Electrochemical Properties of Cathode Material LiFePO₄ with Ti Substitution

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Ti substituted LiFePO₄ with nominal composition Li₁₋₄yTi₄FePO₄ (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 increase of Ti⁺⁺⁺⁺ amount leads to the expansion of the LiFePO₄ lattice monotonically, but the XAS reveals that small amount of doped Ti can also form TiO₂-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. Li₀.₉₆Ti₀.₀₁FePO₄ exhibits the optimized electrochemical performance.

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Lithium iron phosphate, LiFePO₄, 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), high cycle life, high thermal stability, cost-effectiveness, nontoxicity, and environmental friendliness. However, there are two main problems hindering its practical applications: low electronic conductivity and poor lithium ion diffusion rate. Strategies to increase electronic conductivity include cation doping on both Li⁺ and Fe⁺⁺ sites by multivalent cations and carbon coating. It has been demonstrated that both routes can increase the electronic conductivity by a factor of up to an order of magnitude of 10². 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%.

Recently, Meethong et al. reported the high solubility of aliovalent solutes (Mg⁺⁺, Al⁺⁺, Zr⁺⁺, and Nb⁺⁺⁺) on both Li (M1) and Fe (M2) sites along with appropriate charge-compensation vacancies, which demonstrates the possibility of aliovalent doping in this family of compounds. Results on Zr⁺⁺ substitution on Li site and Li-vacancy compensation show high solubility of at least 12 atomic percent Zr doped increases cycling kinetics, and expand Li diffusion channels. However, this mechanism of crystal-chemical modification has not been generally accepted in lithium transition metal olivines. Ti⁺⁺⁺⁺ has an even smaller 6-fold ionic radius (0.0605 nm) in comparison with Zr⁺⁺ (0.072 nm). Therefore, doping with Ti⁺⁺⁺⁺ causes a decrease in charge and discharge capacities. At 0.1 C rate, the charge/discharge capacities are improved. Li₀.₉₆Ti₀.₀₁FePO₄ exhibits the optimized electrochemical performance.

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Recently, Meethong et al. reported the high solubility of aliovalent solutes (Mg⁺⁺, Al⁺⁺, Zr⁺⁺, and Nb⁺⁺⁺) on both Li (M1) and Fe (M2) sites along with appropriate charge-compensation vacancies, which demonstrates the possibility of aliovalent doping in this family of compounds. Results on Zr⁺⁺ substitution on Li site and Li-vacancy compensation show high solubility of at least 12 atomic percent Zr doped increases cycling kinetics, and expand Li diffusion channels. However, this mechanism of crystal-chemical modification has not been generally accepted in lithium transition metal olivines. Ti⁺⁺⁺⁺ has an even smaller 6-fold ionic radius (0.0605 nm) in comparison with Zr⁺⁺ (0.072 nm). Therefore, doping with Ti⁺⁺⁺⁺ 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 Ti⁺⁺⁺⁺ doping is on Li site with Li-vacancy compensation.

Experimental

Ti substituted LiFePO₄ samples with nominal composition Li₁₋₄yTi₄FePO₄ (y = 0, 0.01, 0.02, 0.03, 0.04 and 0.05) were synthesized by solid-state reaction using Li₂CO₃ (99.999%, Alfa Aesar), NH₄H₂PO₄ (98%, Alfa Aesar), 2H₂O (99%, Alfa Aesar), NH₄HCO₃, and Li₂CO₃ (98%, Alfa Aesar) as the starting materials. Stoichiometric mixture in ethanol was high energy ball-milled for 90 minutes by a SPEX 8000 Mixer/mill. Drilled metal vials and balls were used as milling medium. The mass ratio of ball to powder mixture was 2:1. 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 (PTFE; 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) – dimethylcarbomate (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 mVs. 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 Li₁₋₄yTi₄FePO₄ samples for energy calibration. The energy resolution (ΔE/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.

Results and Discussion

Phase and structure.— The measured XRD patterns are shown in Fig. 1. For all the samples measured, a small amount of Fe$_2$P 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. The background was fitted by a fifth order polynomial and the Pseudo-Voigt profile was chosen to fit the peak shape. Both LiFePO$_4$ (space group Pnma) and Fe$_2$P (space group P6$_2$m) 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 Ti$^{4+}$ has a smaller ionic radius (0.0605 nm) than Li$^{1+}$ (0.076 nm), the contraction of lattice is expected as a result of substituting Ti for Li. With the increase of Ti$^{4+}$ doping amount, the amount of Li vacancies increases in a faster rate, which causes the expansion of the olivine unit cell. The unit cell volume $V$ shows a Vegard’s law behavior, that is, a linear dependence on $y$. Such a linearity was observed previously for the Zr doped LiFePO$_4$ series.

Valence state of Fe and Ti.— In Figure 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$_{0.04}$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 LiFePO4 samples is Fe2+. Therefore, Ti-incorporation in LiFePO4/C does not change the valence state of Fe ions. This result supports that the valence of Ti in Li1-4yTiyFePO4 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.

To clarify the valence state of Ti and answer the aforementioned question, Ti K-edge XAS spectrum for Li0.96Ti0.01PO4 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 Li0.96Ti0.01PO4 and Ti4+O2-anatase and Ti4+O2-rutile are almost the same value (∼4982 eV), indicating the valence of Ti in Li0.96Ti0.01PO4 is 4+. A close comparison between the spectrum for Li0.96Ti0.01PO4 and that for Ti4+O2-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 LiFePO4 compound could be in the form of TiO2-anatase impurity.

**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 LiFePO4 at 0.1 C rate are 145 mAh/g and 138 mAh/g, as shown in Fig. 6. With the increase of Ti4+ doping amount, the initial charge and discharge capacities decrease monotonically, which indicates that Ti4+ doping intended at Li site with Li-vacancy compensation reduces the capacity at low C rate. However, this trend changes at higher C rate as shown in Fig. 7. The charge and discharge capacities of un-doped sample decrease dramatically as C rate increases. The capacities of LiFePO4 are about 120, 95, 70, and 44 mAh/g at 0.2 C, 0.5 C, 1 C, and 2 C rates, respectively. For Ti4+ 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) Li0.96Ti0.01FePO4 has much higher capacity at 0.5 C, 1 C, and 2 C rates. The capacities of Li0.96Ti0.01PO4 at 0.2 C, 0.5 C, 1 C, and 2 C are 116, 107, 96, and 77 mAh/g, respectively.

**Cyclic voltammetry performance.**—Cyclic voltammetry measurements were carried out to identify the characteristics of the redox reactions for all samples as shown in Fig. 8. The anodic current peak and the cathodic current peak of pristine LiFePO4 locate at 3.66 V and 3.24 V, which leads to the potential separation of 0.42 V.

With the increase of Ti4+ 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 Ti4+ amount accordingly decrease. However, only the sample with 1 at.% Ti4+ 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.% Ti4+ doping. Besides, the cyclic voltammograms of the samples with 3, 4, and 5 at.% Ti4+ doping show a small secondary anodic/cathodic peak couple at 2.83 V and 2.76 V, and the peak current value increases monotonously with the increase of doping amount.

**Electrochemical impedance analysis.**—The Nyquist plot of EIS of all samples (Fig. 9, 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. Modeled by using Randle equivalent circuit, the refined Nyquist plots (Fig. 9, 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.

Conclusions

Pristine and Ti substituted LiFePO$_4$ samples with nominal composition Li$_{1-4y}$Ti$_y$FePO$_4$ ($y = 0, 0.01, 0.02, 0.03, 0.04$, and $0.05$) were synthesized by solid-state reaction. XRD refinement shows the expansion of lattice unit cell volume with the increase of Ti amount. 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.

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References