



A Novel Concept for the Synthesis of an Improved LiFePO_4 Lithium Battery Cathode

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This paper describes the synthesis and the properties of a kinetically improved LiFePO_4 cathode material. The novel aspect of the synthesis is based on a critical step involving the dispersion of metal (e.g., copper or silver) at a very low concentration (1 wt %). This metal addition does not affect the structure of the cathode but considerably improves its kinetics in terms of capacity delivery and cycle life. Such an enhancement of the electrochemical properties has been ascribed to a reduction of the particle size and to an increase of the bulk intra- and interparticle electronic conductivity of LiFePO_4 , both effects being promoted by the finely dispersed metal powders. This improved conductivity favors the response of LiFePO_4 , thus substantiating its interest as new cathode for advanced lithium ion batteries.

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Among the several materials under development for use as cathodes in lithium ion batteries, the LiFePO_4 of the phospho-olivine family proposed by Goodenough and co-workers¹ appears particularly interesting due to the low cost and the environmental compatibility of its basic constituents. On the other hand, this cathode may be affected by a loss of capacity with increasing current density, associated with diffusion-controlled kinetics of the electrochemical process.¹ Ways to bypass the above-mentioned kinetic limitations may consist in operating at medium-high temperature. We have demonstrated the validity of this approach by reporting high rate performance of a lithium polymer battery based on a nanocomposite membrane as the polymer electrolyte and on the LiFePO_4 phospho-olivine as the cathode.² However, due to the obvious temperature constraints, this approach cannot be practically extended to lithium ion batteries directed to a wide market.

Another way of improving the rate performance of the LiFePO_4 material is that of enhancing its ionic/electronic conductivity by suitable preparation procedures. This strategy has been first suggested by Armand and co-workers,^{3,4} who reported improvement in kinetics of the electrochemical reaction following the addition of an electronically conductive substance during the synthesis. This approach has been followed by other authors.^{5,6} Recently, Yamada *et al.*⁷ have shown that the control of the annealing temperature and, thus, ultimately of the particle size, is a crucial condition for assuring high performance of the LiFePO_4 cathode material.

These literature results clearly indicate the critical importance of providing a proper morphology of LiFePO_4 to assure its performance as an effective cathode in lithium cells. In this paper we propose to improve the electrochemical kinetics of the LiFePO_4 electrode by a specifically designed preparation procedure that considers the dispersion of low particle size metal (copper or silver, respectively) powders during the sol-gel formation of the LiFePO_4 particles. The basic idea is that these metal powders may act as nucleation sites for the growth of the LiFePO_4 particles, helping in obtaining samples with low and uniform size, as well as in enhancing their overall electronic conductivity.

To date, the enhancement of the kinetics of the LiFePO_4 powder electrode has been attempted by carbon dispersion and/or by carbon coating³⁻⁶ and, to our knowledge, the metal dispersion approach has never been proposed for improving the performance of this important electrode material. The results reported in this paper, although

preliminary, are convincing in demonstrating that this new type of "metal-added" LiFePO_4 cathode shows unique properties in terms of cycle life and rate capabilities.

Experimental

The LiFePO_4 cathode samples were obtained by a sol-gel route using either acetates or nitrates as precursors. The main strategies used in our laboratory for the sol-gel preparation of lithium-ion electrode materials have been described in a previous publication.⁸ For the synthesis of the material discussed in this work, a solution of $\text{Li}(\text{OH})$ and $\text{Fe}(\text{NO}_3)_3$ was first added to ascorbic acid and then to H_3PO_4 . Note that, due its peculiar reducing and complexing properties, the ascorbic acid is able to reduce Fe^{3+} to Fe^{2+} at this step of the preparation route, this in turn allowing to avoid the use of the generally very expensive Fe^{2+} precursors otherwise necessary to assure the proper course of the synthesis.

The pH of the resulting solution was adjusted by addition of ammonia. Then metal (copper or silver, respectively, Aldrich pure products, 0.1 μm average particle size, 1 wt %) powder was dispersed in the solution and a gel was obtained by heating at 60°C. This gel was further heated at 350°C for 12 h under nitrogen flux to prevent iron(II) oxidation. The powder was then annealed at 800°C for 24 h, still under nitrogen flux, to obtain the final metal-added LiFePO_4 samples. Metal-free samples were also prepared with the same procedure for comparison purposes.

Depending on the synthesis conditions, the particle size of the final LiFePO_4 powder samples were within a few micrometers. This is shown in Fig. 1, which reports a typical high-resolution scanning electron microscopy (HRSEM) photograph of an Ag-added LiFePO_4 sample.

X-ray powder analysis of the metal-added samples showed an absence of parasitic peaks and good correspondence with the reference LiFePO_4 pattern, demonstrating that single phase with no evidence of impurity compounds are obtained and, thus, that the low content of added metal does not modify the ordered olivine structure of the lithium iron phosphate. Further investigation by high resolution X-ray analysis, as well as by energy dispersive X-ray spectrometry (EDS), confirmed that copper and silver, respectively, are in the metallic form and dispersed as submicrometric particles.

The electrodes for the electrochemical tests were assembled in a film-type configuration by casting on an aluminum current collector a *N*-methylpyrrolidone (NMP) slurry of the LiFePO_4 active material (85 wt %) mixed with a carbon (M.M.M. Carbon Belgium Super P, 12 wt %) conductive additive and a poly(vinyl difluoride) PVdF, Solvay Solef 6020, 3 wt %) binder.

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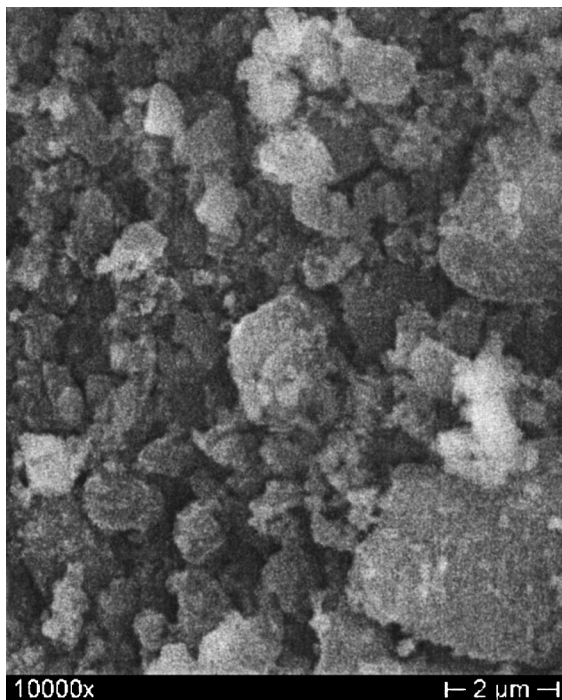


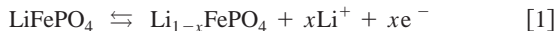
Figure 1. HRSEM image of a silver-added LiFePO₄ powder sample.

These film-type LiFePO₄ electrodes were assembled in electrochemical cells with a lithium metal counter electrode (and, occasionally, a lithium metal reference electrode) separated by a felt imbedded by an electrolyte consisting of a 1 M LiClO₄ solution in an ethylene carbonate-diethyl carbonate, EC-DEC (1:1) mixture.

The assembly of the cell prototypes was carried out in an environmentally controlled dry box. The cathode performance was investigated in terms of cyclic voltammetry (CV), charge-discharge curves, and cycle life. The CV tests were run by standard electrochemical equipment and the cycling tests by a Maccor Battery Cycler instrument.

Results and Discussion

As shown by Goodenough and co-workers,¹ the electrochemical process of LiFePO₄ may be described as a two-phase redox reaction of the type



where the maximum exchange of 1 mol of Li per formula unit ($x = 1$) corresponds to a theoretical specific capacity of 170 mAh g⁻¹.

Figure 2 shows a low-rate (5 μA), quasi-thermodynamic charge-discharge cycle of a standard LiFePO₄ electrode. The trend is similar to that commonly reported for this electrode,^{1,9,10} *i.e.*, a flat voltage profile that evolves around 3.45 V vs. Li, which in turn is representative of an electrochemical process based on the coexistence of the two structurally similar phases. However, and again as typically reported,¹ even at this low rate the amount of cycled lithium is limited to $x = 0.7$, this corresponding to a capacity of 120 mAh g⁻¹, *i.e.*, well below the theoretical capacity. These poor kinetics are associated with the fact that the electrochemical reaction involves a first-order transition from LiFePO₄ (triphylite) to FePO₄ (heterosite), these two phases coexisting in single material particles. The associated lithium extraction process is accompanied by the movement of the interface between the two phases and a limit may be reached where the process becomes controlled by the diffusion of lithium across the relatively small free volume in the triphylite

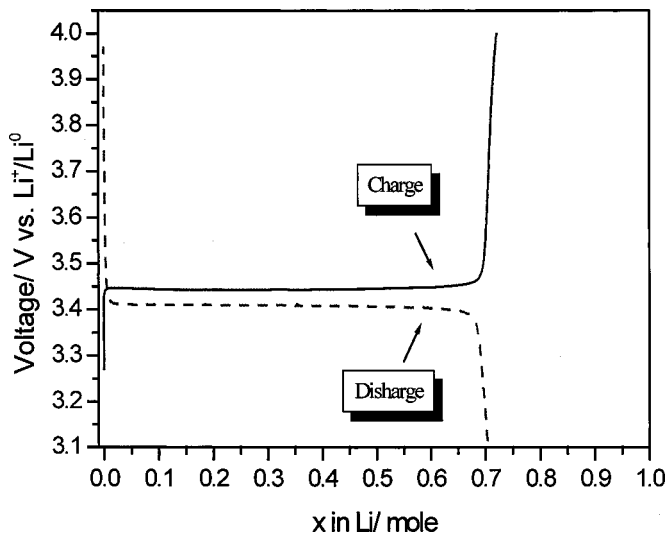


Figure 2. Charge-discharge cycle of a “standard” LiFePO₄ electrode at room temperature and at 5 μA. Li counter electrode. LiClO₄ EC-DEC (1:1) electrolyte.

framework.¹ In addition, and as pointed out by various authors,^{1,4,10} the electronic conductivity of Li_{1-x}FePO₄ progressively decreases as the value of x increases and this also contributes to limit the extent and the rate of the overall electrochemical process.

Figure 3 compares the low rate discharge of the above described common LiFePO₄ electrode with that of a Cu-added LiFePO₄ electrode. The increase in capacity when passing from the standard to the modified electrode is clearly shown; a change from 120 to 145 mAh g⁻¹ is observed. This difference is obviously associated with the presence of the metal, this confirming its role in optimizing the morphology of the LiFePO₄ electrode material and, thus, in enhancing the kinetics of its electrochemical process.

This proposed model requires further experimental control. It is difficult to obtain precise information by standard X-ray or SEM analysis due to the low content of the metallic powders as well as to their low particle size. However, preliminary results obtained by high resolution X-ray, as well as by EDS, have confirmed that the

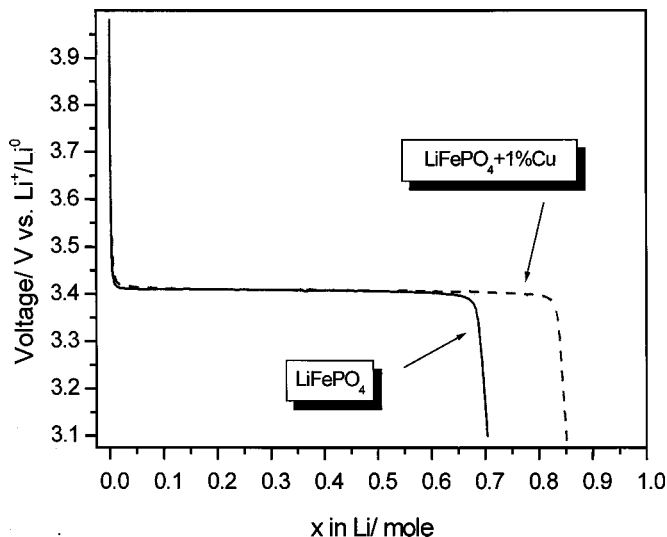


Figure 3. Discharge curves of a “standard” LiFePO₄ electrode and of a modified, Cu-added LiFePO₄ electrode at room temperature and at 5 μA. Li counter electrode. LiClO₄ EC-DEC (1:1) electrolyte.

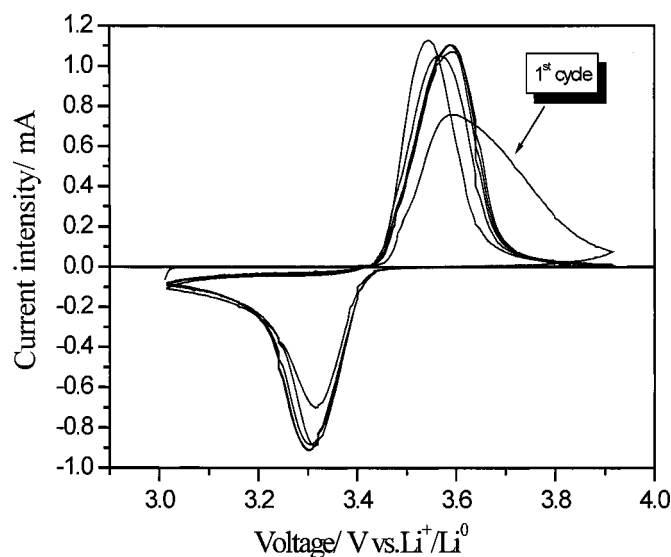


Figure 4. CV of a Cu-added LiFePO_4 electrode in a LiClO_4 EC-DEC (1:1) electrolyte cell. Li counter and reference electrodes. Room temperature. Scan rate 0.1 mV s^{-1} .

metallic powders are dispersed in the form of submicrometric particles in the LiFePO_4 mass. Figure 1, which shows an HRSEM analysis of a silver-added LiFePO_4 powder sample, confirms the distribution and the low particle size of the electrode.

Figure 4 shows a typical CV of a metal (Cu)-added LiFePO_4 cathode. While the reproducibility of the peaks is representative of the reversibility of the modified electrode, the 0.25 V separation between the anodic and cathodic peaks is representative of its good kinetics, especially considering that the electrochemical process involves diffusion of lithium ions in a solid phase and electron jumping across a poorly conducting compound.

These enhanced kinetics reflect in capacity improvement, as shown by Fig. 4, as well as in rate improvement, as shown by Fig. 5 that reports the capacity delivery during cycling at a C/5 rate of a Cu-added LiFePO_4 electrode, again in comparison with that delivered by a standard, metal-free electrode under similar conditions.

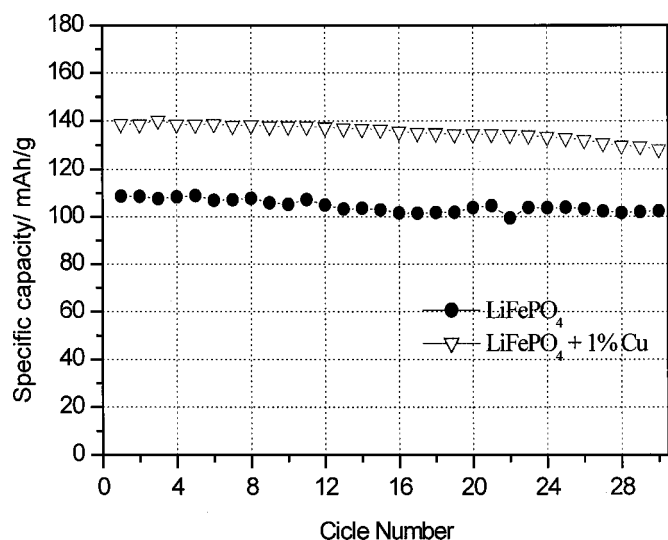


Figure 5. Capacity vs. cycle number of a “standard” LiFePO_4 electrode and of a modified, Cu-added LiFePO_4 electrode at room temperature and at C/5 rate. Li counter electrode. LiClO_4 EC-DEC (1:1) electrolyte.

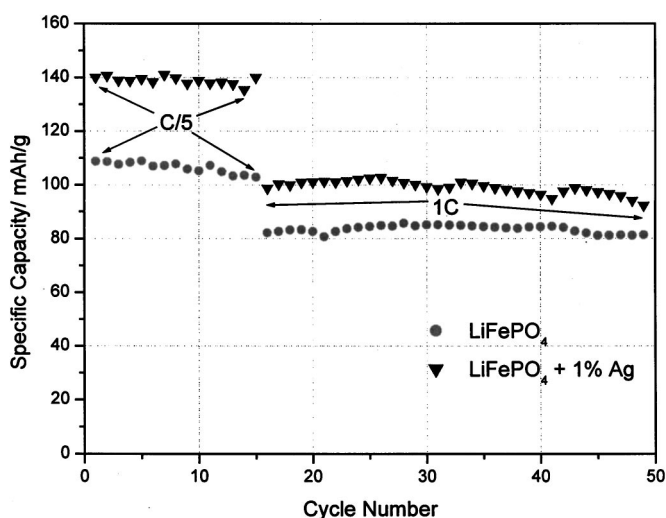


Figure 6. Capacity vs. cycle number of a “standard” LiFePO_4 electrode and of a modified, Ag-added LiFePO_4 electrode at room temperature and at C/5 and 1C rates. Li counter electrode. LiClO_4 EC-DEC (1:1) electrolyte.

The above results demonstrate that the new types of “metal-added” LiFePO_4 cathode show substantial improvements in capacity and in rate capabilities. The beneficial role of the dispersed metal powders may be tentatively explained by assuming that these powders act as nucleation sites for the growth of the LiFePO_4 compound, this helping in obtaining samples with low and uniform particle size, as well as in enhancing their overall electronic conductivity. In addition, the dispersion of the metal powders is also expected to provide contact bridges between the LiFePO_4 particles, this reducing the interparticle resistance and, thus, to assure the progress of the electrochemical reaction throughout the electrode mass.

The proposed electronic conductivity enhancement model although supported by the results reported in this paper, requires further work for the final confirmation. In addition, some concern may arise on the use of copper in view of its possible oxidation in course of long term operation.

Work is currently in progress in our laboratory to substantiate the model. A preliminary approach has been that of testing the effect induced by the dispersion of metals other and electrochemically more stable than copper, such as silver. In fact, if the action of the metal dispersion is the promotion of low particle size associated with the reduction of the LiFePO_4 interparticle resistance, one should expect to obtain the kinetics enhancement effect using any metal conductive additive other than copper. In addition, the use of silver should prevent any side oxidation phenomena. We have verified these assumptions by the synthesis and the characterization of Ag-added LiFePO_4 electrode samples. Figure 6 compares the capacity vs. cycle number for a Ag-added LiFePO_4 electrode in comparison with that provided by a standard, metal-free electrode under similar conditions. A capacity improvement is clearly shown both at medium (C/5) and, particularly, at high (1C) rates, this providing further support to the validity of the electronic conductivity enhancement model. In addition Fig. 6 shows that this improvement is maintained for a long number of cycles, this demonstrating the stability of the silver-added LiFePO_4 electrode.

Conclusion

The results reported demonstrate that the electrode response of the phospho-olivine LiFePO_4 electrode may be enhanced by the addition of dispersed metal powders during the course of a specially designed synthesis procedure. The metal dispersion does not affect the structure of the LiFePO_4 electrode material but it appears to

favor the growth of low size particles and to decrease the interparticle resistance. This in turn favors the progress of the electrochemical process throughout the bulk of the electrode with the final result of enhancing its overall capacity. This has been verified by using copper and silver, respectively, metal dispersions. In both cases, substantial capacity improvement has been experimentally demonstrated. Work is in progress in our laboratory to confirm the capacity enhancement model and to explore the relevance of the metal-added, modified LiFePO_4 electrodes for the development of advanced lithium-ion batteries. In this respect, particular attention will be devoted to the optimization of the metal dispersion, both in terms of the selection of the most favorable type of metal and of the determination of its most efficient loading.

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