

## Structural Effects of Carbonization of LiFePO<sub>4</sub> Nanoparticles

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Developing cathode materials with high energy densities is one of the key challenges for adopting the lithium-ion battery technology for green transportation. LiFePO<sub>4</sub> (LFP) is one of the prominent material used as the active element of the positive electrode in lithium-ion and/or polymer batteries. The presence of the poly-anion phosphate group is of great interest, because it insures that this compound is considerably more stable at the end of charging than the close-packed oxide cathode materials. However, LFP has disadvantages of low intrinsic electrical conductivity, poor Li<sup>+</sup>-ion transport and sensitivity to impurities. These major problems are currently overcome using efficient synthesis method and coating the particles with conductive carbon, so that capacities close to the theoretical predictions can be achieved [1].

In this work, we report the effect of carbonisation at the surface of LFP cathode materials prepared by hydrothermal (HT) steering-assisted method that maintained the solution agitation during the sample synthesis. The structural characterization of C-LFP, surface morphology and electrochemical cycling are studied as a function of the synthesis conditions.

Carbonisation of LFP nanoparticles was performed by mixing HTLFP and 10% lactose in aqueous solution for 5 min. After drying at 95°C under N<sub>2</sub> atmosphere, the slurries were heated at different steps of temperature up to 700°C with purge between each step.

The XRD diagrams of LFP samples before and after the carbonization are shown in Figs. 1-2. The carbon coating significantly decreases the amount of Li<sub>3</sub>PO<sub>4</sub> impurities (Fig. 1). Also, we note for most of the peaks a shift towards lower *d* spacing and, as expected, a small decrease (4.8%) of the crystallite size after carbonization at 700°C. Detailed XRD patterns of carbonized nanoparticles exhibit well-resolved the Bragg lines at ca. 2θ=73-74°. This is attributed to the better crystallinity of carbonized LFP nanoparticles. Also, it has been demonstrated that the carbon coating cures the disordered surface layer [2]. If the size of the

particles is further reduced, the surface over volume ratio is increased, and the effect is even more spectacular.

This effect is simply due to the fact that the “surface over volume” ratio, i.e. the ratio between the volumes occupied by the 3 nm-thick surface layer and the core region, increases when the size of the particle is reduced. For big particles where this surface over volume is negligible, the contribution of the surface layer to the electrochemical performance is negligible. However, for particles of diameter 40 nm, this surface over volume ratio is 0.11, which is non-negligible, and the contribution of the surface layer is responsible for lower specific capacity.

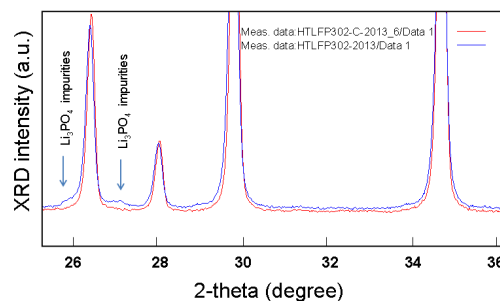


FIG. 1. XRD patterns showing the decrease of Li<sub>3</sub>PO<sub>4</sub> impurities for carbonized LFP nanoparticles.

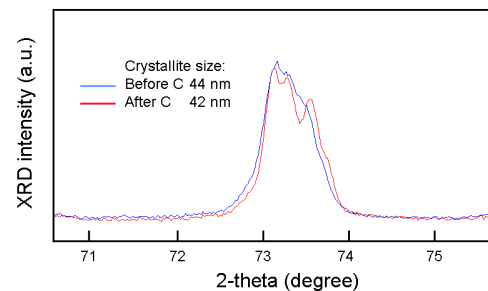


FIG. 2. XRD patterns showing the better crystallinity of carbonized LFP nanoparticles.

## References

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