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Novel Synthesis of $LiFePO_4$ and $Li_4Ti_5O_{12}$ from Natural Ilmenite

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A new process for comprehensively utilizing ilmenite is studied. $FePO_4 \cdot xH_2O$, and Ti-containing precursors are prepared from the iron-rich lixivium and titanium hydrolysate, which are obtained from ilmenite by mechanical activation and leaching. ICP analysis confirms that the $FePO_4 \cdot xH_2O$ contains small amounts of Al and Ti (Fe:Al:Ti = 100:1.69:1.09) and that the Ti-containing precursor contains a small amount of Si (Ti:Si = 100:0.86). $LiFePO_4$ and $Li_4Ti_5O_{12}$ synthesized from the as-prepared precursors exhibit well-crystallized structure, nanoscale particles, and excellent electrochemical properties.

It is well known that there are many difficulties in utilizing abundant and low-grade titanic minerals such as ilmenite, due to high impurity content. Generally, ilmenite ($FeTiO_3$) is used for the production of synthetic rutile and titanium pigment,[1–3] in which titanium is utilized but iron is removed as waste slag or Fe_2O_3 with high impurities. Unfortunately, these wastes are less marketable and difficult to utilize because of their high impurity content, which causes not only severe environmental problems but also the waste of iron resource.

In this study, we propose a novel and inexpensive process to comprehensively utilize ilmenite to prepare a promising cathode material $LiFePO_4$[4,5] and a candidate anode material $Li_4Ti_5O_{12}$[6,7] for lithium-ion batteries. There are no complex purifying procedures during the whole route, because a proper amount of impurities (such as Al, Ti, Fe, etc.) can benefit the electrochemical performance of the final products.[4–6] Almost all of the titanium and iron of ilmenite could be utilized by this process, and the ultimate products are high value-added.

Natural ilmenite from Panzhihua, Sichuan, China, was used as raw material. The particle size was 50–200 µm, and the chemical composition was as follows (wt %): 47.60 TiO_2, 32.81 FeO, 7.25 Fe_2O_3, 5.64 MgO, 3.35 SiO_2, 1.66 Al_2O_3, 0.70 CaO, and 0.663 MnO_2. A planetary ball mill with a rotation speed of 200 rpm was employed for the mechanical activation. Four milling cells were fixed on the platform, and each cell was a 500-mL stainless steel vessel filled with 250 g Φ 20 mm, 200 g Φ 10 mm, and 50 g Φ 5 mm steel balls. The milling was operated in air with ball/ilmenite mass ratio of 20:1 for 2 h. The milled ilmenite was leached in a 500-mL round-bottomed flask attached to a refluxing condenser. First, 240 g of 20 wt % hydrochloric acid was heated to 100 °C, and then 40 g of milled ilmenite was added to the solution under vigorous stirring. After 2 h, the slurry was rapidly cooled and filtered, and then iron-rich filtrate and titanium hydrolysate were obtained.

$FePO_4 \cdot xH_2O$ precursor was synthesized by the following procedures: (1) The lixivium (filtrate) was diluted with deionized water to obtain 0.25 M (Fe) solution; (2) H_3PO_4 (85 wt %) was added to the solution in a molar ratio for $Fe:PO_4 = 1:1.1$; (3) sufficient H_2O_2 (30 wt %) was added into the solution to ensure all Fe^{2+} turning to Fe^{3+}; (4) then $NH_3 \cdot H_2O$ (2 M) was added dropwise into the solution to control the pH at 2.0 ± 0.1, subsequently a cream-colored precipitate formed immediately; (5) after being stirred for 30 min, the precipitate was filtered, washed three times with deionized water, and dried at 80 °C. Thus, $FePO_4 \cdot xH_2O$ precursor was obtained. Later, Li_2CO_3 and oxalic acid were ball milled with the precursor for 4 h in stoichiometric ratio (Li:Fe:C = 1:1:1.8), and the obtained mixture was calcinated at 600 °C for 12 h under argon atmosphere. After being cooled to room temperature, the final product $LiFePO_4$ was obtained.

Ti-containing precursor was prepared by the following procedures: (1) The hydrolysate was washed with 5 wt % HCl and dried at 80 °C; (2) 10 g of hydrolysate was mixed with 100 mL of deionized water, then $NH_3 \cdot H_2O$ (10 M) was added dropwise to the suspension to control the pH at 8–9; (3) 80 g of H_2O_2 (30 wt %) was added to the mixture under vigorous stirring to form peroxo-titanium complex; (4) after being stirred for 30 min at 50 °C, the suspension was filtered; (5) the obtained filtrate was boiled for 15 min, then a yellow precipitate formed; (6) the precipitate was filtered and dried at 80 °C, thus the Ti-containing precursor was obtained. Later, the precursor was ball milled with Li_2CO_3 for 4 h in stoichiometric ratio (Ti:Li = 5:4.16), and the obtained mixture was calcinated at 800 °C for 16 h in air. Thus, the final product $Li_4Ti_5O_{12}$ was obtained.

Elemental content, structure, morphology, and electrochemical properties of the samples were tested by ICP, XRD, SEM, and a battery test system, respectively. Further experimental details can be found in our previous work and Supporting Information.[8,9]

Table 1 lists the leaching ratio of all the elements. It was found that most of the Fe, Mg, Al, Ca, and Mn are lixiviated from ilmenite during the leaching process, while little Ti and Si are extracted. The low leaching rate of Ti is ascribed to the coupled dissolution and hydrolysis reaction; namely, titanium is first dissolved as $TiOCl_2$ and then hydrolyzed as TiO_2.[1,9]

The molar ratios of different elements in lixivium and $FePO_4 \cdot xH_2O$ are compared in Table 2. As shown, the iron-rich lixivium contains large quantity of impurities; however, only a small amount of Ti and Al are precipitated in $FePO_4 \cdot xH_2O$, which is due to the various solubility products of phosphates. The results are consistent with our previous work.[8] Table 2 also shows the molar ratio of different elements in titanium hydrolysate and Ti-containing precursor. It is noted that the titanium hydrolysate contains major impurities, Fe and Si, and small amounts of other

Table 1. The leaching ratios (lixivium/ilmenite) of all the elements

	Ti	Fe	Mg	Si	Al	Ca	Mn
Leaching ratio/%	1.07	96.5	98.5	0.01	96.8	96.1	98.9

Table 2. The molar ratios of Ti, Fe, Mg, Si, Al, Ca, and Mn in ilmenite lixivium, $FePO_4 \cdot xH_2O$, titanium hydrolysate, and Ti-containing precursor

	Ti	Fe	Mg	Si	Al	Ca	Mn
Ilmenite lixivium	1.10	100	27.1	≈0	5.88	2.23	1.50
$FePO_4 \cdot xH_2O$	1.09	100	≈0	≈0	1.69	≈0	≈0
Titanium hydrolysate	100	3.20	0.31	9.42	0.14	0.07	0.01
Ti-containing precursor	100	≈0	≈0	0.86	≈0	≈0	≈0

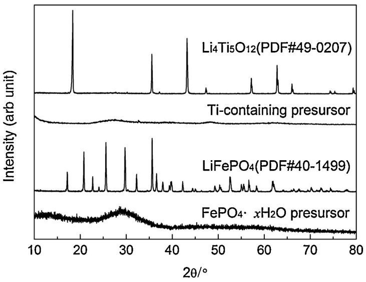

Figure 1. XRD patterns of $FePO_4{\cdot}xH_2O$ precursor, $LiFePO_4$, Ti-containing precursor, and $Li_4Ti_5O_{12}$.

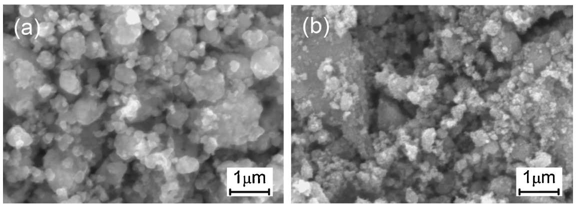

Figure 2. SEM images of (a) $LiFePO_4$ and (b) $Li_4Ti_5O_{12}$ powders.

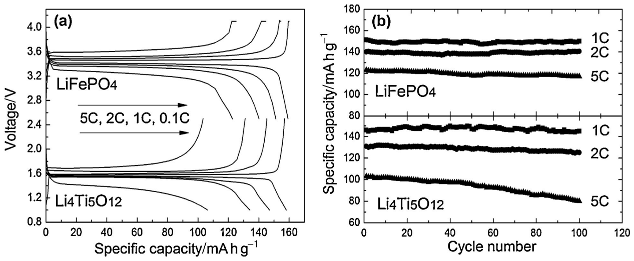

Figure 3. Initial charge and discharge curves (a) and cycling performance (b) of $LiFePO_4$ and $Li_4Ti_5O_{12}$ at different C rates.

elements, whereas the Ti-containing precursor only contains a small amount of Si. During ligand leaching, titanium hydrolysate is reacted with H_2O_2 at proper pH (8–9) to form peroxotitanium complex solution, whereas most of the impurities are still in the slag, except a little Si is dissolved under weak alkaline condition. Thus, titanium is purified from the other impurities.

XRD patterns of the as-prepared $FePO_4{\cdot}xH_2O$, $LiFePO_4$, Ti-containing precursor, and $Li_4Ti_5O_{12}$ are shown in Figure 1. It can be seen that there is no evidence of diffraction peaks in $FePO_4{\cdot}xH_2O$ and Ti-containing precursor, indicating that they are amorphous. XRD pattern of $LiFePO_4$ shows that all the diffraction peaks are indexed to an orthorhombic system with the space group *Pnma*, and no impurities are detected. It demonstrates that Al^{3+} and Ti^{4+} ions have entered into the lattice of $LiFePO_4$.[9] Previous studies have shown that Al^{3+} and Ti^{4+} could be doped at Li site, Fe site, or both,[4,5] but in either case, it will induce the formation of cation-deficient solid solution, which can benefit the electrochemical performance of $LiFePO_4$. Furthermore, chemical analysis revealed 0.89 wt % of carbon in the $LiFePO_4$, but it was not detected by XRD, indicating that it is amorphous. The lattice parameters of $LiFePO_4$ obtained from the Rietveld refinement: $a = 10.3182$, $b = 6.0031$, $c = 4.6948$ Å and $V = 290.80$ Å^3, are similar to those in a previous report.[5] From the XRD pattern of $Li_4Ti_5O_{12}$, it can be seen that all the diffraction lines are in good agreement with the spinel $Li_4Ti_5O_{12}$ (cubic, space group $Fd\bar{3}m$). No other impurity is detected, indicating that Si has doped into the lattice of $Li_4Ti_5O_{12}$.[9] The cell constants of $Li_4Ti_5O_{12}$, $a = 8.346$ Å and $V = 581.35$ Å^3, are smaller than the data reported by Ohzuku et al.,[7] which should be ascribed to Si doping.

Figure 2 shows the SEM images of $LiFePO_4$ and $Li_4Ti_5O_{12}$. As shown, $LiFePO_4$ exhibits a uniform 100–800 nm sphere-like microstructure. $Li_4Ti_5O_{12}$ shows a porous structure with grain-size distribution range from 50 nm to 2 µm. The porous structure is ascribed to the large quantities of gases produced during annealing. The pores, when filled with electrolyte, are responsible for the easy Li-ion exchange.

Figure 3 shows the electrochemical performance of $LiFePO_4$ and $Li_4Ti_5O_{12}$ at room temperature. $LiFePO_4$ shows an initial discharge capacity of 159.2, 151.2, 140.0, and 122.7 mA h g^{-1} at 0.1C, 1C, 2C, and 5C rates, respectively. After 100 cycles, the sample retains a capacity of 150.1, 140.5, and 117.1 mA h g^{-1} at 1C, 2C, and 5C rates, respectively, which is 99.3%, 100.4%, and 95.4% of its initial capacity at the corresponding C rate. The excellent rate ability and cycle performance of $LiFePO_4$ should be ascribed to Al–Ti doping, nanoscale particles, and carbon coating.[9] On the other hand, $Li_4Ti_5O_{12}$ shows an initial charge capacity of 156.9, 145.3, 131.0, and 103.3 mA h g^{-1} at 0.1C, 1C, 2C, and 5C rates, respectively. After 100 cycles, the sample maintains a capacity of 144.3, 125.1, and 80.1 mA h g^{-1}, namely, 99.3%, 95.5%, and 77.5% of its initial capacity at 1C, 2C, and 5C rates, respectively. $Li_4Ti_5O_{12}$ sample shows excellent performance at moderate current rates (1C and 2C); nevertheless, the properties at high current rates (above 5C) still need to be improved. Considering the $Li_4Ti_5O_{12}$ sample possesses high crystallinity, fine particles, and porous microstructure, the poor electrochemical properties at high current rates may be ascribed to Si doping, which needs further study.

$FePO_4{\cdot}xH_2O$ with trace Al and Ti, and Ti-containing precursor with a small amount of Si is prepared from natural ilmenite. (Al, Ti)-doped $LiFePO_4$ and Si-doped $Li_4Ti_5O_{12}$ are synthesized from the obtained precursors. Both materials show excellent electrochemical properties at 0.1–2C rates. $LiFePO_4$ also shows good performance at 5C, but the performance of $Li_4Ti_5O_{12}$ at higher current rates (above 5C) still needs to be improved.

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9 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.