



## Electrochemical kinetics of nanostructure LiFePO<sub>4</sub>/graphitic carbon electrodes



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### ABSTRACT

Lithium cation insertion/deinsertion reaction kinetics in a LiFePO<sub>4</sub> (LFP)/graphitic carbon composite material were electrochemically studied with a cavity microelectrode (CME). The LFP/graphitic carbon composite has a core LFP (crystalline/amorphous)/graphitic carbon shell structure. In the crystalline and amorphous LFP phase, different reaction mechanisms were observed and characterized. While the reaction mechanism in the crystalline LFP phase is controlled by Li<sup>+</sup> diffusion, the amorphous LFP phase shows a fast, surface-controlled, pseudocapacitive charge-storage mechanism. This pseudocapacitive behavior is extrinsic in origin since it comes from the presence of Fe<sup>3+</sup> defects in the structure. These features explain the ultrafast performance of the material which offers interesting opportunities as a positive electrode for assembling high power and high energy hybrid supercapacitors.

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### 1. Introduction

Electric double-layer capacitors (EDLCs) are energy storage devices offering extremely fast charging-discharging characteristics, remarkable stability and long cycle life [1]. Thus, EDLCs are mainly used in applications where instant power is required for short time [2]. However, the low energy density of EDLCs still limits their range of applications. A promising route to increase the energy density of supercapacitors is designing hybrid supercapacitors where an activated carbon electrode is combined with a fast, faradic charge storage electrode [3]. Pseudocapacitive materials with fast redox reactions confined at the surface of materials have been proposed as the faradic electrode, such as transition metal oxides [4–7] or two-dimensional transition metal carbides [8,9]. However, most of these pseudocapacitive materials operate in aqueous electrolytes, thus limiting their practical interest for high-energy supercapacitor applications. V<sub>2</sub>O<sub>5</sub> [10], H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> [11,12] and TiO<sub>2</sub>(B) [13,14] were among the first materials showing pseudocapacitive behavior in Li<sup>+</sup> containing nonaqueous electrolytes. Although high capacity (200 mAh g<sup>-1</sup>) was obtained, cyclability and power performance are still a concern [15]. More recently, the fast pseudocapacitive behavior of orthorhombic Nb<sub>2</sub>O<sub>5</sub> was identified in

nonaqueous electrolyte, which was explained by a Li<sup>+</sup> pseudo-intercalation mechanism [16]. The high discharge rates (up to 1000 C) make this material interesting as a negative electrode for hybrid devices [17].

Recently, we used the ultracentrifugation technique to prepare a LiFePO<sub>4</sub> (LFP)/graphitic carbon composite material. This material showed ultrafast charge/discharge rates (35 mAh g<sup>-1</sup> at 300 C), comparable to activated carbons used in EDLCs [18]. LFP/graphitic carbon composite has a core LFP (crystalline/amorphous)/graphitic carbon shell structure that offers both high reversibility and high rate capability. Unlike conventional LFP where Li<sup>+</sup> intercalation is achieved at constant potential through a two-phase reaction mechanism, the galvanostatic charge/discharge profile of the composite showed different electrochemical signatures. Three various regions were observed: one plateau at a constant potential of 3.4 V corresponding to the crystalline LFP phase and two sloping profiles below and above 3.4 V corresponding to amorphous LFP containing Fe<sup>3+</sup> defects and graphitic carbon phases, respectively [18]. The Li<sup>+</sup> diffusion coefficient in the sloping potential region of the amorphous LFP phase (10<sup>-11</sup> cm<sup>2</sup> s<sup>-1</sup>) was found to be two orders of magnitude higher than that of crystalline LFP core phase (10<sup>-13</sup> cm<sup>2</sup> s<sup>-1</sup>). Such a high Li<sup>+</sup> diffusivity was assumed to be mainly responsible for the high rate capability of the composite but the charge storage mechanisms in the different potential regions have still to be understood. In this paper, the electrochemical kinetics of LFP/graphitic carbon composite was investigated using the cavity microelectrode

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(CME) technique [19]. We identified two different behaviors and kinetic regimes. The  $\text{Li}^+$  intercalation in the core crystalline LFP phase is a diffusion-limited process while a surface charge storage pseudocapacitive mechanism drives the kinetics in the sloping potential region. This fast, extrinsic pseudocapacitive process originating from the presence of  $\text{Fe}^{3+}$  defects in the amorphous LFP phase [18] explains the high power performance of the LFP/graphitic carbon composite.

## 2. Experimental

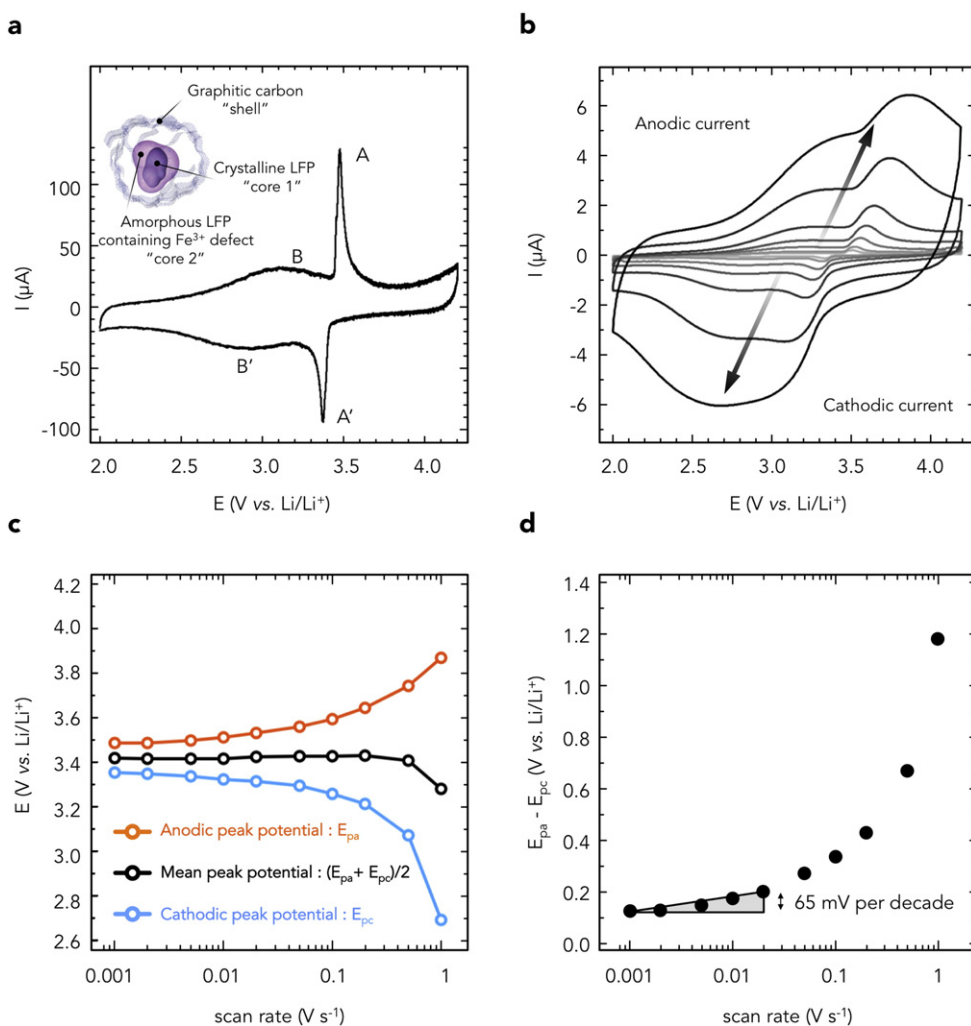
The synthesis procedure of the LFP/graphitic carbon composite using ultracentrifugation technique [20] was reported elsewhere [18]. The electrochemical tests with CME were performed at room temperature in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) containing 1.0 M of  $\text{LiPF}_6$ , which was purchased from KISHIDA CHEMCAL Co., Ltd. (battery grade). The CME consists of a thin platinum wire ( $\Phi = 60 \mu\text{m}$ ) with a cavity of  $30 \mu\text{m} \Phi$  and  $40 \mu\text{m}$  deep sealed in a glass [19].

## 3. Results and discussion

Fig. 1a (inset) shows a schematic of the prepared LFP composite material [18]. The core of the composite contains a nanocrystalline LFP phase (core 1) surrounded by an amorphous LFP phase containing

$\text{Fe}^{3+}$  defect (core 2). Fig. 1a shows the cyclic voltammogram (CV) for LFP/graphitic carbon composite in a two-electrode cell at a low scan rate of  $0.1 \text{ mV s}^{-1}$  in the 2.0 V–4.2 V potential range. The set of redox peaks (peak A and A') observed at 3.4 V vs.  $\text{Li/Li}^+$  corresponds to the core crystalline LFP phase. Below 3.4 V, the CV is characterized by the presence of two redox waves at about 3 V (peak B and B'), leading to a symmetric, capacitive-like CV signature where the charge changes with the applied potential. Previous *in-situ* XAFS measurements have shown a continuous change in the oxidation state of Fe in this potential range [18]. Accordingly, the electrochemical signature can be assigned, in a first approach, to a pseudocapacitive behavior. This pseudocapacitive behavior is extrinsic in origin, since it is related to the presence of  $\text{Fe}^{3+}$  defects in the structure [15,21,22]. The capacitive current observed below 2.5 V and beyond 3.4 V corresponds to the double-layer capacitance of the graphitic carbon shell, since no change in the oxidation state of Fe was observed [18]; it accounts for about 25% of the total capacity.

The LFP/graphitic carbon composite was studied using a CME in a three-electrode mode configuration, at various scan rates from 10 to  $1000 \text{ mV s}^{-1}$  (Fig. 1b). Even at  $1000 \text{ mV s}^{-1}$ , both set of peaks A and B can be observed despite a merging of two peaks at such high scan rates. Fig. 1c shows the changes of the peak potentials (A and A') as a function of the scan rate. The peak separation ( $E_{\text{pa}} - E_{\text{pc}}$ ) is 132 mV at  $1 \text{ mV s}^{-1}$  and increases with the scan rate with a slope of about



**Fig. 1.** (a) Cyclic voltammogram of  $\text{LiFePO}_4/\text{graphitic carbon}$  at  $0.1 \text{ mV s}^{-1}$  in 1 M  $\text{LiPF}_6$  EC + DEC (vol 1:1) electrolyte using coin-type-cell configuration, where Li foil was used as a negative electrode. (b) Cyclic voltammograms of  $\text{LiFePO}_4/\text{graphitic carbon}$  at 10, 20, 50, 100, 200, 500,  $1000 \text{ mV s}^{-1}$  in same electrolyte using cavity microelectrode. A  $1 \text{ cm}^2$  rolled platinum foil and a piece of lithium metal were used as a counter and reference electrodes, respectively. (c) Changes of the anodic (orange) and cathodic (blue) peak potentials, and mean peak potential ( $= (E_{\text{pa}} + E_{\text{pc}})/2$ , black) as a function of the scan rate. (d) Change of the peak separation ( $E_{\text{pa}} - E_{\text{pc}}$ ) as a function of the scan rate.

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