Effect of LiI Amount to Enhance the Electrochemical Performance of Carbon-Coated LiFePO₄


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We used the wet chemistry method with different amounts of LiI to prepare LiFePO₄ and carbon-coated LiFePO₄ (LiFePO₄/C) samples. The lithiation process of LiI for preparing the LiFePO₄ is proposed. We found that the amount of LiI greatly affected the purities of products. The LiFePO₄/C sample showed constant values of current density during potential cycling up to 35 cycles as compared to LiFePO₄, suggesting that the LiFePO₄/C has better electrochemical performance. The obtained maximum capacity for LiFePO₄/C can be approached to the theoretical capacity of 170 mAh/g. Moreover, Brunauer-Emmett-Teller measurements of LiFePO₄ and LiFePO₄/C showed a surface area of 6.7 and 50 m²/g, respectively. It is reasonable to believe that the excellent performance of the compound developed in our work can be attributed to the smaller particle size coated with conductive carbon achieved by the controlling LiI in the sol-gel method.

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X-ray absorption experiments were carried out at the Wiggler beam line BL17C of the National Synchrotron Radiation Research Center, Taiwan. The electron storage ring was operated at energy of 1.5 GeV with a beam current of 300 mA. A Si_{111} double-crystal monochromator was employed for energy selection with a resolution of around 2 × 10^{-4}. The X-ray absorption near-edge spectrum (XANES) at the Fe K-edge was recorded at room temperature in transmission mode using gas-filled ionization chambers to measure the intensities of the incident and transmitted X-ray beams. After background subtraction, the XANES spectra were normalized with respect to the edge jump.

The cyclic voltammetry (CV) measurements were obtained by a cyclic voltammeter (digital potentiostat DP 8R and Autolab model PGSTAT20) in the open circuit mode range from 2.0 to 4.5 V vs Li^+ / Li at a 0.5 mV s^{-1} scan rate. The electrochemical impedance spectrum (EIS) measurement was obtained by an Autolab potentiostat PGSTAT20 with a frequency response analyzer. The frequency range is between 1 MHz and 0.1 Hz. To determine actual carbon content in the LiFePO_4 / C composite, elemental CHN analysis was performed on “Haraeus CHN-O Rapid” analyzer. The elementary CHN analysis result for carbon content (%) was tested. The exact value of carbon content was around 3.7% in the sintered sample with white sugar.

Results and Discussion

X-ray diffraction.— Figure 1 shows the XRD patterns of LiFePO_4 synthesized with different amounts of LiI. It can be seen that a well crystalline, single phase of LiFePO_4 can be obtained with 2.5 M LiI. The impurity phase of Fe_2P_2O_7, as shown by arrows in Fig. 1, was found in the products when the amount of LiI was less than 2.5 M. The impurity phase might originate from the decomposition of some amounts of unreacted amorphous FePO_4 phase when the amount of LiI is not enough for the reaction. Moreover, Li_3PO_4 impurity phase was found above 4.0 M, which may be due to the phosphatic ions reacting with an excess amount of LiI, as shown by the stars in Fig. 1. These results indicate that the sample purity is affected by different amounts of LiI.

Lithiation mechanism studies.— In the following discussion, we propose the lithiation process and discuss the suitable synthesis conditions to prepare highly crystalline LiFePO_4. The lithiation process and possible proposed chemical reaction equations are listed below and are indicated by the rectangles with the dashed line in Fig. 2. The different amounts of LiI dissolved in CH_3CN turned into the Li^+ and I^- ions as shown in Eq. 1. Afterward we added LiI solutions drop by drop to the amorphous FePO_4 to prepare LiFePO_4. The addition of LiI to FePO_4 will change the color gradually to dark-red because of the generation of I_2 in CH_3CN solution, as shown in Eq. 2. The grass-green color is the lithiation product of amorphous FePO_4 due to Li^+ ions and e^-, as shown in Eq. 3. When the amount of LiI was less than 2.5 M, the unreacted amorphous phase of FePO_4 is reduced to Fe_2P_2O_7 in the reduction conditions, as shown in Eq. 4. When the amount of LiI was above 4.0 M, the excess phosphatic ion will react with the LiI to form the Li_3PO_4 impurity phase. All the different amounts of LiI (1.0, 2.5, 4.0, and 4.5 M) are according to the molar amount of FePO_4

\[2\text{LiI}_{(\text{CH}_3\text{CN})} \rightarrow 2\text{Li}^+_{(\text{CH}_3\text{CN})} + 2\text{I}^-_{(\text{CH}_3\text{CN})}\]  

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**Figure 1.** XRD patterns of LiFePO_4 with different amounts of LiI: (a) LiI = 1.0 M, (b) LiI = 2.5 M, (c) LiI = 4.0 M, and (d) LiI = 4.5 M. The impurity phase of Fe_2P_2O_7 is marked by arrows, and the impurity phase of Li_iPO_4 is marked by stars.

**Figure 2.** (Color online) The probable lithiation processes with different amounts of LiI used to prepare LiFePO_4.
The results indicated that the lithiation effect of LiI and the compared with different amounts of LiI, 1, 2.5, 4.0, and 4.5 M, respectively. The electrochemical performance. As shown in Fig. 1, both LiFePO 4 measured for each oxidation peak as a function of cycle number. The current density is also shown in the inset of Fig. 4, which is measured in situ XANES results of LiFePO 4 during the discharge process in order to determine the oxidation state of Fe.\(^{15}\) Hence, the pre-edge and near-edge features of LiFePO 4/C were compared at different voltages as shown in Fig. 5. The Fe pre-edge part (labeled A in the inset) around 7112 eV corresponds to the 1s-3d transition, which is an electric-dipole-forbidden process but quadrupole allowed. A weak absorption at this energy is due to the mixing of the Fe 3d orbitals with 4p orbitals (3d-4p mixing) of the surrounded oxygen atoms, which split the 3d orbital into \(t_{2g}\) and \(e_g\) states. The observed splitting of the 3d state can be assigned to the FeO\(_6\) octahedral crystal field splitting of the \(t_{2g}\) and \(e_g\) energy level in the LiFePO 4/C structure. Comparison of the pre-edge feature of LiFePO 4/C during discharge with that of the standard LiFePO 4 before discharge clearly shows that the oxidation state of Fe in LiFePO 4 has shifted from a higher to a lower energy. It indicates that the reduction of Fe has occurred in LiFePO 4/C during the lithium-ion insertion into the crystal structure, which is in line with our assumption of intercalation of Li\(^+\) into the crystal structure. The near-edge part (labeled B in the inset) at 7114 eV as shown in Fig. 5 also shifted from higher to lower values.

**In situ XANES analysis.—** Figure 5 shows room-temperature in situ XANES results of LiFePO 4/C at different voltages used to study the structural and electronic modification occurring around the Fe center during the discharge process of LiFePO 4/C. Because XANES can give valuable information about the local environment around the Fe during potential cycling, we have recorded in situ XANES at the Fe K-edge during the discharge process in order to determine the electronic modifications occurring during the discharge of LiFePO 4/C. It is generally assumed that the pre-edge and near-edge (normalized absorption value 0.5) features are sufficient to determine the oxidation state of Fe;\(^{15}\) hence, the pre-edge and near-edge features of LiFePO 4/C were compared at different voltages as shown in Fig. 5. The Fe pre-edge part (labeled A in the inset) around 7112 eV corresponds to the 1s-3d transition, which is an electric-dipole-forbidden process but quadrupole allowed. A weak absorption at this energy is due to the mixing of the Fe 3d orbitals with 4p orbitals (3d-4p mixing) of the surrounded oxygen atoms, which split the 3d orbital into \(t_{2g}\) and \(e_g\) states. The observed splitting of the 3d state can be assigned to the FeO\(_6\) octahedral crystal field splitting of the \(t_{2g}\) and \(e_g\) energy level in the LiFePO 4/C structure. Comparison of the pre-edge feature of LiFePO 4/C during discharge with that of the standard LiFePO 4 before discharge clearly shows that the oxidation state of Fe in LiFePO 4 has shifted from a higher to a lower energy. It indicates that the reduction of Fe has occurred in LiFePO 4/C during the lithium-ion insertion into the crystal structure, which is in line with our assumption of intercalation of Li\(^+\) into the crystal structure. The near-edge part (labeled B in the inset) at 7114 eV as shown in Fig. 5 also shifted from higher to lower values.

**CV analysis.—** Figure 4 shows the cyclic voltammograms of the LiFePO 4 and LiFePO 4/C samples at a scan rate of 0.5 mV s\(^{-1}\). The current density is also shown in the inset of Fig. 4, which is measured for each oxidation peak as a function of cycle number. The electrochemical properties of LiFePO 4 and LiFePO 4/C were performed in the range of 2.0–4.5 V vs Li\(^+\)/Li at a 0.5 mV s\(^{-1}\) scan rate for the 35 cycles. LiFePO 4 without carbon showed much loss in electrochemical activity during potential cycling up to 35 cycles. However, LiFePO 4/C showed constant values of current density, indicating the better and stable electrochemical performance of the cathode film.

**AC impedance analysis.—** Figure 3 shows the NyQuist plots of LiFePO 4 and LiFePO 4/C samples. The high frequencies are shifted in the negative direction on the real axis of the LiFePO 4/C sample. All plots exhibit a depressed semicircle in the high-frequency region, which is attributed to the enhancement of the charge-transfer process.

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\begin{align*}
2\text{I}_2(\text{CH}_3\text{CN}) &\rightarrow I_2(\text{CH}_3\text{CN}) + 2e^- \quad [2] \\
4\text{FePO}_4(s) + 2\text{Li}^+ + 2e^- &\rightarrow 2\text{LiFePO}_4(s) + 2\text{FePO}_4(s) \quad [3] \\
2\text{FePO}_4(s) &\rightarrow \text{Fe}_2\text{P}_2\text{O}_7(s) + 1/2\text{O}_2 \quad [4]
\end{align*}
\]

\(2\text{I}_2(\text{CH}_3\text{CN}) \rightarrow I_2(\text{CH}_3\text{CN}) + 2e^- \quad [2]
\]

\(4\text{FePO}_4(s) + 2\text{Li}^+ + 2e^- \rightarrow 2\text{LiFePO}_4(s) + 2\text{FePO}_4(s) \quad [3]
\]

\(2\text{FePO}_4(s) \rightarrow \text{Fe}_2\text{P}_2\text{O}_7(s) + 1/2\text{O}_2 \quad [4]
\]
processes are also investigated in detail. BET analysis showed that the particle size of LiFePO$_4$/C was significantly reduced by addition of carbon. The enhanced electrochemical activity can be attributed to the decreased particle size and the formation of cavity architecture with carbon coating in the LiFePO$_4$/C. The improved charge transfer due to carbon was also confirmed by CV, EIS, and a galvanic profile test. These results suggest that the carbon formed a cavity architecture with carbon-coating in the LiFePO$_4$ sample, causing improvement in the electrochemical performance of cathode materials. Such a modification route for reducing the particle size and forming the cavity architecture of LiFePO$_4$ could be useful for its use as an alternative cathode material in reversible lithium batteries.

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