

Performance of LiFePO_4/C and Carbon Fibers Composite as Cathodes in Lithium-ion Batteries and Battery Modeling

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Currently, the cathode material LiFePO_4/C is the most promising active material for high-power lithium-ion batteries for electric vehicle applications and it has been observed that its response is also dependent on the nature of the carbon used as support. This paper presents the preliminary results from the synthesis of LiFePO_4 supported on carbon fibers where phosphate and fibers are synthesized together at a single stage. The electrodes built with this material have a good electrochemical response with the typical behavior of LiFePO_4 . In addition, the behavior of these materials has been characterized from the viewpoint of the electrochemistry of charge/discharge processes in order to provide knowledge for the global modelling of batteries. A Battery Management System (BMS) is also currently being developed in order to control the operating conditions and the state of charge of Li-ion batteries. The development of a BMS requires an adequate modelling of the dynamic accumulation processes taking place in the battery. A general model has been derived and validated in terms of the experimental performance of a Li-ion battery and some results are presented below.

Introduction

The LiFePO_4/C composite is currently the most promising active material for cathodes of high-power lithium-ion batteries, mainly because of its composition (nontoxic), low price and good chemical and thermal stability during cycling. But it has been observed that the response of these materials is also dependent on the nature of the carbon used as support (1). In this paper we present the results of the preliminary synthesis of LiFePO_4 supported on carbon fibers wherein the phosphate and the carbon fibers are synthesized simultaneously in a single step. This is carried out by combining two synthesis techniques. One is the glycine-assisted combustion (2) and the other is the decomposition of porous polymers (3). Here cotton fibers were used as porous polymer that carbonizes during LiFePO_4 sintering at 750 °C under argon atmosphere. The material obtained was physically characterized (SEM, EDS, TEM) and electrochemically characterized by the usual techniques for lithium-ion battery electrodes (charge-discharge cycling, cyclic

voltammetry and EIS). Electrodes show a good response and the typical electrochemical behavior of these materials.

Experimental

Sample Preparation

The samples were prepared by solid-state glycine-assisted synthesis under argon flowing atmosphere, but the reagents were dissolved in water. An [0.5 M] aqueous solution of LiNO_3 , $\text{NH}_4\text{PO}_4\text{H}_2$, $\text{FeC}_6\text{H}_6\text{O}_7$ and glycine was totally absorbed on cotton fibers, transferred to the tube furnace, dried at 300°C for 5 h under Ar atmosphere and sintered at 750°C for 6 h. Afterwards, the sample was ground in a ball mill for 1 h. The samples were physically characterized by XRD, TEM, and SEM.

Electrochemical characterization

The electrodes for electrochemical measurements were prepared by mixing the prepared LiFePO_4/C composite with Super C carbon and PVDF binder in a weight ratio of 80:10:10 together with N-methyl-pyrrolidinone solvent. A thin layer of the mixture was coated by doctor blade on aluminum foil, dried and pressed. The experiments were performed in a metal three-electrode El-Cell® test cell assembled in Ar atmosphere glovebox with O_2 and H_2O concentration < 1ppm, using metallic lithium as counter and reference electrodes. The voltammograms were recorded at 0.1 mV/s, 1 mV/s and 10 mV/s between 2.7 V and 4.2 V. For charge/discharge cycles a current of 1 C was used, with cutoff potentials of 2.7 V and 4.2 V. The rate capability experiments were recorded with the same charge rate and cutoff potential with discharge rates C/5, C/2, C, 2C, 5C and 10 C. Electrochemical impedance spectroscopy was performed using 5 mV sine voltage excitation amplitude in the frequency range 10 kHz to 5 mHz. Measurements were made at various states of charge at OCV.

Results and discussion

As shown in Figure 1(a) the material obtained from the combination of both synthesis procedures maintains the fibrillar structure of the selected polymer (cotton fibers). This material is basically composed of carbon fibers that are decorated with LiFePO_4 particles as shown in more detail in Figure 2(a). From the EDS spectra, an atomic ratio P:Fe close to 1:1 is obtained, indicating that the stoichiometric ratio approaches that expected for LiFePO_4 (Figures 1(b) and 2(b)). Looking in detail at Figure 1(b) corresponding to the EDS spectrum of a broad field, the carbon content would be quite high compared with the optimum for this type of electrode. From the calcination of the samples, carbon content higher than 50% was determined. Initially this would imply that the electrodes prepared with these samples should provide a response with lower capacities than those expected for LiFePO_4/C electrodes.

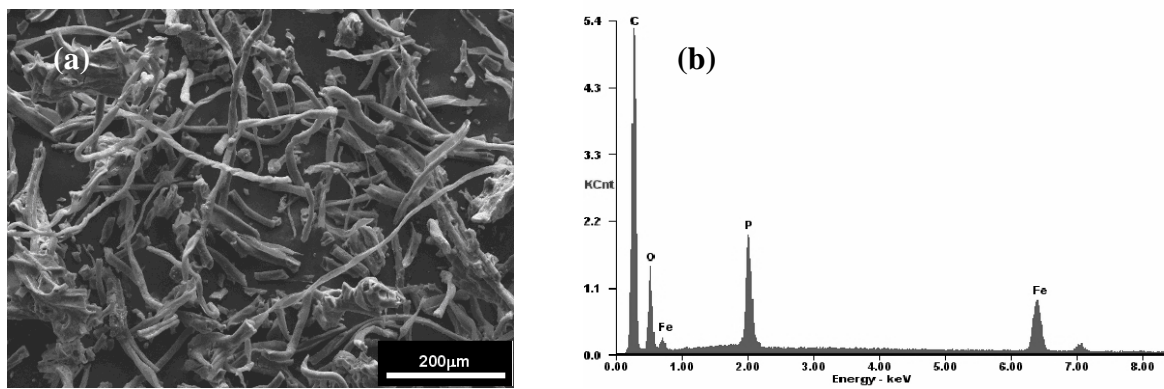


Figure 1. (a) SEM images of the obtained samples and (b) EDS spectra from the image.

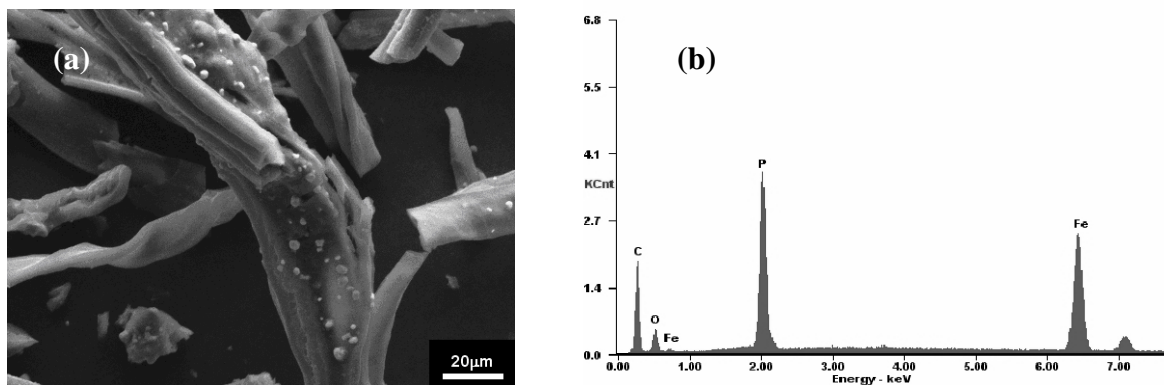


Figure 2. (a) SEM image with higher magnification and (b) EDS spectra from the image.

The electrodes show a plateau potential at 3.4 V with good cyclability (Figure 3), but the capacity was lower than that estimated for LiFePO_4 . This response was assumed taking into account the amount of carbon on the samples.

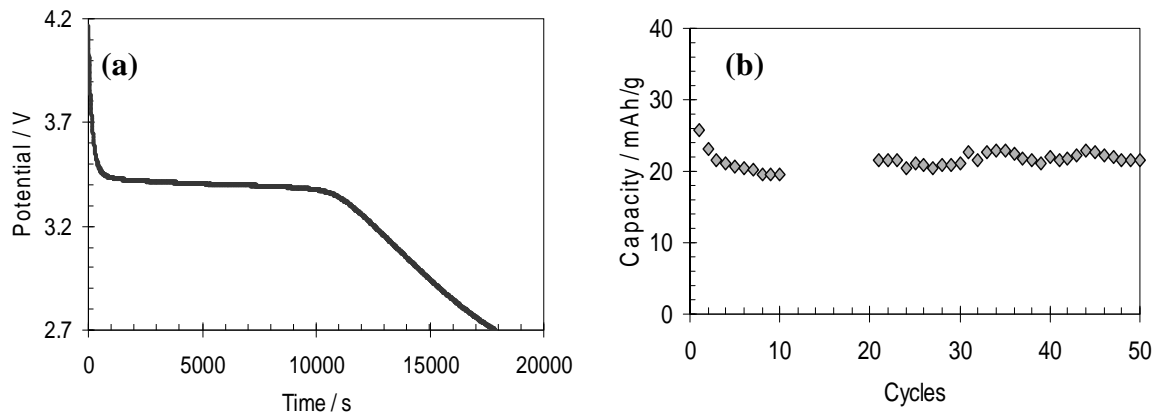


Figure 3. (a) Galvanostatic discharge at C/5 and (b) discharge capacity vs. cycles at 1C.

The reversibility and the kinetic behavior of these materials were the typical response of LiFePO_4/C because these experiments are not seriously influenced by the concentration of active material on the electrodes (Figure 4).

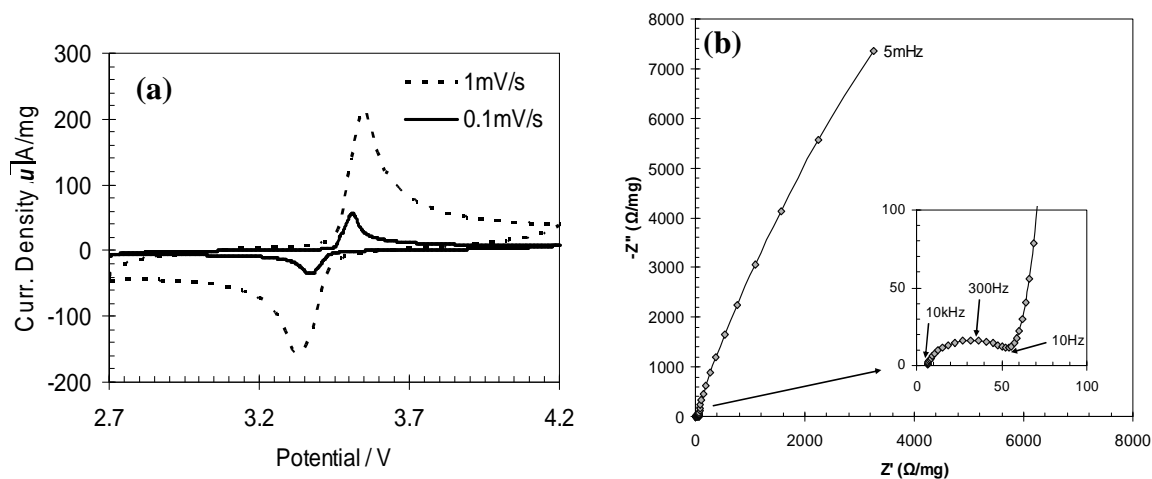


Figure 4. a) Cyclic Voltammograms at 0.1 and 1 mV/s at 25°C. b) EIS Nyquist diagrams at high frequencies and entire range of frequencies

Battery Model Formulation for BMS

A general model has been derived, which describes the accumulation process in the electrodes of a Li-ion battery as a series combination of a pure integrator and a high pass filter coupled to a static nonlinearity function, I_f (Butler-Volmer type equation). In the model only the dynamics of the controlling electrode is taken into account. This model has been validated in terms of the experimental performance of a Li-ion battery. Figure 5 depicts a scheme of the complete battery model. In the figure the term r accounts for the ohmic resistance between electrodes, $G(s)$ corresponds to the Laplace transform of the high pass filter, and $1/(Q_{max}s)$ is the Laplace transform of the integrator

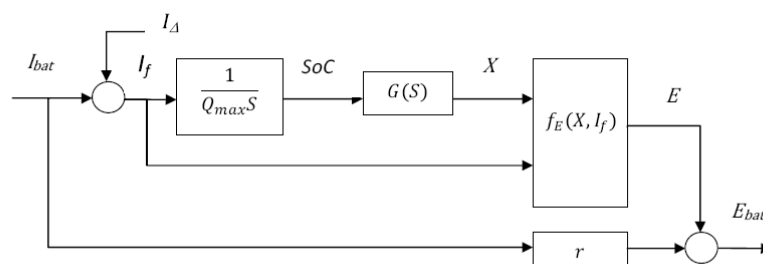


Figure 5. Battery Model

Figures 6 and 7 show a validation of the proposed model in terms of the simulation of the potential response to a given current perturbation signal using a commercial Li-ion battery.

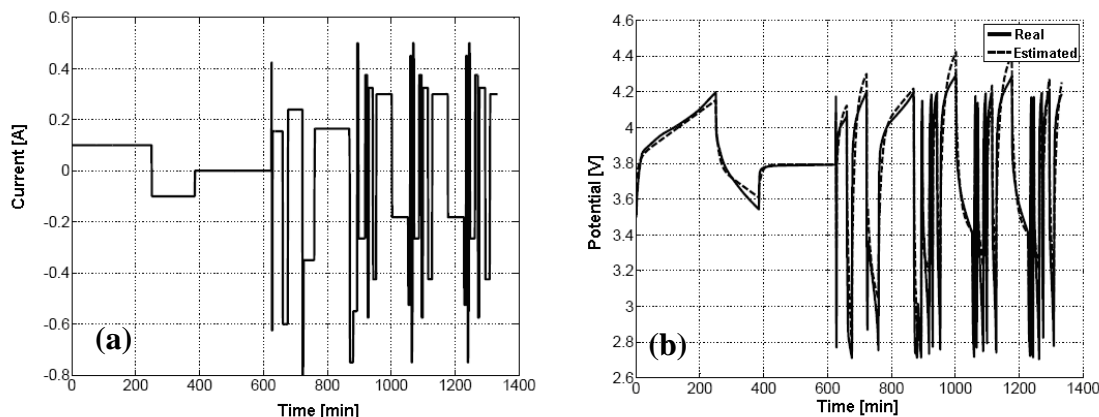


Figure 6. Study of commercial Li-ion battery: (a) applied current and (b) measured and predicted potential response.

Conclusions

This paper presents the preliminary results from the synthesis of LiFePO_4 supported on carbon fibers where phosphate and fibers are synthesized together at a single stage. Cotton fibers were used as porous polymer that carbonizes during LiFePO_4 sintering at $750\text{ }^\circ\text{C}$ under argon atmosphere. The electrodes built with this material have a good electrochemical response with the typical behavior of LiFePO_4 . Results have demonstrated that these materials have electrochemical properties comparable to those typically produced by the commercial method. A general model has been derived and validated in terms of the experimental performance of a Li-ion battery, some results are presented.

Acknowledgments

This work was supported by the Consejo Nacional de Investigaciones Científicas y Técnicas of Argentina, and the Agencia Nacional de Promoción Científica y Tecnológica. The authors thank the Innovation and Technology Transfer Project in Priority and Areas of the UNLP, GACR P102/10/2091 and the bilateral cooperation with the Faculty of Electrical Engineering and Communications, Brno University, Czech Republic.

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