

Phospho-Olivine as Advanced Cathode Material for Lithium Batteries

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Abstract

Nano-sized and micron-sized LiFePO₄ electrode materials were prepared by a sol gel and coprecipitation reactions. An improvement of the cycling and rate performances in lithium cells was observed for the carbon coated LiFePO₄ materials. The coating process uses a solid/gas-phase reaction which consists of decomposing propylene gas, as carbon source, inside a reactor containing olivine LiFePO₄ materials. Optimized LiFePO₄ electrode cells, cycled at RT between 3.0 and 4.3 V at a C/10 rate, do not show any sign of capacity fade during the first 50 cycles. Combination of the high volumetric energy density and low cost preparation method makes the micron-sized LiFePO₄ olivine an attractive safe cathode for lithium-ion batteries.

Introduction

Lithium iron oxide compounds had been extensively investigated as cathode materials for lithium batteries during the last decade [1-3]. The aim was to search for new positive electrode materials that can replace LiCoO₂ because of cost and safety issues. LiFeO₂ was prepared by ionic exchange with α -NaFeO₂ but was found metastable and then had led to non-conclusive battery performance [4]. α -FeOOH (Akaganeite) has an attractive open structure with large tunnels [5]. However, the insertion of lithium ions in the material occurs at lower potential with poor reversibility. From a structural standpoint, the antagonist change of the bond structure in iron oxide materials seems to reasonably predict the operating electrochemical potential of Fe⁴⁺/Fe³⁺ and Fe³⁺/Fe²⁺ redox couples. Indeed, Fe⁴⁺/Fe³⁺ couple tends to lie too far below the Fermi level of metallic lithium. On the contrary, Fe³⁺/Fe²⁺ couple tends to lie too close to it, which lowers the voltage to non-useful limits. To reduce the margin of this antagonist

effect, Goodenough et al. [2-3] introduced phosphorus in order to reduce the covalency of the Fe-O bond that faces stronger covalent P-O bonds. Since then, interest in phosphate compounds as insertion material for lithium batteries has led to a large number of studies [2-3, 6-9].

Lithium extraction from the phospho-olivine LiFePO₄ occurs at a constant voltage 3.45 V and gives rise to FePO₄ at the end of the oxidation of all divalent iron ions. The theoretical capacity value is 170mAh/g, and experimentally, 95% of this capacity can be achieved. The electrochemical stability of this system is not altered by the generation of Fe³⁺ ions unlike when highly oxidizing Ni⁴⁺ ions are involved during the charge of LiMO₂ (M= Ni, Co) layered material [10-11]. Moreover, the voltage window in the case the olivine is not so high as to accelerate the electrolyte aging, and not so slow as to sacrifice the energy density of the cell. Also, the material is much less prone to thermal runaway and is inexpensive and environmentally benign. Since cost and abuse tolerance are critical measures in an overall battery product, it is important to improve the cycling characteristics of LiFePO₄, to allow it to gain wide acceptance in the lithium-ion battery market. Performance improvements over uncoated

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electrodes were observed in this study, and the chemical/physical characterization of these coatings has provided insight into the morphology and conductivity improvement mechanism of the carbon-coated LiFePO₄.

Experimental

Nanosized LiFePO₄ was first prepared by a solid-state reaction involving a mixture of iron(II) oxalate, ammonium di-hydrogen phosphate, and lithium carbonate in a stoichiometric molar ratio (1:1:1). The precursors were mixed overnight by ball milling in acetone. The obtained gel was first dried at 60 °C under vacuum, then thoroughly reground, before being heated under purified N₂ gas for 24 h at 700 °C. Micron-sized LiFePO₄ powders were synthesized via co-precipitation by reacting iron nitrate nonahydrate and phosphoric acid. Aqueous of 1:1 molar ratio solution of 2M concentration were pumped into a continuously stirred tank reactor. Then, FePO₄ hydrate immediately started to form as the chelating solution NH₄OH solution was pumped into the reactor. The obtained precursor was mixed with a stoichiometric amount of Li₂CO₃, and then calcined for 15 h at 700 °C in a furnace purged with an Ar/H₂ mixture.

The resulting LiFePO₄ powder was subsequently coated with a carbon film using a gas-phase decomposition process. The general technique consists of feeding a mixture of N₂ and propylene, C₃H₆, as the carbon source gas into a preheated reactor furnace containing the olivine material. The temperature for decomposing C₃H₆ gas and depositing a few mono-layers of carbon at the surface of olivine particle was set at 700 °C. Thermal gravimetry analysis showed that the carbon amount was typically around 3 wt.% of the final olivine composite material.

Powder X-ray diffraction (Siemens D5000 diffractometer) was used to analyze the crystal structure and the phase composition of the lithiated compounds. Cu-K α was used as the radiation source. The samples were scanned from 2 θ =10° to 100° at a slow scan rate of 20s per 0.02°.

The scanning electron microscope (SEM, Hitachi S-4700-II) at the Electron Microscopy Center at Argonne National Laboratory was used to analyze the sample morphology and surface cross section. The chemical composition of the studied samples were checked quantitatively by inductively

coupled plasma /atomic emission spectrometry (ICP/AES) within a 5% measurement uncertainty.

Electrochemical measurements were carried out on CR2032-type coin cells (1.6 cm²). The positive electrodes were made of 80 wt.% active oxide materials, 10 wt.% acetylene black as the conductive agent, and 10 wt.% polyvinylidene difluoride binder. In the case of the carbon coated olivine material, no additional carbon black was added during the preparation of the electrodes. The electrolyte was 1.2M LiPF₆ dissolved in a (3:7 volume ratio) mixture of ethylene carbonate and ethyl methyl carbonate. The cells were assembled with lithium metal as the negative electrode and were tested in the voltage ranges of 2.5-4.3 V.

Results and discussion

Fig. 1 shows the x-ray diffraction patterns of LiFePO₄ olivine before and after the carbon coating experiment. The x-ray diffraction peaks for LiFePO₄ can be indexed in the orthorhombic system (space group Pnma) with cell parameters: a = 5.983, b = 10.289, and c = 4.670 Å. After the carbon coating process, the olivine structure was maintained with no evidence of impurities that may be caused by the reduction of iron during the coating process (Fig.1). In LiFePO₄, divalent iron atoms occupy corner-sharing octahedral running as planes parallel to c axis whereas lithium atoms occupy chains of edge-sharing octahedra parallel to c axis (Fig.2). The [PO₄] tetrahedra connect the lithium octahedral and forms along with iron octahedra available spaces for lithium mobility. Fig. 3 shows an SEM photograph of nano-sized and micron-sized LiFePO₄ materials studied here. The average particle size of the olivine material was around ~200 nm for the nano-sized LiFePO₄ and 5 μ m for the micron-sized LiFePO₄. The packing densities of these materials were 0.6 g/cm³ (nano-sized material) and 1.5 g/cm³ (micron-sized material).

Rationale for carbon coating using a vapor-phase process was the improvement in electrical conductivity at the surface of LiFePO₄ material. The vapor-phase process allowed a smooth continuous film of carbon to be deposited. Furthermore, since it is a gas-solid reaction, the gas can penetrate and coat inner pore areas of the powder. This effective carbon-coating process requires less weight percentage of total carbon in the electrode, thus offering an advantage over solution deposition methods that would typically

require a greater weight percent of carbon loading during electrode processing. Note that the amount of carbon in the final electrodes was only about 3 wt.% which is equal to the amount of carbon that coated the material during the decomposition of the propylene gas. Performance improvements over uncoated electrodes were observed in this study.

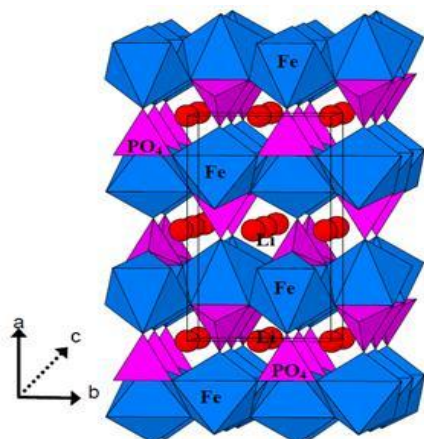


Fig. 1. Spatial representation of the LiFePO_4 structure

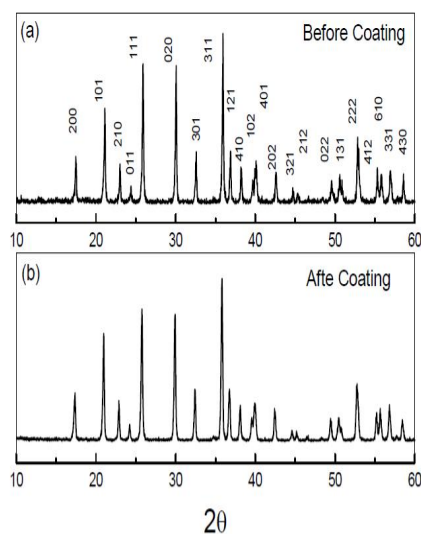


Fig. 2. X-ray patterns of (a) uncoated LiFePO_4 and (b) carbon coated LiFePO_4

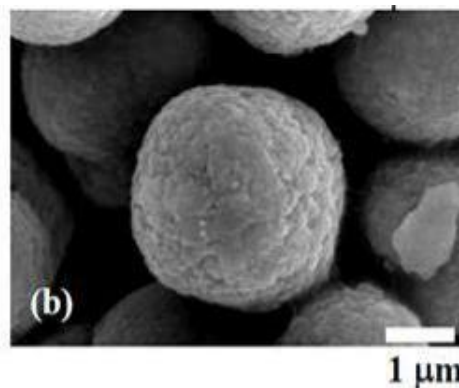
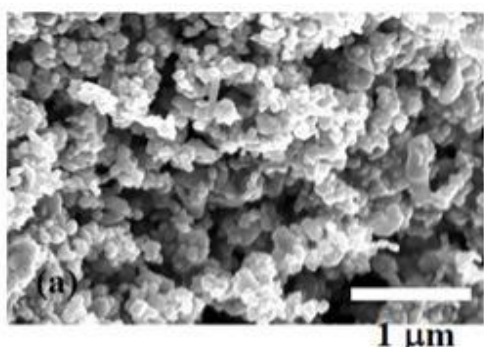


Fig. 3. SEM images of nano-sized LiFePO_4 and micron-sized LiFePO_4

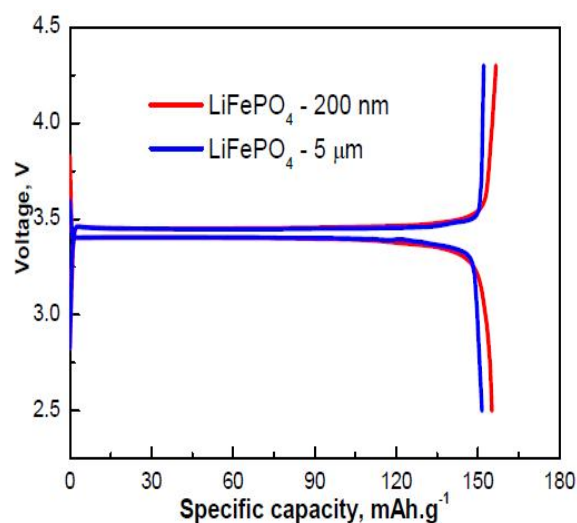


Fig. 4. Voltage vs. specific capacity of nano-sized and micron-sized LiFePO_4

Fig. 4 shows typical charge and discharge curves of nano-sized and micron-sized LiFePO_4 cell with a lithium metal counter electrode. The cell showed capacities of 150 mAh/g at C/10 rate which is comparable to the reported performance from other carbon coated olivine obtained by different methods [12-17]. The only difference in the cells is that in our electrode, no carbon black additive was added during the process of making the electrodes while most of the performance related to other carbon coated olivine was carried out in electrodes that contained between 10 to 15% additional carbon black additive. The cells based on our nano-sized and micron-sized LiFePO_4 materials shows also excellent cycleability at room temperature with no capacity fade after 70 cycles indicating stable electrochemical properties (Fig. 5). In this case, the cells were cycle at the C/10 rate within a voltage window of 2.5 to 3.7V.

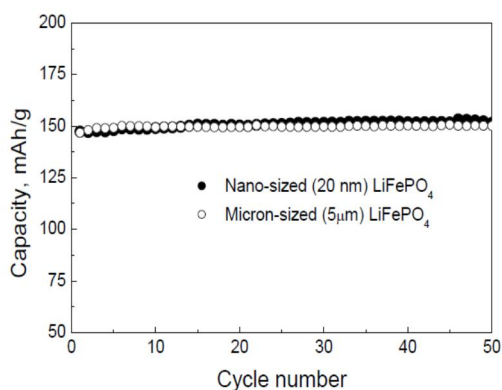


Fig. 5. Cycling performance of nano-sized and micron-sized LiFePO_4

The approach of synthesizing nano-sized and micron-sized LiFePO_4 is based on enhancing the power capability of latter without jeopardizing its volumetric energy density. In general, the electrochemical performance of an electro-active material strongly depends upon not only its intrinsic properties such as the chemical composition and crystalline structure, but also its textural and morphological properties, which are greatly dependent on the fabrication methods available in the field of materials science. Primarily because of their physical properties, nano-sized LiFePO_4 provides a higher electro-active surface for faster lithium ions diffusion whereas micron-sized LiFePO_4 provides a higher packing density for greater energy storage. Because both nano-sized and micron-sized LiFePO_4 delivered similar specific capacities (~ 150 mAh/g), the volumetric energy density depends upon the value of the packing density and is expected to be much greater in the case of the micron-sized material, i.e. 310 Wh/L (nano-sized material) and 775 Wh/L (micron-sized material).

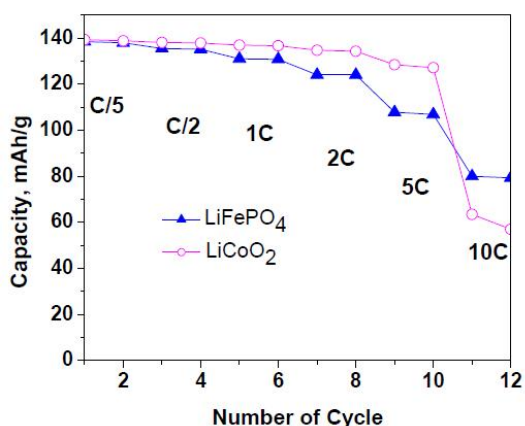


Fig. 6. Rate capability of carbon coated LiFePO_4 compared to LiCoO_2 electrode

Fig.6 shows the rate capability of carbon-coated LiFePO_4 material compared to the commercially available LiCoO_2 . The cells were cycled twice starting from under C/5 to 10C rates. The coated- LiFePO_4 exhibited better capacity retention under the 10C rate which attests to the effectiveness of the carbon coating process in improving the overall electronic conductivity of LiFePO_4 .

Conclusion

Here, we have introduced an inexpensive route to make nano-sized and micron-sized LiFePO_4 and easy carbon coating technique for the LiFePO_4 material. We have also demonstrated that the olivine (Pnma LiFePO_4) structure is not affected by the coating process. The optimized olivine electrode delivers a capacity of 150 mAh/g at room temperature. The micron-sized LiFePO_4 has a packing density of 1.5 g/cm³ which will translate into a higher active material loading and energy density in the full-size battery.

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