

## Urgency of LiFePO<sub>4</sub> as cathode material for Li-ion batteries

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**Abstract.** The energy crisis involving depletion of fossil fuel resource is not the sole driving force for developing renewable energy technologies. Another driving force is the ever increasing concerns on the air quality of our planet, associated with the continuous and dramatic increase of the concentration of greenhouse gas (mainly carbon dioxide) emissions. The internal combustion engine is a major source of distributed CO<sub>2</sub> emissions caused by combustion of gasoline derived largely from fossil fuel. Another major source of CO<sub>2</sub> is the combustion of fossil fuels to produce electricity. New technologies for generating electricity from sources that do not emit CO<sub>2</sub>, such as water, solar, wind, and nuclear, together with the advent of plug-in hybrid electric vehicles (PHEV) and even all-electric vehicles (EVs), offer the potential of alleviating our present problem. Therefore, the relevant technologies in LiFePO<sub>4</sub> as cathode material for Li-ion batteries suitable to the friendly environment are reviewed aim to provide the vital information about the growing field for energies to minimize the potential environmental risks.

**Keywords:** LiFePO<sub>4</sub>; cathode material; Li-ion batteries; nanotechnology

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### 1. Introduction

The three principal alternatives to fossil fuels as an energy source are nuclear, solar, and wind energy. Each of these requires energy storage, and the most versatile way to store energy is as chemical energy. Therefore, the major challenge ahead is the development of effective electronic energy storage (EES) systems (Basic research needs for electronic energy storage 2007, Wikipedia encyclopedia, Goodenough 2007, Armand and Tarascon 2008). Today's EES devices, typically chemical storage (batteries) or electrochemical capacitors (ECs), are not capable of meeting the increasing demand, not to mention the energy storage requirements of the coming future. Portable EES in the form of rechargeable batteries powers the wireless revolution in cellular telephones and laptop computers. With some technical problem solved, it is now enabling the successful development of hybrid electric vehicle (HEV). These developments have stimulated an international race to achieve the PHEV (plug-in hybrid electric vehicles), which would allow commuters to drive to work solely by stored electric power charged from the grid during off-peak hours. However, current battery technology provides only limited vehicle performance and driving range-fewer than 50 miles between charging cycles. Enhanced EES devices are needed to make

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abundant Fe resources in nature (Tarascon and Armand 2001). Most importantly, electrochemical extraction of lithium from the  $\text{LiFePO}_4$  phase is accompanied by a direct transition to the isostructural  $\text{FePO}_4$  (heterosite) phase, in which the  $\text{Fe}^{2+}$  ions are oxidized to  $\text{Fe}^{3+}$ , leaving the olivine framework intact. Thus there is no structural change upon lithium insertion and extraction. The Fe-P-O bonds in  $\text{LiFePO}_4$  are stronger than the Co-O bonds in  $\text{LiCoO}_2$  and thus the oxygen atoms are much harder to remove which consequently leads to a higher stability upon short-circuit, overheating, etc. Only under extreme heating (generally over 800 °C) breakdown occurs.

Therefore,  $\text{LiFePO}_4$  is intrinsically more stable against overcharge or short circuit conditions and has the ability to withstand high temperature operation without decomposing, firing or explosion that sometimes would happen in  $\text{LiCoO}_2$  batteries. As a result,  $\text{LiFePO}_4$  technology possesses excellent safety characteristics which are critically important for EVs and are fundamentally superior to other types of lithium-ion batteries. Furthermore,  $\text{LiFePO}_4$  does not contain any toxic elements. The advantages of traditional lithium-ion coupled with the safety features of phosphates, make  $\text{LiFePO}_4$  technology the most promising power supply for the future EVs (Table 1).

#### 4. Problems encountered and solutions proposed for $\text{LiFePO}_4$

In the lithium metal oxides with either a layered ( $\text{LiMO}_2$ , M = Co, Ni, Mn) or a spinel ( $\text{LiM}_2\text{O}_4$ , M = Mn, Ni) structure, a cubic-close-packed oxygen array provides an edge-sharing network of octahedra for the transition metal ions (Thackeray 2002). These materials are good lithium-ion conductors and they both have inherent good electronic conductivity, two attributes that are essential for providing cells with acceptable energy and power. In particular, the presence of mixed-valent cations, for example,  $\text{Co}^{4+/3+}$  ions in  $\text{Li}_{1-x}\text{CoO}_2$  and  $\text{Mn}^{4+/3+}$  in  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  for  $0 < x < 1$  contributes significantly to the inherent electronic conductivity of the electrodes during charge and discharge. In these structures, electron transfer occurs between the mixed-valent cations on the edge-shared octahedral array. By contrast, the cation arrangement in olivine structure typified by  $\text{LiFePO}_4$  differs significantly from that in the layered and spinel structures (Fig. 1). There is no continuous network of  $\text{FeO}_6$  edge-shared octahedral that might contribute to electronic conductivity; instead, the divalent  $\text{Fe}^{2+}$  ions occupy corner-shared octahedra. During the electrochemical lithium insertion and extraction, the resulting phases,  $\text{LiFePO}_4$  and  $\text{FePO}_4$ , are both poor electronic conductors because they each contain Fe cations with only one oxidation state (2+ or 3+, respectively). Therefore, the olivine-type  $\text{LiFePO}_4$  cathode materials encounter the principal drawback of poor rate capability resulting from its inherent low electronic conductivity ( $10^{-9} \sim 10^{-10} \text{ S.cm}^{-1}$ ) and low  $\text{Li}^+$  ions diffusion rate. This shortcoming has largely hindered its wide application (Whittingham 2004, Thackeray 2002).

To make commercial implementation of  $\text{LiFePO}_4$  materials, in the past few years, tremendous academic efforts have been devoted to tackle the poor rate problems. The important approaches for enhancing the real electronic conductivity include (1) surface coating of the  $\text{LiFePO}_4$  particles with a thin layer of conductive material (carbon (Ravet *et al.* 2001, Chen and Dahn 2002, Wilcox *et al.* 2007), silver (Park *et al.* 2004, Mi *et al.* 2008, Chen *et al.* 2004, Croce *et al.* 2002), or copper (Caballero *et al.* 2006, Morales *et al.* 2007)); (2) making homogeneous composites with conductive polymers, for instance polyacene (PAS) (Xie *et al.* 2006) and polypyrrole (PPy) (Huang and Goodenough 2008, Wang *et al.* 2008, Huang *et al.* 2006, Park *et al.* 2007); (3) formation of nano-or micro-porous structured  $\text{LiFePO}_4/\text{C}$  particles by using sol-gel methods





















