

## A New Synthetic Route to Prepare LiFePO<sub>4</sub> with Enhanced Electrochemical Performance.

Pier Paolo Prosinì<sup>a,b</sup>, Maria Carewska<sup>a</sup>, Silvera Scaccia<sup>a</sup>, Mauro Pasquali<sup>b</sup>, Daniela Zane<sup>c</sup> and Stefano Passerini<sup>a</sup>.

<sup>a</sup> ENEA, Advanced Energy Technologies

C.R. Casaccia, Via Anguillarese 301, Rome 00060, Italy

<sup>b</sup> Dipartimento ICMMPM, Facoltà di Ingegneria,

Università di Roma "La Sapienza", Rome, Italy

<sup>c</sup> Centro Studio per l'Elettrochimica e la Chimica Fisica delle Interfasi, CNR, via C. Laurentiano 7, Rome, Italy.

In recent years, much effort has been made to identify new materials suitable for use as positive electrodes in rechargeable lithium-ion batteries. LiFePO<sub>4</sub> represents an excellent candidate: it is inexpensive, non-toxic, environmentally benign and has a theoretical specific capacity of 170 Ah kg<sup>-1</sup>. Padhi et al. [1] showed that lithium can be extracted from LiFePO<sub>4</sub> and inserted into FePO<sub>4</sub> along a flat potential at 3.5 V vs. Li. They found that the electrochemical extraction of lithium was limited to about 0.6 Li/formula unit. The capacity exhibited from the material was strictly related to the current density used. The observation that the capacity is restored when reducing the discharge current indicates that the loss in capacity is a diffusion-limited phenomenon within a single grain.

Ravet et al. [2] renewed the interest for LiFePO<sub>4</sub> reporting a new synthetic route leading to electronically conductive particles with outstanding electrochemical features.

Yamada et al. [3] investigated the cathode performance of LiFePO<sub>4</sub> as a function of the synthesis temperature. They found that the material synthesized at 550°C showed a reversible capacity at room temperature as high as 160 Ah kg<sup>-1</sup>, otherwise no other details about the discharge rate were given.

In this work we show a new synthetic route to prepare LiFePO<sub>4</sub>. Amorphous FePO<sub>4</sub> was used as precursor. It was obtained by spontaneous precipitation from equimolar aqueous solutions of Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, using hydrogen peroxide as oxidizing agent.

LiFePO<sub>4</sub> was obtained by chemical lithiation of the precursor. The TG/DTA curves of the lithiated compound are displayed in Fig. 1. Over the temperature range from ambient to 550 °C there is not appreciable weight loss in the TG curve. The corresponding DTA curve shows an exothermic effect at 470 °C that is related to the crystallization of the compound.

Crystalline LiFePO<sub>4</sub> was obtained by heating the amorphous compound at 550°C for 1h under reducing atmosphere. It showed enhanced electrochemical performance in terms of specific capacity and charge/discharge rate.

Figure 2 shows the voltage profiles as a function of the specific capacity for two different charge/discharge rates. The material was able to delivered about 140 Ah kg<sup>-1</sup> when discharged at 3C rate. The capacity increased at almost the full capacity when the discharge rate was set at C/10. The practical specific energy at this discharge rate was 530 Wh kg<sup>-1</sup>.

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## References

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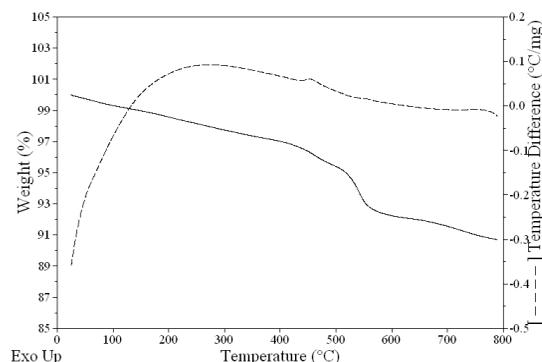


Figure 1. TG/DTA curves for amorphous lithium iron phosphate. Heating rate : 5°C min<sup>-1</sup> in flowing argon.

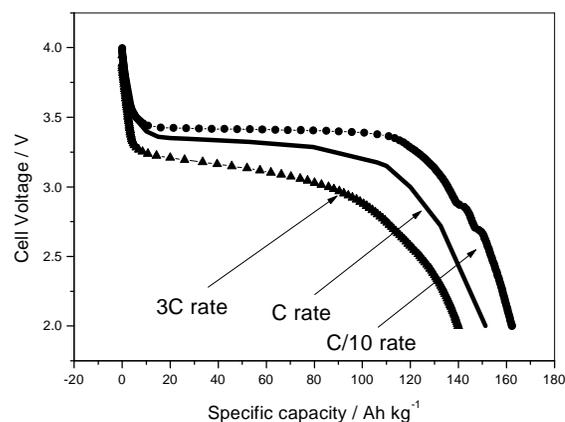


Figure 2. Voltage profile vs. specific capacity for a LiFePO<sub>4</sub> composite cathode under different charge/discharge conditions. Electrode composition: 70 wt. % LiFePO<sub>4</sub>, 20 wt. % carbon black, 10 wt. % teflon. Electrolyte: EC/DEC 1:1 LiPF<sub>6</sub> 1M. Current density: 4.5 mA cm<sup>-2</sup> (3C rate), 1.5 mA cm<sup>-2</sup> (C rate), and 0.15 mA cm<sup>-2</sup> (C/10 rate). Temperature: 20°C. The cathode loading of LiFePO<sub>4</sub> was 9.2 mg cm<sup>-2</sup>.