capabilities.

The low density of LiFePO<sub>4</sub> results in a low volumetric density, and so it is critical that the minimum volume of carbon and Teflon be used in the electrode. Taking the density of LiFePO<sub>4</sub>, Teflon and carbon black as 3.6 g/cm<sup>3</sup>, 2.2 g/cm<sup>3</sup> and 1.8 g/cm<sup>3</sup>, respectively, then an electrode containing 10 wt.% carbon and 5 wt.% Teflon, will have a volumetric energy density 25% less than the theoretical value. This assumes that all the particles pack equally efficiently, which is unlikely to be the case with the poor packing associated with carbon, particularly with decomposed sugar.

Several studies [18,35,39–41] have been reported on a number of other iron phosphates including amorphous and

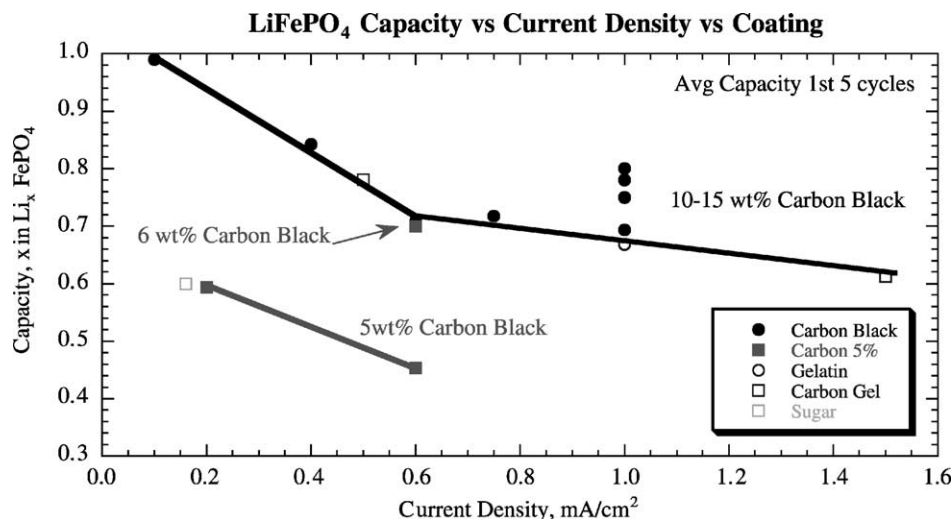


Fig. 8. Impact of carbon-based conductive diluent added to the LiFePO<sub>4</sub> particles on electrochemical performance as a function of the discharge rate.

crystalline  $\text{FePO}_4 \cdot n\text{H}_2\text{O}$  and Giniite [42]. This work will not be further described here, except to note that capacities approaching 1Li/Fe can be obtained and that the capacity can be maintained over extensive cycling. However, in almost all cases [35] the crystalline density, 2.6–3.1 g/cm<sup>3</sup>, is significantly less than that, 3.7 g/cm<sup>3</sup>, of  $\text{LiFePO}_4$  itself, which will still further decrease the already low volumetric storage capacity. So it is unlikely that such materials will find general use.

#### 4. Conclusions

Lithium iron phosphate cathodes can be readily cycled up to at least 1 mA/cm<sup>2</sup> at room temperature with over 70% theoretical capacity. The means of adding the conductive carbon diluent appears not to be important, but may have a deleterious impact on the volumetric energy density. The orthorhombic iron phosphate is thermodynamically unstable but kinetically stable relative to the trigonal quartz form. Lithium iron phosphate on over-discharge loses capacity due to the formation of lithium phosphate. The layered nickel manganese oxides appear to be best described as manganese stabilized nickel dioxides and have a higher capacity than the iron phosphate; they also have a significantly higher volumetric energy density due to their more compact structures, 140% (on an Ah/cm<sup>3</sup> basis) and 165% (on a kWh/cm<sup>3</sup> basis) relative to  $\text{LiFePO}_4$  at 1 mA/cm<sup>2</sup> and 21 °C. The stabilized  $\delta$ -phase vanadium oxides have still higher capacities, 180 and 140% relative to  $\text{LiFePO}_4$  on an Ah/cm<sup>3</sup> and Wh/cm<sup>3</sup> basis, respectively, but these come at a lower cell voltage.

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