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Raman and XRD studies on the influence of nano silicon surface modification on Li^+ dynamics processes of $LiFePO_4$

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ABSTRACT

In this letter, Li^+ ion kinetic processes of $LiFePO_4$@C and $LiFePO_4$@C modified by nano silicon ($LiFePO_4$@C/Si) have been systematically investigated by X-ray diffraction, Raman spectra and Electrochemical impedance spectroscopy (EIS), respectively. The experimental results indicate that, (1) $LiFePO_4$@C/Si possesses faster charged and discharged velocity than $LiFePO_4$@C; (2) the nano silicon surface modification induces the larger diffusion coefficient and less activation energy of Li ions, which promotes Li^+ ion transfer rate; (3) it suppresses effectively the Fe dissolution and enhances the stability of $LiFePO_4$ phase and cycle performance; (4) there exists the best silicon surface modification content (Si content = 2.46 at.%) in enhancing the electrochemical performances of $LiFePO_4$. Additionally, it is suggested that constant-voltage charge is with some time indispensable for a fully delithiation of the $LiFePO_4$ material.

1. Introduction

Since the pioneering work in 1997 published by Padhi et al., lithium iron phosphate $LiFePO_4$ has become the most promising positive-electrode materials for the next generation of lithium-ion batteries due to its remarkable thermal stability, relatively high theoretical specific capacity of 170 mA h/g and flat charge-discharge profile at about 3.4 V vs. Li^+/Li [1,2]. However, the low electrical conductivity and slow lithium ion diffusion hindered its wide applications in the stored energy. In order to improve the electrochemical performances of $LiFePO_4$, many efforts have been made to increase the conductivity of $LiFePO_4$ by coating with electronic conducting agents [3–7], doping with metal and nonmetal ions [8,9], as well as decreasing its particle size down to nanometers [10–11]. Especially, Armand et al. found that a carbon coating $LiFePO_4$ synthesis simultaneously increases the electronic conductivity and prevents the growing particle, which is also a significant breakthrough for the applications of $LiFePO_4$ [3]. And after that, a lot of the surface modification technologies have been developed for enhancing the electrochemical performances of $LiFePO_4$ [12–15]. It is suggested that the purity of phase, the smaller particle size, uniformity of coating, reduced agglomeration and so on are significant for getting better electrochemical properties.

In order to understand the lithium intercalation/deintercalation mechanism, a two-phase reaction has been suggested [16–20], where there exist very narrow solid solutions in the vicinity of the end members $LiFePO_4$ and $FePO_4$. Moreover, Chen et al. confirmed the easy diffusion of lithium in the tunnels parallel to the *b* direction and found that lithium is extracted at the phase boundary parallel to the *bc* plane that progresses in the *a* direction on reaction [21]. By X-ray diffraction and electron microscopy, Delmas et al. found the coexistence of fully intercalated and fully deintercalated individual particles [20]. On this basis, a reaction mechanism with 'domino-cascade model' was constructed, which is hoped to try to understand the dynamics processes involved in electrochemical cycling starting from $LiFePO_4$ nanoparticles.

The phase changes of $LiFePO_4$ in Li^+ intercalation/deintercalation have been studied by ensemble averaging methods including XRD [20], Mossbauer [17] and electrochemistry [22]. However, there exist limitations in observing the surface related properties of cathode material using these methods. Fortunately, Raman spectroscopy provides a more localized technology to study the surface phase change and microstructures during charge and discharge [23]. By Raman spectroscopy, they found the incomplete delithiation of large $LiFePO_4$ due to the 1D channel blocking with anti-site defects. In Raman studies of $LiFePO_4$, both internal and external modes were suggested. In the internal modes, the very sharp band at 951 cm^{-1} is attributed to the Ag mode of ν_1, while the two weaker bands at 995 and 1067 cm^{-1} are thought to belong to the antisymmetric stretching modes of the PO_4^{3-} anion (ν_3). These three peaks at 953, 995 and 1067 cm^{-1} are considered to be characteristic for $LiFePO_4$. In the external modes, the peaks at 175 cm^{-1}, 244 cm^{-1} and 305 cm^{-1} correspond to translation of Fe,

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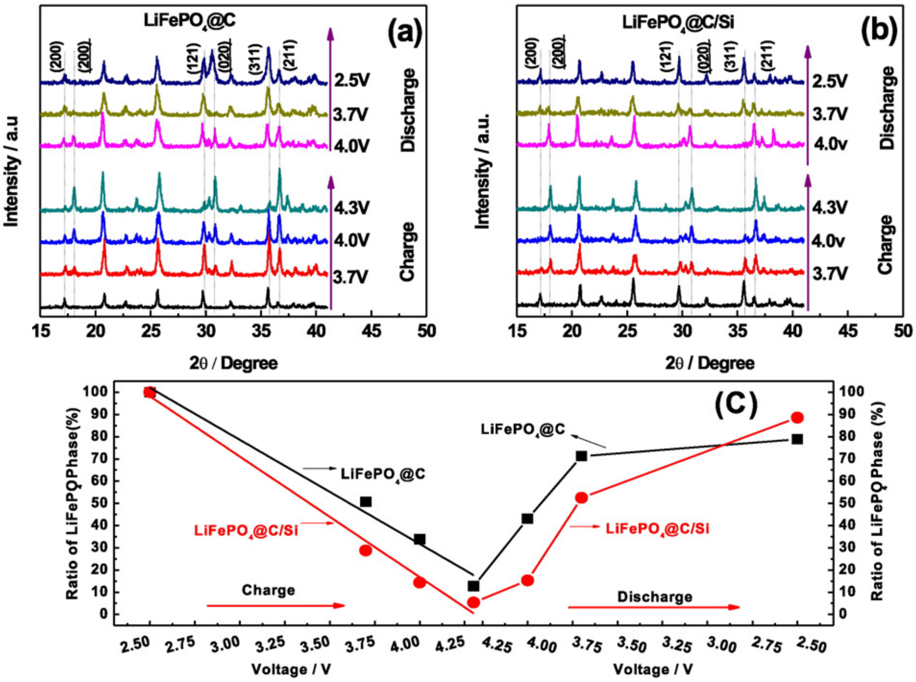

Fig. 1. XRD patterns of (a) LiFePO$_4$@C and (b) LiFePO$_4$@C/Si galvanostatically charged to $V_c = 3.7$ V, 4.0 V and 4.3 V at 2C rate, then kept at this voltage until the current was less than 0.2C, and galvanostatically discharged down to $V_{dc} = 4.0$ V, 3.7 V and 2.5 V at 2C rate respectively. (c) The graphic of LiFePO$_4$ phase as a function of voltage.

coupled translation of Fe and PO_4^{3-}, which indicates a phase change from LiFePO$_4$ to FePO$_4$. Additionally, Bai et al. still observedα-Fe$_2$O$_3$ phase with Raman peaks of 211 and 279 cm^{-1} in the thermal effect of pure, C-coated and Co-doped LiFePO$_4$ [24].

To our knowledge, the dynamics processes of LiFePO$_4$ phase change upon Li$^+$ extraction and insertion have been performed largely by XRD, Raman spectroscopy. However, the influence of the surface modification on the dynamics processes of LiFePO$_4$ phase change has hardly been studied. In this letter, Li$^+$ ion kinetic processes of LiFePO$_4$@C and LiFePO$_4$@C/Si electrodes are systematically investigated by X-ray diffraction, Raman spectra and Electrochemical impedance spectroscopy (EIS), respectively. The experimental results indicate that LiFePO$_4$@C/Si has faster charged and discharged velocity than LiFePO$_4$@C. Moreover, it is found that the nano silicon surface modification induces the lower activation energy of Li ions diffusion, which promotes Li$^+$ ion transfer rate. At last, it is observed that the nano silicon modification suppresses effectively the Fe dissolution and enhances the stability of LiFePO$_4$ phase and cycle performance.

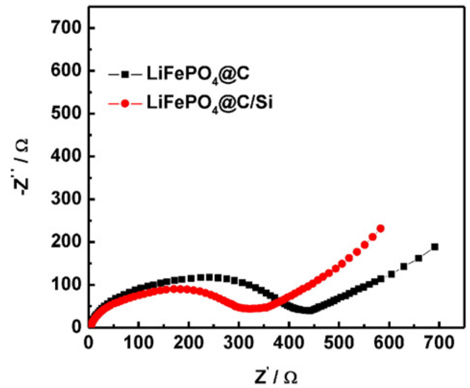

Fig. 2. The typical nyquist plots of LiFePO$_4$@C and LiFePO$_4$@C/Si in the fully discharge state after 1 cycle at 2C rate.

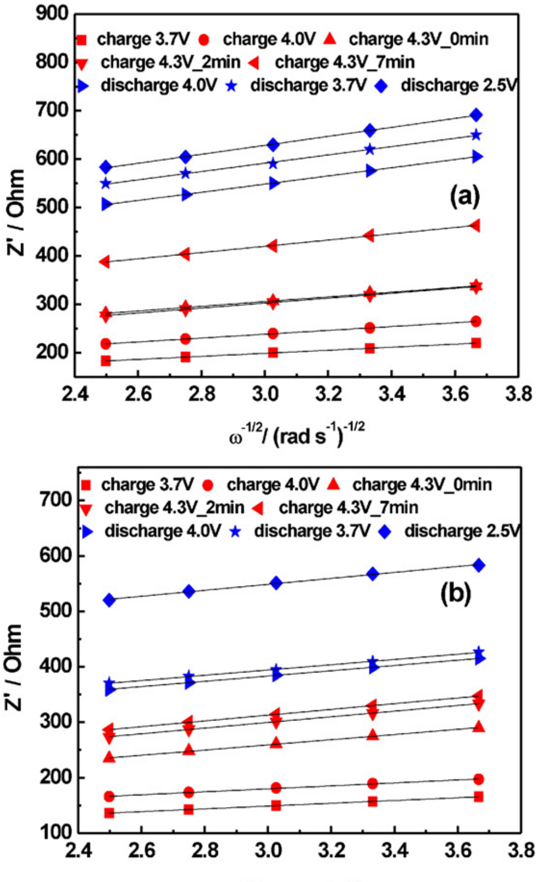

Fig. 3. Z′ vs. $\omega^{-1/2}$ plots in the low frequency of (a) LiFePO$_4$@C and (b) LiFePO$_4$@C/Si.