



Full paper

Origin of phase inhomogeneity in lithium iron phosphate during carbon coating

Yulong Liu^a, Jiajun Wang^a, Jian Liu^a, Mohammad Norouzi Banis^a, Biwei Xiao^a, Andrew Lushington^a, Wei Xiao^{a,b}, Ruying Li^a, Tsun-Kong Sham^b, Guoxian Liang^{c,*}, Xueliang Sun^{a,*}

^a Department of Mechanical and Materials Engineering, Western University, London, Ontario, Canada N6A 5B9

^b Department of Chemistry, Western University, London, Ontario, Canada N6A 5B7

^c Johnson Matthey Battery Materials Ltd., 280 Ave. Liberté, Candiac, Quebec, Canada J5R 6X1

ARTICLE INFO

Keywords:

LiFePO₄

Carbon coating

Secondary phase

Phase change

Lithium ion battery

ABSTRACT

Phase purity plays a vital role in achieving high capacity and long cycle life for lithium iron phosphate. Given that LiFePO₄ has lower electronic and ionic conductivity, carbon coating on fine particle surface is often used in order to improve the electrochemical performance of LiFePO₄. Unfortunately, the carbon coating process is an inherently reducing process that is difficult to control and often results in the over-reduction of LiFePO₄, turning it into iron phosphide. Our research here demonstrates the formation of a non-conductive Fe₂P₂O₇ phase during the carbon coating process on LiFePO₄. This phase formation is found to be dependent on particle size, temperature, and annealing atmosphere. Furthermore, these changes are found to directly associate with the change of the reducing potential. The finding in this work aims to guide and control the phase purity of carbon coated LiFePO₄ by identifying important parameters that need to be taken under consideration during the carbon coating process in an effort to realize excellent electrochemical performance.

1. Introduction

Carbon surface coating has been widely applied to lithium iron phosphate (LFP) for lithium ion batteries in order to improve electronic conductivity as well as provide favourable surface chemistry [1]. LFP, possessing an intrinsically lower electronic conductivity of 10⁻⁹ S cm⁻¹, has been effectively improved by carbon coating [2,3]. Since pioneering work conducted by Ravet et al. demonstrates excellent electrochemical performance after carbon coating on the LFP, [4,5] research in this field has attracted great attentions. Most reports are focused on the understanding the influence of carbon coating on bulk LFP rather than surface effects [5–8]. However, changes to stoichiometry and/or the formation of secondary phases on the surface/interface of LFP have been unclear due to the complex nature of the carbon coating procedure [9–12]. This process comprises of several reactions occurring simultaneously and is reliant on many factors such as volatility of lithium, [13,14] deposition/diffusion of carbon, [15,16] and redox of iron and/or phosphors [17]. Given the electrochemical importance of secondary phases, researchers have attempted to synthesize the LFP with alternative phase composition. Further, the influences of secondary phase on the electrochemical performance have been

reported by many groups [16,17]. Previously, a Fe₂P₂O₇ secondary phase was detected on the surface of hydrothermal synthesized LFP. The origin of such impurity phase formation was that more Fe_{Li} anti-site was formed at lower temperature than high temperature solid state reactions [18–20]. However, there is a lack of in-depth understanding on the complex relationship between phase distribution and particle size [12,15,21]. Furthermore, the precise control over the formation of secondary/impurity phases still remains elusive and difficult. As a result, a holistic understanding of surface phase homogeneity on LFP will greatly improve product uniformity for mass-production [22,23].

Recently, our work demonstrated the formation of a secondary surface impurity phase of Fe₂P₂O₇ when carbon coating on LFP. This process was hypothesized to occur due to loss of lithium oxide at high temperature [24]. With advanced in-depth characterization techniques, surface chemistry change was clearly visualized and recorded on the flat surface of ingot samples. The phase distribution on the surface of LFP was found to become inhomogeneous following the coating process as a result of C/LFP interface reactions. This Fe₂P₂O₇ phase is expected to be electrochemically inert, with no contribution to the capacity of LFP. The emerging question of importance that arises out of this study is what surface properties allow for the facile formation of secondary

* Corresponding authors.

E-mail addresses: Guoxian.Liang@matthey.com (G. Liang), xsun@eng.uwo.ca (X. Sun).

phases and how can this formation be reduced or eliminated during LFP manufacturing. In an effort to address these questions, we systematically investigate the formation and stability of $\text{Fe}_2\text{P}_2\text{O}_7$ phase on commercial powder samples by developing a procedure that includes a wide range of reaction conditions aimed at controlling or eliminating $\text{Fe}_2\text{P}_2\text{O}_7$ phase by tuning carbon coating parameters. In addition, LFP ingot sample prepared by melt casting method, with a large flat surface, is also used to obtain detailed surface chemistry changes that occur during the carbon coating process, thus providing crucial information toward important parameters that lead to changes at the surface/interface [25–28].

With fine tuning of carbon coating condition, a full diagram of $\text{Fe}_2\text{P}_2\text{O}_7$ phase existing region is outlined with respect to different coating parameters. Highly pure LFP particles with different size could be achieved by controlling the carbon coating process. From a thermodynamic point of view, we give a single unified mechanism that could be used to describe the formation of $\text{Fe}_2\text{P}_2\text{O}_7$ phase under different circumstance. Furthermore, we use LFP ingot sample to demonstrate the direct visualization of phase changes during the carbon coating process. The methodology utilized in this work on multi-element phase equilibrium systems under reducing atmosphere and/or high temperature can be useful for material systems that require control over phase purity and stability during carbon coating.

The origin of such impurity phase formation was that more FeLi antite site was formed at lower temperature than high temperature solid state reactions [18–20].

2. Results

Detailed physical investigation of the $\text{Fe}_2\text{P}_2\text{O}_7$ phase change in different size LiFePO_4 (LFP) is presented in Fig. 1. LFP particles with different size were achieved by ball milling LFP ingot sample, with a range from micron (19 μm) to nano (60 nm) (Size distribution in Fig. S1). The relationship between particle size and $\text{Fe}_2\text{P}_2\text{O}_7$ formation were investigated by XRD, patterns of carbon-coated LFP powders were collected in Fig. 1a. Small peaks in the XRD within the range of 28–33° (grey area) increase in intensity with increasing LFP particle size. This range of peaks can be assigned to $\text{Fe}_2\text{P}_2\text{O}_7$ (JCPDS no 76-1762), suggesting that increased LFP size results in high amount of $\text{Fe}_2\text{P}_2\text{O}_7$. As LFP particle sizes decrease, $\text{Fe}_2\text{P}_2\text{O}_7$ peaks diminish and are virtually non-existent at sizes below 150 nm (See the circle inset in Fig. 1a). To obtain further evidence for the size-dependent relationship on the formation of $\text{Fe}_2\text{P}_2\text{O}_7$ phase, three samples of size 560 nm, 150 nm, and 60 nm were characterized using high resolution transmission electron microscope (HRTEM, Fig. 1b). For 560 nm LFP, two sets of diffraction patterns are observed. One can be assigned to bulk phase LiFePO_4 while the other is attributed to $\text{Fe}_2\text{P}_2\text{O}_7$ impurity phase (inset of 560 nm LFP in Fig. 1b), indicating the co-existence of these two phases. Interestingly, HRTEM reveals the presence of a thin carbon layer approximately ~2 nm in thickness. This layer is closely followed by a thin strip of $\text{Fe}_2\text{P}_2\text{O}_7$. In contrast, the smaller particles (60 nm) or the critical size (150 nm) particles show no evidence of $\text{Fe}_2\text{P}_2\text{O}_7$ impurity (150 nm LFP and 60 nm LFP in Fig. 1b), remaining as pure LiFePO_4 phase. The carbon layer covered on the two different LFP particles is ~5 nm (150 nm LFP) and ~8 nm (60 nm LFP), respectively, suggesting thicker carbon layer for a smaller LFP. It is evident that the impurity phase $\text{Fe}_2\text{P}_2\text{O}_7$ formation during carbon coating process is size dependent and the critical size is 150 nm. With such a value in mind, we can instruct the manufacturer to produce the right size for impurity free LFP with suitable tap density.

$\text{Fe}_2\text{P}_2\text{O}_7$ is an electrochemically inert phase and therefore influences electron and lithium transportation, leading to decreased capacity and cycling stability. To investigate this effect, electrochemical performance of LFP particles with different sizes were evaluated at a current density of 0.1 C (1 C = 170 mA g^{-1}), as shown in Fig. 1c. Clearly, smaller particle sizes deliver increased capacity compared to their larger-sized

counter parts. For example, 19 μm LFP particles only deliver a discharge capacity of 100 mAh g^{-1} in the first cycle with capacity fading to 61 mAh g^{-1} after 100 cycles (capacity retention of 61%). On the contrary, the 60 nm LFP sample exhibits a very stable discharge capacity of 160 mAh g^{-1} , with 100% capacity retention after 100 cycles. The other different-sized LFP (from 150 nm to 560 nm) follow the same trend in between the 19 μm -size and 60 nm LFP. However, the performance here includes the influence of impurity phase and particle size. In the next section, we will exclude the influence of particle size, as the smaller size LFP is impurity free while the bigger size LFP has different level of impurity, which makes the evaluation of impurity phase difficult.

Additionally, temperature plays an important role in the formation of $\text{Fe}_2\text{P}_2\text{O}_7$ impurity phase during the carbon coating process. The 19 μm LFP particles were initially studied to determine the influence of temperature on the formation of $\text{Fe}_2\text{P}_2\text{O}_7$, Fig. 2a illustrated the phase change of LFP during carbon coating. XRD patterns are taken within a temperature range of 400–850 °C with a 50 °C interval. From the peaks shape between 28° and 33° in Fig. 2a, it can be clearly seen that the $\text{Fe}_2\text{P}_2\text{O}_7$ impurity phase changes with temperature. Diffraction peaks for $\text{Fe}_2\text{P}_2\text{O}_7$ impurities begin to appear at 450 °C and their intensities become stronger as annealing temperatures reach 750 °C. Interestingly, the diffraction peaks for $\text{Fe}_2\text{P}_2\text{O}_7$ impurity disappears at temperatures above 800 °C (inset in Fig. 2a in the range of 28–33°). Sensitivity of detecting $\text{Fe}_2\text{P}_2\text{O}_7$ impurity as a function of temperatures provides important insight on surface chemistry of LFP during the carbon coating process, therefore, we further investigate the phase evolutions as a function of temperature using an *in-situ* XRD heating stage (Fig. S2). From these experiments we observe the same phase change trend as *ex-situ* XRD samples, suggesting instability of $\text{Fe}_2\text{P}_2\text{O}_7$ phase at high temperature. Furthermore, we also extended the same experiment to smaller LFP particles. The similar trend of appearance and disappearance of $\text{Fe}_2\text{P}_2\text{O}_7$ impurity with temperatures is observed in LFP particles with smaller size (560 nm and 50 nm LFP) at 400–800 °C. The difference among these three size LFP samples is that the critical temperature for disappearance of $\text{Fe}_2\text{P}_2\text{O}_7$ impurity decreases with smaller LFP particle sizes. (See Fig. S3a and b).

To obtain further evidence of surface changes, sub-micron particles (560 nm LFP) were chosen as a suitable model for morphology and crystal structure investigation. From SEM images of 560 nm LFP (Fig. S3c), no obvious surface chemistry changes were observed for two different temperature (700 °C and 800 °C) coated LFP samples. Slight particle growth for samples annealed at 800 °C is observed by estimating the size-distribution, it is a phenomenon commonly found for nano LFP. Therefore, detailed structural information through HRTEM and SAED characterizations were performed to verify surface chemistry changes. A clear difference in both the SAED patterns and HRTEM images of two coated samples can be seen in Fig. 2b. Compared with 700 °C LFP samples, the SAED pattern for 800 °C LFP samples shows only one set of diffraction peaks, which can be identified and indexed as LFP. Furthermore, HRTEM images reveal LFP pure surface with no trace of $\text{Fe}_2\text{P}_2\text{O}_7$, covered with a thick ~6.6 nm carbon layer, which is consistent with XRD analysis in Fig. 2a.

As demonstrated earlier, LFP performance is influenced by the amount of $\text{Fe}_2\text{P}_2\text{O}_7$ impurity as well as LFP particle size. To exclude the influence of particle size, we examined the electrochemical performance of 19 μm LFP treated under different temperatures (Fig. 2c). It seems that electrochemical performance can be correlated to amount of $\text{Fe}_2\text{P}_2\text{O}_7$ impurity phase. Our results demonstrate that an increased amount of impurity leads to quick capacity decay and loss of reversible capacity. Furthermore, rate performance testing on the 700 °C, 800 °C samples and 750 °C sample with more $\text{Fe}_2\text{P}_2\text{O}_7$ indicates that a diminished performance is observed for 750 °C sample with the increase of impurity content, especially at higher rate. This phenomenon may be ascribed to the inert nature of $\text{Fe}_2\text{P}_2\text{O}_7$. During electrochemical cycling, $\text{Fe}_2\text{P}_2\text{O}_7$ impurity phase impedes lithium-ion mobility and inhibits its

Download English Version:

<https://daneshyari.com/en/article/7952835>

Download Persian Version:

<https://daneshyari.com/article/7952835>

[Daneshyari.com](https://daneshyari.com)