

# Characterisation and performance studies of a $\text{LiFePO}_4$ cathode material synthesized by microwave heating

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## Abstract

Lithium iron phosphate with incorporated carbon,  $\text{LiFePO}_4\text{-C}$ , was synthesized by the microwave-assisted method. X-ray diffraction analyses showed higher crystallization degrees for samples submitted to higher irradiation times. A particle-agglomerated morphology was associated as revealed by scanning electron microscopy. The electrochemical characteristics of a composite cathode containing the synthesized product were evaluated. The two-phase electrochemical process between  $\text{FePO}_4$  and  $\text{LiFePO}_4$  was evidenced in the cycling voltammogram profile and its reversibility and stability were demonstrated. An additional redox reversible reaction was revealed and assigned to another phosphate present in the synthesized product. The charge/discharge performance study indicated a good capacity retention after the initial cycles where capacity fading was associated to the resistance of a SEI film that forms and grows on the cathode's surface. Results obtained by electrochemical impedance analysis before and after cell's cycling are discussed.

**Keywords:**  $\text{LiFePO}_4$  cathode, nanocomposites, Li-ion batteries, Microwave heating, Charge-discharge cycles

## 1 Introduction

Among various energy storage technologies, rechargeable lithium-ion batteries have been considered as an effective solution to the increasing need for high-energy and power densities in electrochemical power sources. A battery cell with a  $\text{LiCoO}_2$  cathode was extensively used for portable applications. However, the toxicity and high cost of cobalt, the poor thermal stability that leads to safety hazards associated with battery fires and the limited availability in nature of the  $\text{LiCoO}_2$  and other lamellar compounds of the same family, have been the motivation for the research of novel cathode materials. Recently, due to its long lifespan, abundant resources, low toxicity and high thermal stability, the olivine lithium iron phosphate ( $\text{LiFePO}_4$ ) has emerged as the critical cathode material for applications such as large-scale power storage or electric transportation (e.g., electric vehicles and hybrid electric vehicles). This compound has also a high-lithium intercalation voltage (around 3.5 V vs.  $\text{Li/Li}^+$ ) and a large theoretical specific capacity ( $170 \text{ mAhg}^{-1}$ ) [1]. As a result, there is a large demand for the production of high-performance  $\text{LiFePO}_4$  powders. The limited low conductivity of pure  $\text{LiFePO}_4$  can be addressed by modifying the powders structure using novel fabrication technologies. Advantages requirements for a good synthetic method are low energy consumption cost and reduced processing time. Microwave processing is a self-heating process that occurs through the absorption of electromagnetic energy.

Since, the microwave energy is directly absorbed by the sample, uniform and rapid heating can be achieved within a short time period. The energy consumption and cost are lower than those required for furnace heating. In addition, it is a low temperature process with good repeatability, which does not require a reductive gas for the synthesis of  $\text{LiFePO}_4$ .

In the present work, a carbon  $\text{LiFePO}_4$  material obtained using a microwave assisted synthesis was incorporated into a two terminal Swagelok cell using a Li foil as anode and a Celgard membrane embedded in ionic liquid N-methyl-N-propylpyrrolidinium bis(fluorosulfonyl)imide (Py13-FSI) together with the lithium bistrifluoromethane-sulfonamide salt (LiTFSI) as electrolyte. Characterisation and battery performance tests results are discussed.

## 2 Experimental

The first step for the  $\text{LiFePO}_4$  synthesis with incorporated carbon was the mixing of precursors (ferrous oxalate, ammonium dihydrogen phosphate, lithium carbonate and dextrose - the source of carbon) by ball-milling with addition of a solvent (ethanol) for a generating dispersion, followed by solvent evaporation. It was used a value of 5.9 of BPR (*ball-to-powder* ratio) and a rotation speed of 300 rpm for 6 hours. Mixed precursors were then pelletized in several forms for the next step, the microwave heating, in order to get the carbon modified nanocrystalline  $\text{LiFePO}_4$  ( $\text{LiFePO}_4\text{-C}$ ). It was

used a modified domestic microwave oven for the heat treatment with an applied maximum power level of 500 W. The effects of microwave time and sample configuration were evaluated by the acquired results from X-ray diffraction analyses performed on each obtained product.

The product selected from the ones that originated the best synthesis results was incorporated in a composite cathode material (80%) with 15% of carbon and 5% of PVdF. A lithium secondary battery was then prepared with this cathode and with a metallic lithium foil as the anode. It was used as electrolyte, a membrane Celgard® 2400 with the ionic liquid N-methyl-N-propylpyrrolidinium bis (fluoro-sulfonyl)imide with the lithium bistrifluoromethanesulfonamide salt, Py13-FSI/LiTFSI. This set, anode (Li foil) / Celgard with electrolyte / cathode (composite with synthesized  $\text{LiFePO}_4\text{-C}$ ), was built and placed in a two terminal Swagelok cell for characterisation and battery performance tests.

The synthesized  $\text{LiFePO}_4\text{-C/LiTFSI-Py13-FSI}$  interface was also characterised by Electrochemical Impedance Spectroscopy (EIS). The EIS spectra were obtained by a Solartron 1250 Frequency Response Analyser coupled to a Solartron 1286 Electrochemical Interface in a 0.005-65000 Hz frequency range and with a sinusoidal excitation voltage applied to the cell of 5 mV rms. The equivalent circuit parameters were estimated by using Complex Non-Linear Squares fitting.

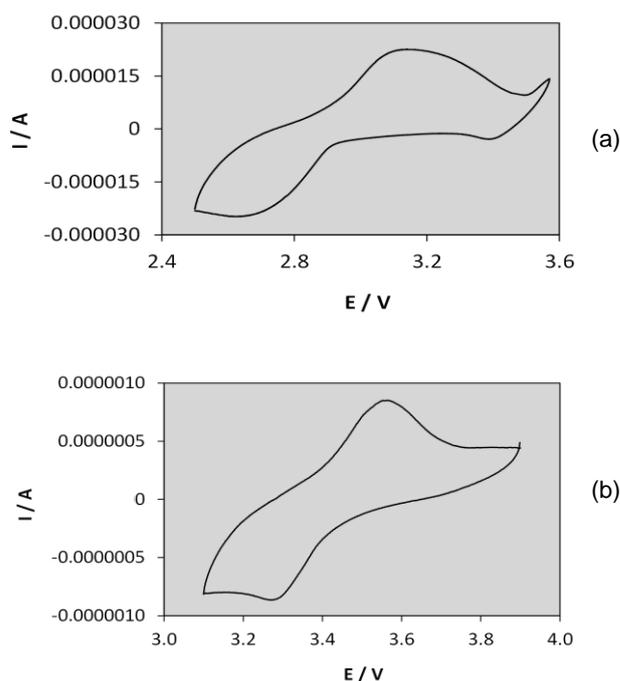
### 3 Results

For most experimental conditions tested, structural characterisation by X-ray diffraction proved that the olivine phase  $\text{LiFePO}_4$  was synthesized with a crystallisation degree depending on the microwave irradiation time, even though other crystalline phosphates were also obtained as sub-products. The materials synthesized with higher microwave times showed higher crystallisation degrees. Scanning electron microscopy (SEM) showed an uneven surface and, overall, a particle-agglomerated morphology with inhomogeneous particle size distribution. Smaller submicron particles with a size between 50 and 150 nm are bounded on the surface of larger ones (600 nm - 3  $\mu\text{m}$ ). Distributed in the sample are few fragments with sizes as big as 15  $\mu\text{m}$ , also with smaller particles on their surface.

Just after the Li /  $\text{LiFePO}_4$  cell preparation, EIS characterisation took place. Impedance spectra typically exhibited a depressed semicircle in the high frequency region, attributed to the electrode/electrolyte charge transfer process. A constant phase element was used instead of the double layer capacitance to account for the porous nature of the cathode. At lower frequencies, a

Warburg element was fitted corresponding to the solid-state diffusion of  $\text{Li}^+$  on the cathode.

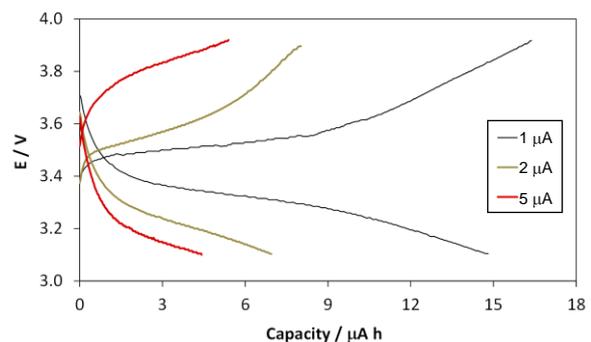
Cyclic voltammetry was also applied to the Swagelok cell in the 2.5 - 3.9 V potential range. The existence of two redox processes (Fig.1) was revealed and confirmed by galvanostatic charge and discharge tests. It is associated to Li ions intercalation to/extraction from two different compounds in the synthesized cathode product. One of them, the  $\text{LiFePO}_4$  with its expected two-phase electrochemical process between  $\text{FePO}_4$  and  $\text{LiFePO}_4$ , was evident in the 3.3-3.5 V potential range.



**Fig. 1.** Cyclic voltammograms of a synthesized  $\text{LiFePO}_4\text{-C}$  electrode measured with a scan rate of  $5\text{mVs}^{-1}$  in two different voltage potential ranges.  $E=2.5\text{-}3.6\text{ V}$  (a);  $E=3.1\text{-}3.9\text{ V}$  (b).

The good reversibility and stability of the  $\text{LiFePO}_4$  redox processes were established by results from continuous cycles of potentiodynamic tests.

The electrochemical performance of the  $\text{LiFePO}_4$  was evaluated, between 3.1 and 3.9 V, at room temperature, by galvanostatic charge and discharge measurements. Typical curves for different current values applied on cell cycling are presented in Fig. 2.



**Fig. 2.** Charge/discharge curves of the synthesized LiFePO<sub>4</sub>-C electrode at different applied currents.

The capacity loss occurring during the first few cycles performed at 2  $\mu\text{A}$  was attributed to possible losses of cycling lithium due to the growth of a SEI film that can be formed on the cathode's surface and consumes lithium. EIS analysis, done after cell cycling, confirmed the potential presence of this surface passivation layer. After about 9 cycles, the remaining reversible capacity was maintained up to the final performed cycle at that current. The coulombic efficiency presented, throughout all used discharge and charge rates, a value between 0.9 and 1.0, indicating good reversibility between the intercalation and extraction processes for all performed cycles. It was then inferred that the capacity decline with the current rate (or applied current) increase is not the result of damage, but rather reflects the lithium transport limitation in the LiFePO<sub>4</sub> compound.

Optimisation conditions for getting a better cathode material are put forward.

#### 4 Final Remarks

A LiFePO<sub>4</sub>-C composite cathode material was successfully synthesized using the microwave heating process, preceded by mixture and activation of precursors by ball-milling. SEM observations showed a surface presenting a particle-

agglomerated morphology with inhomogeneous particle size distribution.

The cathode electrochemical characterisation, performed between 2.5 and 3.9 V, revealed the existence of two redox processes in two different potential ranges, one of them belonging to the two-phase transformation between FePO<sub>4</sub> and LiFePO<sub>4</sub>.

Good reversibility was evidenced by the charge/discharge behaviour at different current rates applied to the test cell, with the coulombic efficiency presenting a value very close to unity.

Good capacity retention after 9 cycles performed at 2  $\mu\text{A}$ , with no noticeable fading after that, expresses the stability of the redox processes occurring in the battery cell. The cell impedance is almost constant thereafter and it is presumed that the formed SEI film stops growing.

Modifying the synthesis conditions, namely more rigorous atmosphere control minimizing oxygen and the quantity of carbon used for decreasing the particle size, while at the same time obtaining a LiFePO<sub>4</sub> compound with more homogeneous surface, are features to be taken into account in future work in order to get higher cell capacity values and rate capability improvement.

#### 5 Acknowledgements

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#### 6 References

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