Synthesis and Characterization of Li$_{1-4y}$Ti$_y$FePO$_4$ as Cathode Materials for Lithium-Ion Batteries

Hui Fang$^1$, Gan Liang$^1$, Liang Zhao$^2$, Timothy Wallace$^1$, Hanu Arava$^1$, Lu-Lu Zhang$^3$, Alexander Ignatov$^4$, and Mark C. Croft$^{4,5}$

$^1$ Department of Physics, Sam Houston State University, Huntsville, TX 77341, USA
$^2$ Department of Physics and Astronomy, Rice University, Houston, TX 77005, USA
$^3$ College of Mechanical and Material Engineering, Three Gorges University, 8 Daxue Road, Yichang, Hubei 443002, China
$^4$ Department of Physics and Astronomy, Rutgers University, Piscataway, NJ 08854, USA
$^5$ NSLS, Brookhaven National Laboratory, Upton, NY 11973, USA

Li$_{1-4y}$Ti$_y$FePO$_4$ ($y = 0, 0.01, 0.02, 0.03, 0.04$, and $0.05$) cathode materials were prepared by solid-state reaction. The as-prepared samples were characterized by X-ray diffraction, X-ray absorption spectroscopy, cyclic charge-discharge, cyclic voltammograms, and electrochemical impedance spectroscopy. The x-ray diffraction results indicate that the Ti$^{4+}$ incorporates into the LiFePO$_4$ lattice, but the XAS reveals that small amounts of doped Ti can also form TiO$_2$-anatase impurities. At 0.1 C rate, doping of Ti causes a decrease in charge and discharge capacities. However, at higher C rate, the charge/discharge capacities are improved. 1 at.% doping sample Li$_{0.96}$Ti$_{0.01}$FePO$_4$ exhibits the optimized electrochemical performance.

1. Introduction

Lithium iron phosphate, LiFePO$_4$, with olivine structure has emerged as one of the most promising cathode materials for large-scale applications of lithium-ion batteries such as hybrid vehicle and electric vehicle due to its high theoretical capacity (about 170 mAh/g), long cycle life, high thermal stability, cost-effectiveness, nontoxicity, and environmental friendliness (1, 2). However, there are two main problems hindering its practical applications: low electronic conductivity and poor lithium ion diffusion rate (3). Strategies to increase electronic conductivity include cation doping on both Li$^+$ and Fe$^{2+}$ sites by multivalent cations (3-7) and carbon coating (8-10). It has been demonstrated that both routes can increase the electronic conductivity by a factor of up to an order of magnitude of $10^8$. However, the cation doping route has an advantage over the carbon coating route because the latter could result in an energy density loss up to 30 volume%.

Recently, Meethong et al. reported the high solubility of aliovalent solutes (Mg$^{2+}$, Al$^{3+}$, Zr$^{4+}$, and Nb$^{5+}$) on both Li (M1) and Fe (M2) sites along with appropriate charge-compensation vacancies (11), which demonstrated the possibility of aliovalent doping in this family of compounds. Results on Zr$^{4+}$ substitution on Li site and Li-vacancy
compensation show high solubility of at least 12 atomic percent Zr doping, increased cycling kinetics, and expand Li diffusion channels (11). However, this mechanism of crystal-chemical modification has not been generally accepted in lithium transition metal olivines (12, 13). Ti⁴⁺ has an even smaller 6-fold ionic radius (0.0605 nm) in comparison with Zr⁴⁺ (0.072 nm). Therefore, doping with Ti⁴⁺ may lead to even better electrochemical properties of LiFePO₄. In this research, we systematically studied the structural and electrochemical properties of Ti-doped LiFePO₄ system for which Ti⁴⁺ doping is on Li site with Li-vacancy compensation.

2. Experimental

Li₁₋₄yTiyFePO₄ (y=0, 0.01, 0.02, 0.03, 0.04 and 0.05) samples were synthesized by solid-state reaction using Li₂CO₃ (99.999%, Alfa Aesar), FeC₂O₄·2H₂O (99%, Alfa Aesar), NH₄H₂PO₄ (98%, Alfa Aesar), and Ti(OCH₃)₄(CH₃OH)₂ (95%, Alfa Aesar) as the starting materials. Stoichiometric mixture in ethanol was high energy ball-milled for 90 minutes by a SPEX 8000 Mixer/mill. Hardened steel vial and balls were used as milling medium. The mass ratio of ball to powder mixture was 20 to 1. After ball milling, the mixture was heated at 350 °C for 10 hours under high purity Argon to decompose the carbonate, oxalate, and ammonium. The decomposed mixture powder was baked at 700 °C for 5 hours in flowing Argon to form the desired compound.

The crystal structure of the samples was studied by X-ray diffraction (XRD). Room temperature powder XRD was performed on a Rigaku D/Max diffractometer with Cu Kα beam (λ = 1.5418 Å) and graphite monochromator. The measurements were carried out with 2θ ranging from 10° to 60° and step size of 0.02°. Data were collected with a dwelling time of 2 seconds at each point in order to ensure high peak intensity. Electrochemical properties were characterized on CR2032 coin cells assembled in a glove box filled with high purity Argon gas. The cathodes were made by mixing active material (75 wt.%), carbon black (20 wt.%), and binder (PTEF; 5 wt.%). A Celgard 2400 microporous membrane was used as separator, and lithium ribbon was used as anode. The electrolyte employed in this study was 1M LiPF₆ solution in ethylene carbonate (EC) – dimethylcarbonate (DMC; 1:1 in volume). The cathode performance was investigated in terms of galvanic charge - discharge and cycle life by using an Arbin Instrument BT-2000 between 2.5 and 4.1 V versus Li/Li⁺ at room temperature. Cyclic voltammetry was carried out by using a Gamry Reference 600 Potentiostat between 3.0 and 4.5 V at the scan rate of 0.1 mV/s. Electrochemical impedance spectroscopy (EIS) was measured also by the Gamry Reference 600 Potentiostat. The amplitude of the AC signal was 5 mV over the frequency range between 0.01 Hz and 100 kHz.

The valence states of Fe and Ti were studied by x-ray absorption spectroscopy (XAS) measurement. The Fe K-edge and Ti K-edge XAS measurements were performed in fluorescence mode at beam line X-19A of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. A double-crystal Si (111) monochromator was used for energy selection, which was detuned by reducing the incident photon flux about 20% from its maximum value to suppress contamination from harmonics. A FeO standard for Fe K-edge and a Ti-foil standard for Ti K-edge, respectively, were run simultaneously with the Li₁₋₄yTiyFePO₄ samples for energy calibration. The energy resolution (∆E/E) of the X-19A beam line was 2×10⁻⁴, corresponding to about 1.4 eV and 1.0 eV at Fe K-edge and Ti K-edge, respectively. All of the XAS spectra presented in this paper were
background subtracted and normalized to unity in the continuum region about 100 eV above the edge.

3. Results and Discussion

3.1. Phase and Structure

The measured XRD patterns are shown in Fig. 1. For all the samples measured, a small amount of Fe₂P impurity was found; the corresponding peaks are too tiny to be visible in Fig. 1. Rietveld analysis was performed to determine the lattice parameters of each sample, using the RIETICA software package (14). The background was fitted by a fifth order polynomial and the Pseudo-Voigt profile was chosen to fit the peak shape. Both LiFePO₄ (space group \( Pnma \)) and Fe₂P (space group \( P6/2m \)) phases were included in the refinement (Fig. 2). The results are plotted in Fig. 3. The values of the lattice parameters \( a \) and \( b \) decrease as \( y \) increases from 0 to 0.01 and then increase with the increase of \( y \) from 0.01 to 0.05; the parameter \( c \) exhibits a systematic, linear increase with the increase of \( y \) from 0 to 0.05. Since Ti⁴⁺ has a smaller ionic radius (0.0605 nm) than Li¹⁺ (0.076 nm) (15), the contraction of lattice is expected as a result of substituting Ti for Li. With the increase of Ti⁴⁺ doping amount, the amount of Li vacancies increases in a faster rate, which causes the expansion of the olivine unit cell (11). The unit cell volume \( V \) shows a Vegard’s law (16) behavior, that is, a linear dependence on \( y \). Such linear relationship was observed previously for the Zr doped LiFePO₄ series (11).

Figure 1. XRD patterns of Li\(_{1-4y}\)Ti\(_y\)FePO₄ \((y = 0, 0.01, 0.02, 0.03, 0.04, 0.05)\) samples, with \( hkl \) indices of major reflection peaks marked.
Figure 2. Rietveld refined XRD pattern of LiFePO$_4$ sample. The raw data, calculated pattern and difference between them were marked by black cross, red line and green line, respectively. The blue tick marks underneath the pattern indicates the calculated peak position of LiFePO$_4$ (above) and Fe$_2$P (below) phases.

Figure 3. Lattice parameters and unit cell volume of Li$_{1-y}$Ti$_y$FePO$_4$ (y = 0, 0.01, 0.02, 0.03, 0.04, 0.05). The straight lines are guides for the eyes, showing the nearly linear dependence on y.
3.2. Valence State of Fe and Ti

In Fig. 4, the Fe K-edge spectra for the pristine LiFePO$_4$ and the Li$_{1-4y}$Ti$_y$PO$_4$ with $y = 0.01$ sample are shown along with the spectra of reference compounds Fe$^{2+}$O and Fe$^{3+}$PO$_4$·H$_2$O for comparison. The spectra for the pristine and Ti-doped sample are almost identical, indicating that the valence value for Fe is the same for both of them. The primary indicator of valence variation is the chemical shift in the main portion of the edge to higher energy with increasing valence. Fig. 4 clearly shows that the values of the edge energies (defined as the energy at absorption coefficient $\mu \sim 0.5$) are almost the same ($\sim 7119$ eV) for LiFePO$_4$, Li$_{0.96}$Ti$_{0.01}$PO$_4$ and Fe$^{2+}$O, but are about 6 eV below the edge energy for the Fe$^{3+}$ compound Fe$^{3+}$PO$_4$·H$_2$O. Thus, the formal valence value of Fe in both the un-doped and Ti-doped LiFePO$_4$ is +2. The pre-edge feature located at about 7112 eV is due to $1s \rightarrow 3d$ quadruple transitions and $1s \rightarrow p/3d$ hybridized states via dipole transitions. The low onset energy of the feature also supports the Fe$^{2+}$ valence in the LiFePO$_4$ based materials. (The pre-edge feature of the Fe$^{3+}$PO$_4$·H$_2$O is shifted up in energy). Thus both the main- and pre-edge portions of the Fe K-edge XAS spectra clearly confirm that the valence state of Fe in the pristine and Ti-doped LiFePO$_4$ samples is Fe$^{2+}$. Therefore, Ti-incorporation in LiFePO$_4$/C does not change the valence state of Fe ions. This result supports that the valence of Ti in Li$_{1-4y}$Ti$_y$FePO$_4$ should be +4. However, whether the dopant Ti atoms go into the lattice structure to substitute Li or they exist in other impurity Ti compounds still remain a question.

Figure 4. X-ray absorption spectra at Fe K-edge for LiFePO$_4$, Li$_{0.96}$Ti$_{0.01}$FePO$_4$, and reference compounds FeO and FePO$_4$·H$_2$O.
To clarify the valence state of Ti and answer the aforementioned question, Ti K-edge XAS spectrum for Li$_{0.96}$Ti$_{0.01}$PO$_4$ was measured and is shown in Fig. 5 along with some reference compounds. It can be seen that the edge energies of the spectra for Li$_{0.96}$Ti$_{0.01}$PO$_4$ and Ti$^{4+}$O$_2$-anatase and Ti$^{4+}$O$_2$-rutile are almost the same value (~4982 eV), indicating the valence of Ti in Li$_{0.96}$Ti$_{0.01}$PO$_4$ is 4+. A close comparison between the spectrum for Li$_{0.96}$Ti$_{0.01}$PO$_4$ and that for Ti$^{4+}$O$_2$-anatase reveals that all the positions of the pre-edge and main edge features for these two spectra are very similar. This result indicates that substantial portion of the Ti ions in the Ti doped LiFePO$_4$ compound could be in the form of TiO$_2$-anatase impurity.

Figure 5. X-ray absorption spectra at Ti K-edge for Li$_{0.96}$Ti$_{0.01}$FePO$_4$, and reference compounds TiO$_2$-anatase, TiO$_2$-rutile, and Ti Foil.

3.3. Electrochemical Cycling Performance

Cycling charge-discharge capacities were measured at 0.1 C for 4 cycles followed by 0.2 C, 0.5 C, 1C, and 2 C rates, each with 20 cycles. The initial charge and discharge capacities for LiFePO$_4$ at 0.1 C rate are 145 mAh/g and 138 mAh/g, as shown in Fig. 6. With the increase of Ti$^{4+}$ doping amount, the initial charge and discharge capacities decrease monotonically, which indicates that Ti$^{4+}$ doping at Li site with Li-vacancy compensation reduces the capacity at low C rate. However, this trend changes at higher C rate (Fig. 7 and Fig. 8). The charge and discharge capacities of un-doped sample decrease dramatically as C rate increases. The capacities of LiFePO$_4$ are about 120, 95, 70, and 44 mAh/g at 0.2 C, 0.5 C, 1 C, and 2 C rates, respectively. For Ti$^{4+}$ doped samples, the charge and discharge capacities at all C rates employed in this study decrease monotonically along with the increase of doping amount. Compared with un-doped
sample, 1 at.% doped sample (y = 0.01) Li_{0.96}Ti_{0.01}FePO_4 has much higher capacity at 0.5 C, 1 C, and 2 C rates. The capacities of Li_{0.96}Ti_{0.01}FePO_4 at 0.2 C, 0.5 C, 1 C, and 2 C are 116, 107, 96, and 77 mAh/g, respectively.

Figure 6. Initial charge and discharge curves of the Li_{1-4y}Ti_{y}FePO_4 (y = 0, 0.01, 0.02, 0.03, 0.04, 0.05) at 0.1 C rate.

Figure 7. The cycling charge capacity of Li_{1-4y}Ti_{y}FePO_4 (y = 0, 0.01, 0.02, 0.03, 0.04, 0.05) at 0.2 C, 0.5 C, 1 C, and 2 C rates.
3.4. Cyclic Voltammetry Performance

Cyclic voltammetry measurements were carried out to identify the characteristics of the redox reactions for all samples as shown in Fig. 9. The anodic current peak and the cathodic current peak of pristine LiFePO$_4$ locate at 3.66 V and 3.24 V, which leads to the potential separation of 0.42 V. With the increase of Ti$^{4+}$ doping amount, the potential of the anodic peaks progressively decrease while the potential of the cathodic peaks increase. Therefore, the potential intervals with the increase of the Ti$^{4+}$ amount accordingly decrease. However, only the sample with 1 at. % Ti$^{4+}$ doping (y = 0.01) shows the comparable peak current value to that of the pristine sample, while the peak current values of other doping amount are significant smaller. The combined results of the potential interval and current peak value suggest that the reversibility of the electrode reaction is improved by 1 at.% Ti$^{4+}$ doping, which leads to a better electrochemical performance, especially at high C rate. Besides, the cyclic voltammograms of the samples with 3, 4, and 5 at.% Ti$^{4+}$ doping show a small secondary anodic/cathodic peak couple at 2.83 V and 2.76 V, corresponding to LiTi$_2$(PO$_4$)$_3$ phase (18), and the peak current value increases monotonously with the increase of doping amount.
3.5. Electrochemical Impedance Analysis

The Nyquist plot of EIS of all samples (Fig. 10, top) shows an arc in the high-frequency region and a line in the low-frequency region. The arc corresponds to the charge-transfer resistance of the particles in the electrolyte/sample interface (17). Modeled by using Randle equivalent circuit, the refined Nyquist plots (Fig. 10, bottom) suggested that the charge-transfer resistance progressively decreases with the increase of Ti doping amount. The charge-transfer resistance for the pristine sample is 286 $\Omega$. For 1% and 2% Ti doped samples, the charge-transfer resistances are 262 $\Omega$ and 214 $\Omega$, respectively. When Ti doping amount increases to 4% and 5%, the charge-transfer resistances decrease to 98 $\Omega$ and 93 $\Omega$. The decrease of the charge-transfer resistance may attribute to the improved electric conductivity and the impurities caused by Ti doping. However, with the increasing Ti content, the charge/discharge capacity decreases, which attributes to the LiTi$_2$(PO$_4$)$_3$ with low capacity (18).

4. Conclusions

Pristine and Ti doped Li$_{1-4y}$Ti$_y$FePO$_4$ ($y = 0, 0.01, 0.02, 0.03, 0.04$, and $0.05$) samples were synthesized by solid-state reaction. XRD refinement shows the expansion of lattice unit cell volume, which suggests the incorporation of Ti into the lattice. The valence of Ti is +4, and the incorporation of Ti does not change the Fe valence. With the increase of Ti doping amount, the charge/discharge capacities decrease progressively at 0.1 C rate, while at faster C rate, 1%, 2%, and 3% Ti doped samples exhibit higher capacities, which may attribute to the improvement of electric conductivity. CV results suggest that 1% doped sample Li$_{0.96}$Ti$_{0.01}$FePO$_4$ possesses the optimized electrochemical performance, which is in agreement with the cyclic charge/discharge measurement. EIS results also reveal that Ti doping enhances the electronic conductivity.
Figure 10. Nyquist plots of the measured impedance spectra (top) and the refined impedance spectra (bottom) by using Randle circuit showed as the insertion in the figure of Li_{1-4y}Ti_{y}FePO_{4} (y = 0, 0.01, 0.02, 0.03, 0.04, 0.05).

Acknowledgments

This work was supported by National Science Foundation under Grants (No. CHE-0718482), an award from Research Corporation for Science Advancement, and an ERG grant from Sam Houston State University.
References