
Production of LiFePO_4 by using steelmaking slag as a phosphorus source

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Synopsis:

The usage of LiFePO_4 (LFP) battery cathodes for electric vehicles (EVs) has increased in recent years. Phosphorus for LFP will be required for a comparable amount of fertilizer. However, the economically minable phosphate rock mines are decreasing, and the market for phosphorus is already tight. Thus, it is urgently necessary to promote the production of LFP based on secondary phosphorus resources. In this study, the production of LFP using phosphorus recovered from steelmaking slag was investigated. After selective leaching of steelmaking slag, the phosphorus in the extract is precipitated as FePO_4 by titration with FeCl_3 at $\text{pH}=3$. The FePO_4 was mixed with $\text{LiOH}\cdot\text{H}_2\text{O}$ and glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) and heat treated at 700°C to prepare LFP. The FeCl_3 titration amount should be controlled within 0.6 stoichiometric mole ratio of Fe^{3+} to phosphorus to avoid the Fe_3PO_7 generation. The glucose should be mixed at the mole ratio of $\text{FePO}_4/\text{C}=1.0$ to prevent the Fe^{3+} from being over-reduced to Fe. The other elements, Ca, Si, Mg, Al, and Mn in the slag extract, did not affect the crystallization process and the structure of FePO_4 and LFP. The present study confirmed the feasibility of using steelmaking slag as a source of phosphorus for the preparation of LFP.

Keywords:

Battery cathode materials; Steelmaking slag; Phosphorus; FePO_4 ; LiFePO_4

1. Introduction

1. 1 LiFePO₄ (LFP) as a cathode material in electric vehicles (EVs)

EVs have developed rapidly in recent years to meet the CO₂ issue.^{1,2)} The global stock of EVs, including battery electric vehicles (BEV) and plug-in hybrid electric vehicles (PHEV), is expected to reach 220 million by 2030. The rapid development of EVs relies on the stable electrode materials supply. At this moment, metals such as Mn, Co, and Ni have been used as cathode material in EV batteries, however, they are facing depletion and are soon difficult to obtain, making them expensive.³⁻⁶⁾ Therefore, there is a strong need for cathode materials made from inexpensive and stably available materials that do not contain these rare metals. LFP attracts attention as a cathode electrode material to replace the rare metal-based ones, and already about 60% of cathode electrode material in China is LFP.^{1,2)} With EV production increasing rapidly, a huge amount of LFP, or phosphorus will be required. It is predicted that the primary demand for phosphorus flow in the LFP production will reach 3Mt by 2050.⁷⁾ This undoubtedly brings great pressure to the utilization and distribution of phosphorus resources.

1. 2 Phosphorous utilization risk

Not only for LFP, phosphorus is an essential element in modern society.⁸⁾ Currently, within all of the phosphorus extracted from the phosphate rock, more than 80% of phosphorus is used in agriculture fields (mainly fertilizer) and less than 20% in industry usage (chemicals, semiconductors, surface treatment of steel sheets, etc.), and there has been no severe competition between them.^{9,10)} However, the phosphorus demand for LFP is expected so huge, that there is an expected risk of an unprecedented crisis in which competition with phosphorus for fertilizer will occur.¹¹⁾

To avoid this crisis with the limited resources of phosphate ores, we need to find new phosphorus resources. One is the recycling of spent LFP, but it will take several decades until the used LFP is put on the market.¹²⁻¹⁴⁾ An alternative approach is to use domestic secondary phosphorus resources until the spent LFP is put on the market. Waste ash, the incinerated sewage sludge and animal manure,

is currently considered a promising secondary phosphorus resource^{15–18}). At the same time, steelmaking slag has also attracted increasing attention recently^{19–24}).

1. 3 Using steelmaking slag as the phosphorus source to synthesize LFP

Steel products reach over 1.8 billion tons per year worldwide.²⁵) Along with steel production, a huge amount of slags are also produced. Due to the free CaO and MgO in steelmaking slag resulting in powdering easily, it is difficult to utilize steelmaking slag as construction materials.^{26,27}) The large amount of steelmaking slag has mainly been disposed of in the isolated area. The slag's long-term disposal limits space utilization and pollutes the environment.

The steelmaking slag also contains phosphorus which originates from the iron ores and requires to be removed in the steel products to get rid of brittleness.²⁸) The phosphorus content in the iron ore is greatly enriched in the steelmaking slag after the dephosphorization treatment and exists as P_2O_5 at approximately 2 to 10 mass%. The content of phosphorus also restricts the usage of steelmaking slag. Once phosphorous is separated from steelmaking slags, the steelmaking slag can be reused in the sinter ore plant as well as in architectural engineering. Thus, many studies have been conducted to separate the phosphorus from the steelmaking slag.^{19,22,29–32}) As one of the recovery processes, phosphorous was captured as $FePO_4$ from slag leaching extract. Since $FePO_4$ is known to be the precursor material for producing LFP based on its olivine structure,^{33,34}) steelmaking slag can be used as a phosphorus resource to prepare LFP.

In this case, however, the other elements in the slag are indispensable, and the effect of these on LFP characteristics must be investigated. It is reported that the appropriate element doping in lithium iron phosphate has a certain effect on the improvement of its electrochemical performance at different extents.^{35–37}) For example, Mn^{2+} was reported to influence both electronic and ionic conductivities,^{38,39}) The mechanism of influence of elements' doping on the electrochemical properties of LFP has not been well studied, but the usage of the elements in steelmaking slag as

doping elements to enhance the electrochemical properties of lithium iron phosphate may make the steelmaking slag more attractive.

For the LFP-producing process up until now, FePO_4 has been produced using the co-precipitation method using high-purity H_3PO_4 and FeCl_3 . In the steelworks, there is not only phosphorous-containing steelmaking slag but also a large amount of FeCl_3 produced from mill scale during hot rolling in the steelworks.

In this study, we produce FePO_4 , which is the starting material for LFP production, using a phosphorus extraction solution recovered from slag and a FeCl_3 solution, and then added Li components to create LFP at a low cost. The slag was firstly leached and then titrated by FeCl_3 to extract the phosphorus as FePO_4 . Although the FeCl_3 solution generated within the steelworks has a high purity, the slag extract contains various impurities in addition to phosphorus. Therefore, when using slag extract as a phosphorus raw material, one of the objectives of this study is to evaluate the influence of these impurities on FePO_4 production. The FePO_4 was then mixed with $\text{LiOH}\cdot\text{H}_2\text{O}$ and glucose to produce the LFP at 700°C . By controlling the experimental conditions, the final production showed the feasibility of using slag as the phosphorus source to produce LFP without impurities.

2. Experimental methods

2.1 Materials and procedures

The composition of the steelmaking slag before heat treatment is shown in Table S1-(1). For selective leaching of the slag, it was pretreated through the programmed heating and cooling process.²²⁾ After the furnace was heated to 1600°C in air, the alumina crucible loaded with the slag was slowly put into the furnace. The slag melted at 1600°C and then it was cooled at $3^\circ\text{C}/\text{min}$ to room temperature. During the slow cooling process, the glassy phase containing iron developed, and is hard to dissolve. Consequently, the dissolution of Fe using acid afterward would be suppressed.²²⁾ After the heat treatment, the components of the slag changed due to the oxidation and are shown in Table S1-(2). As shown in Table S1-(2), the total Fe (T-Fe), including the formation of FeO and

metallic Fe (M-Fe) was fully converted into Fe₂O₃. The free CaO and MgO (f-CaO, f-MgO) were converted into stabilized gangue phases and the magnesia crucible increased the MgO content in the slag.

The slag was then crushed and screened under 53μm for selective leaching. The slag was first added to the distilled water at 100 mL per gram slag. With the stirring of the impeller, the 1M HNO₃ was titrated into the water till pH decreased from 11 to 3. According to the equilibrium calculation in the former work,²²⁾ pH=3 is the most suitable condition for selectively leaching the phosphorus in steelmaking slag sufficiently using HNO₃. With pH controlled at 3 by HNO₃, the solution was stirred for 2h. It was then filtered and the leachate was ready for synthesis of FePO₄. The concentration of the elements in the slag leachate is shown in Table 1.

To investigate how the different elements behave during the process, the synthesized extract was analyzed by using chemical agents. Both steelmaking slag extract and synthesized extract were used as the raw material for comparison. Chemical agents Ca(NO₃)₂·4H₂O, Na₂SiO₃, MgCl₂·6H₂O, and H₃PO₄ were used to simulate the steelmaking slag leachate according to the concentration of the primary element, Ca, Si, Mg, and P in the actual slag leachate respectively shown in Table 1. The amounts of the chemical agents for slag synthesis are listed in Table S2. They were mixed in the distilled water together with HNO₃ to maintain the pH = 3. There was a noticeable precipitation of SiO₂ after the mixture. After the filtration, the synthesized extract was prepared.

2. 2 Synthesis of crystallized FePO₄ using slag extract and synthesized extract

When both slag extract and synthesized extract were prepared, the following operation was applied to produce FePO₄. The pH controller was used to maintain the pH of the solution during the precipitation process. 0.2M FeCl₃ was titrated into the slag extract to precipitate the phosphorus by forming the FePO₄·nH₂O precipitation. As for the precipitation reaction in the solution, the Gibbs free energy is given by

$$\Delta G = -\frac{RT}{n} \ln \frac{IAP}{K_{sp}} \quad \text{----- (1)}$$

where R , T , n , IAP , and K_{sp} represent the ideal gas constant, the absolute temperature, the number of ions in the precipitation, the free ionic activities product, and the thermodynamic solubility product of the precipitation phase.⁴⁰⁾ For example, as for one of the precipitation reactions in the solution,



with initial concentration of Fe^{3+} and PO_4^{3-} and $n = 2$ (Fe^{3+} and PO_4^{3-}), the Gibbs free energy could be calculated to determine whether the reaction occur or not at equilibrium situation.

The saturation index (SI) describes the supersaturation or undersaturation of a dissolved salt that deviates from the equilibrium state. It is calculated by the ion activity product (IAP) of the actual solution and the solubility constant (K_{sp}) as below:

$$SI = \log \frac{IAP}{K_{sp}} \quad \text{----- (3)}$$

Also, the relation between SI and Gibbs free energy shows:

$$\Delta G = - \frac{2.303RT}{n} SI \quad \text{----- (4)}$$

Thus, when $SI = 0$, $\Delta G = 0$. The dissolution of the salt is in equilibrium. When $SI < 0$, $\Delta G > 0$. The salt in the solution cannot precipitate thermodynamically. When $SI > 0$, $\Delta G < 0$. In this case, the salt precipitates. According to the equilibrium calculation by PHREEQC (developed by the United States Geological Survey (USGS)).⁴¹⁾ (Figure 1), the saturation index (SI) shows the statement of the solubilities of the possible precipitations in the solution. The $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ precipitates when $\text{pH} > 3$, and $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ starts to precipitate when $\text{pH} > 5$. At $\text{pH} = 3$, $\text{Fe}(\text{OH})_3$ may not precipitate, but it may at $\text{pH} = 5$. Thus, pH was selected at 3 and 5 to precipitate $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ from the steelmaking slag leachate to avoid the coprecipitation of the different matters and to investigate the behavior of $\text{Fe}(\text{OH})_3$.

The pH of the solution gradually decreased with the titration of FeCl_3 , thus, the whole titration procedure was controlled by adding NaOH to keep the pH still. The amount of the titration of FeCl_3 was selected as 0.6, 1.0, and 1.3 stoichiometric mole ratio to the phosphorus amount in the leachate. After two hours of stirring at 400 rpm, the solution remains emulsion. The emulsion was then filtered

and the precipitation was washed three times with pure water and dried at room temperature, and the amorphous $\text{FePO}_4 \cdot n\text{H}_2\text{O}$ was obtained.

Afterward, the precipitation was placed in an alumina crucible and annealed at 600~700°C for 10 hours in a muffle furnace under an air atmosphere. The amorphous $\text{FePO}_4 \cdot n\text{H}_2\text{O}$ was transformed to crystallized FePO_4 during the annealing procedure.

2. 3 Synthesis of the LFP using crystallized FePO_4

Crystallized FePO_4 was used as the raw material to synthesize the LFP. Li source and the reducing agents were required at this time, which have been chosen as $\text{LiOH} \cdot \text{H}_2\text{O}$ and glucose, respectively. The crystallized FePO_4 both from the slag extract and the synthesized extract were utilized for synthesizing the LFP. The LiFePO_4 formation reaction from this mixture can be presented by



Based on reaction (5), 0.5 mole carbon is required to produce 1 mole LFP from 1 mole FePO_4 . Since glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) contains 6 carbon atoms, C eq. is defined as glucose/12 (mole). To fully utilize the FePO_4 to convert to the LFP, the excess amount of $\text{LiOH} \cdot \text{H}_2\text{O}$ and glucose was mixed more than the required amounts indicated in reaction (5). Since unreacted carbon enhances electrical conduction,³³⁾ its presence does not introduce a major problem.

Then the mixture was placed in the furnace for the high-temperature experiment. The mixture was heated at different temperatures (600, 650, and 700°C) under an Ar atmosphere (>99.9999%) and kept for 10 hours at 400 CCM. LFP could be finally synthesized and analyzed under different circumstances.

Figure. 2 shows the overall experimental flow of the synthesis on LFP using the steelmaking slag.

2. 4 Analysis

An X-ray diffraction measurement with a scan speed of 2°/min over a 2θ range from 10 to 70° was used to check the crystallization of the sample. A scanning electron microscope (SEM) was used

to observe the morphology of the prepared powders. An inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used to analyze the concentration of each element in the solution. The standards with different concentration gradients of Fe, Ca, Si, Mg, and P were prepared, and the samples' content was obtained by comparing the test results with the standards. TEM observation was performed to verify the local distortion and disorder of the crystal structure due to the incorporation of impurities. To analyze the decomposition behavior of $\text{LiOH}\cdot\text{H}_2\text{O}$ and glucose, thermogravimetry (TG) was applied.

3. Results and discussion

3. 1 Synthesis of crystallized FePO_4 from the steelmaking slag extract

The steelmaking slag extract was used to synthesize the FePO_4 by FeCl_3 titration at 1.3 stoichiometric mole ratio to the phosphorus in the extract, which aims to ensure the phosphorus could be captured by Fe^{3+} thoroughly to form the $\text{FePO}_4\cdot n\text{H}_2\text{O}$. When pH was selected as 3, the XRD results of the precipitation before and after the annealing at different temperatures (600°C, 650°C and 700°C) were shown in Figure 3 (a). The particle size of the precipitation formed in the solution was either amorphous or too small to be detected by X-ray, and the XRD result showed an amorphous-like pattern. At this moment, it is required to obtain the crystallized FePO_4 . During the annealing treatment, the crystallization did not occur until the temperature reached 700°C. Also, the crystal water in $\text{FePO}_4\cdot n\text{H}_2\text{O}$ was removed. The heat-treated precipitation was identified as the crystal FePO_4 . The tiny particle of FePO_4 grew up and formed the crystal during the heat procedure. Thus, 700°C was selected for the formation temperature of crystal-structure FePO_4 . As shown in Figure 3 (a), the Fe_3PO_7 peak is also identified. The existence of Fe_3PO_7 will be discussed later.

The particle was further examined by a high-resolution transmission electron microscope (TEM) to observe the crystal structure. The TEM result is shown in Figures 3 (b) and (c). It showed the undistorted structure of FePO_4 . Both XRD and TEM results indicated that the titrated Fe^{3+} captured the phosphorus in the slag extract and formed the crystallized FePO_4 . Along with the formation of

FePO₄, the existence of SiO₂ particles was confirmed by TEM observation (Figure 3 (d)), and silica existed as amorphous silica since it showed concentric broad rings (Figure 3 (e)). Namely, the amorphous silica did not transform to the crystal SiO₂ even at 700°C heat treatment.

3. 2 Influence of the titrated Fe³⁺ on the FePO₄ formation

While crystallized FePO₄ was prepared at the 1.3 stoichiometric mole ratio of Fe³⁺ to phosphorus, the XRD peak at about 29° represents the Fe₃PO₇ formed in the meantime.

Figure 4 (a) shows various compounds composed of Fe₂O₃, FeO, and P₂O₅.⁴²⁾ In this figure, the iron in the compound on the line connecting P₂O₅ and Fe₂O₃ is Fe³⁺, and the iron in the compound on the line connecting P₂O₅ and FeO is Fe²⁺. The compound surrounded by these two lines contains a mixture of Fe²⁺ and Fe³⁺. As can be seen from the figure, the reaction to generate Fe₃PO₇ from its stoichiometry is thought to be due to the reaction of FePO₄ + Fe₂O₃ → Fe₃PO₇. However, Fe₂O₃ is required for this reaction to occur.

The excess of the Fe³⁺ leads to the precipitation of the Fe(OH)₃. As shown in Figure 1, the SI of Fe(OH)₃ at pH=3 is -0.45 which means Fe(OH)₃ is soluble. The results shown in Figure 1 were carried out under the equilibrium conditions. In the actual titration process, however, there will be a local fluctuation of pH, which may lead to Fe(OH)₃ coprecipitation with the FePO₄·nH₂O practically. The Fe(OH)₃ can be converted into Fe₂O₃ during the heating process,



and formed Fe₂O₃ reacted with the FePO₄ to produce the Fe₃PO₇ by the following reaction:⁴³⁾



For the best control of the procedure, the simulated extract was used for analyzing the effect of the amount of the Fe³⁺ addition. The Fe/P ratio has been decreased from 1.3 to Fe/P=1 and 0.6. After applying the same operation to the precipitation, the XRD results showed the disappearance of the peak of Fe₃PO₇ at pH=0.6 as shown in Figure 4 (b).

The extracts before and after the filtration of the precipitation by FeCl_3 were analyzed by an inductively coupled plasma atomic emission spectroscopy (ICP-AES) to evaluate the elements' concentration. The ICP-AES results of different Fe/P ratios are listed in Table S3. The phosphorous content in the solution before precipitation is 90 ppm. For the case of Fe/P=1, 168 ppm of Fe is required to precipitate all of this phosphorous. When Fe/P=1.3, the addition of Fe content for the precipitation is 218 ppm. Therefore, after all 90 ppm of phosphorous is precipitated, 50 (=218-168) ppm of Fe remains. As shown in Table S3, the amount of Fe remaining in the solution is 27 ppm. It is thought that 23 ppm of Fe is precipitated as $\text{Fe}(\text{OH})_3$. When the Fe/P mole ratio was 1, the recovery of P in the solution reached 98%. However, to avoid the production of Fe_3PO_7 , Fe/P mole ratio as 0.6 was chosen. The Fe_3PO_7 may appear if Fe/P mole ratio increases. And less P will be captured if Fe/P mole ratio decreases.

3. 3 Coprecipitation of impurities with FePO_4

The FePO_4 powder synthesized from the steelmaking slag leachate was dissolved in HCl and subject to ICP-AES for analyzing the concentration of the other elements. The results are listed in Table 2. It was presented as the mole ratio using the amount of Fe element as the denominator. As shown in Table 2, the Si, Ca, and Mg components in the steelmaking slag leachate did not tend to co-precipitate with the FePO_4 . Ca was already washed away during three times washing of FePO_4 precipitation with pure water. SiO_2 does not dissolve in HCl. Therefore, SiO_2 was not present in the dissolved solution although SiO_2 coexists with FePO_4 .

The small amount of Al and Mn components co-precipitated and remained with the FePO_4 powder. At present, it is unclear whether Mn and Al are incorporated into FePO_4 or whether they are just attached to the surface, but even if they are incorporated, the amount is small and it is assumed that they will not have a major effect on the crystal formation of FePO_4 .

3. 4 Influence of pH on the FePO_4 formation

According to the equilibrium calculation of slag extracts by PHREEQC, as shown in Figure 1, the $\text{FePO}_4 \cdot n\text{H}_2\text{O}$ had the highest value of SI at pH=5. At pH=5, however, the precipitation for $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ is expected. To evaluate the effect of the pH on the FePO_4 formation, the precipitation was carried out at pH=5.

The XRD results of the precipitation at pH=5 in the slag extract are shown in Figure S1. It showed that FePO_4 was generated, but $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, which is expected to precipitate thermodynamically, did not precipitate.

Compared to $\text{FePO}_4 \cdot n\text{H}_2\text{O}$, more ions are required to form $\text{Ca}_5(\text{PO}_4)_3\text{OH}$. Therefore, from a kinetic point of view, it is thought that the precipitation of $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ is less easy than that of FePO_4 . With pH changed from 3 to 5, according to Figure 1, $\text{Fe}(\text{OH})_3$ trended to precipitate easier. Thus, although the titration amount was controlled as Fe/P=0.6, some amount of $\text{Fe}(\text{OH})_3$ was precipitated for further forming Fe_3PO_7 .

3. 5 Synthesis of LFP from the crystallized FePO_4

The valence of Fe in FePO_4 is 3+, and that in LFP is 2+. Therefore, to produce LFP using FePO_4 as a starting material, it is necessary to reduce Fe^{3+} in FePO_4 to divalent Fe. Thus, the FePO_4 prepared from the slag extract was mixed with $\text{LiOH} \cdot 2\text{H}_2\text{O}$ and glucose ($\text{C}_6\text{H}_{12}\text{O}_6$), and annealed at 700°C to synthesize the LFP. Based on the reaction (5), 0.5 mole carbon is required to produce LFP (1 mole) from FePO_4 (1 mole). To provide sufficient Li and carbon for the reduction of FePO_4 , the mole ratio of FePO_4 : $\text{LiOH} \cdot \text{H}_2\text{O}$: C eq. was set to 1.00: 1.06: 2.00. An experiment with C eq. set to 3.00 was also carried out to see the influence of carbon content.

The products obtained by this process were analyzed by XRD, and the results are shown in Figure 5 (a), which confirmed the formation of LFP. As shown in Figure 5 (a), when the amount of glucose was increased to 3.00 C eq., the Fe^{3+} was partly reduced to Fe. The excess carbon amount increased the reducing potential of the environment and over-reduced the Fe^{3+} to Fe. Thus, the amount of glucose was controlled at the 2.00 C eq.

3. 6 The LFP formation mechanism from FePO₄

The reaction mechanism for producing LFP by carbon reduction of a mixture of FePO₄ and Li(OH) is complex and details have not been established yet. To analyze the LFP formation from FePO₄, the thermogravimetry (TG) analysis was carried out. The TG results of the LiOH·H₂O and glucose are shown in Figure 5 (b). The atmosphere was chosen as N₂ and the heating rate was 5 °C/min from room temperature to 700°C and holding for 10 hours as shown in the red broken line in the figure.

The absorbed water in LiOH·H₂O was initially evaporated until the temperature reached about 100°C. After that, the dehydration of LiOH·H₂O caused 42% weight loss and decomposing to Li₂O. The final weight loss of LiOH·H₂O was 64% as shown in Figure 5 (b). The glucose decomposed gradually from about 200 to 400°C and most of the glucose (C₆H₁₂O₆) was decomposed to carbon at 700°C. The TG result shows that the mixture of FePO₄, LiOH·H₂O, and glucose will be changed to the mixture of FePO₄, Li₂O, and carbon when it reaches 700°C.

The phase diagram of the FePO₄-LiFePO₄ binary system is schematically shown in Figure 6 (a). As shown in the figure, there is a miscibility gap between the FePO₄-based solid solution and the LFP-based solid solution at room temperature. Namely, when the battery proceeds discharging, the cathode LFP solid solution converts to FePO₄ solid solution, and conversely, during charging, the generated FePO₄ solid solution changes to LFP solid solution. While at more than about 350°C, LFP and FePO₄ fully dissolve in each other to form a complete solid solution, Li_{1-x}FePO₄ (0 ≤ x ≤ 1). The Li_{1-x}FePO₄ can be more precisely presented by Li_{1-x}Fe²⁺_{1-x}Fe³⁺_xPO₄.

This means that the formation of LFP from a mixture of FePO₄, C, and Li₂O involves the reduction of Fe³⁺ in FePO₄ to Fe²⁺ by carbon and the progress of Li diffusion into FePO₄, resulting in the formation of a FePO₄-based-solid solution in the early stage. When the Fe²⁺ and Li reach a certain amount in the solid solution, the FePO₄-based-solid solution structure changes to an LFP-based-solid solution structure and finally becomes pure LFP. The LFP formation process proceeds along with

the hatched line from FePO_4 to LFP shown in Figure 6 (b). The schematic $\text{FeO-Fe}_2\text{O}_3\text{-Li}_2\text{O-P}_2\text{O}_5$ system is constructed based on $\text{Fe}_2\text{O}_3\text{-Li}_2\text{O-P}_2\text{O}_5$ system⁴²⁾ and $\text{FeO-Li}_2\text{O-P}_2\text{O}_5$ system⁴²⁾.

The phase development from each FePO_4 particle to LFP during heat treatment at 700°C in the present study is shown in Figure 6 (c). For the comparison, the phase development during charging of the FePO_4 cathode in the battery at room temperature is also schematically shown in Figure 6 (c). In the heat treatment process at 700°C , as shown in Figure 6 (a), the formation of LFP from FePO_4 occurs by the development of $\text{Li}_{1-x}\text{FePO}_4$ solid solution with increasing Li ion in the $\text{Li}_{1-x}\text{FePO}_4$ solid solution⁴⁴⁾. Li ions are disorderly distributed in the solid solution crystal lattice. At the particular Li concentration, the solid solution changes from FePO_4 base crystal structure (cristobalite structure) to LFP-based crystal structure (olivine structure). However, in the formation of LFP from FePO_4 during electron charging process in the battery at room temperature, FePO_4 is directly converted to LFP⁴⁵⁾. Namely, LFP and FePO_4 coexist during the charging process.

4. Conclusions

To meet the huge demand of phosphorous to produce a cathode material LFP used in EVs, the feasibility of LFP production using steelmaking slag was investigated, and obtained results are summarized as follow:

- (1) The procedure to produce LFP from steelmaking slag extract was carried out using FePO_4 as the intermediate product. After the selective leaching of the steelmaking slag by HNO_3 , the FePO_4 was precipitated from the leachate by titration of FeCl_3 . A mole ratio of Fe/P was selected as 0.6 to avoid the further formation of Fe_3PO_7 .
- (2) The elements in the solution, Ca, Si, Mg, Mn, and Al, did not affect the FePO_4 crystallization, and Si and Mg element components even did not coprecipitate with the FePO_4 .
- (3) The prepared crystalized FePO_4 powder was mixed with $\text{LiOH}\cdot\text{H}_2\text{O}$ and glucose ($\text{C}_6\text{H}_{12}\text{O}_6$), and the mixture was heated at 700°C to produce LFP. The transformation from FePO_4 to LFP has a very particular requirement of the amount of glucose to provide the proper reducing environment.

The trivalent iron was reduced to bivalent iron by the carbon decomposed from glucose. It should be controlled carefully at 2.00 C eq. to avoid of the formation of metallic Fe.

(4) Steelmaking slag is conformed to be used as the phosphorus source for synthesizing LFP. By separating phosphorus from steelmaking slag, it also becomes possible to effectively utilize steelmaking slag, whose use has been limited so far.

Supporting information

The compositional changes of the steel slag pretreatment process, the composition of the simulated slag leachate, the ICP results of the titration process and the titration products at a pH of 5 are shown in the supporting information. This material is available on the website.

Statement for conflict of interest

We have no conflicts of interest to disclose.

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440

441

442 Table 1. The concentration of the elements of the steelmaking slag leachate (ppm)

Ca	Si	Mg	P	Fe	Al	Mn
2200	340	200	90	0	1	39

443

444 Table 2. The mole ratio of the elements in the FePO_4 synthesized from the steelmaking slag
 445 leachate

Ca/Fe	Si/Fe	Mg/Fe	P/Fe	Fe/Fe	Al/Fe	Mn/Fe
0	0	0	0.98	1	0.0078	0.0052

446

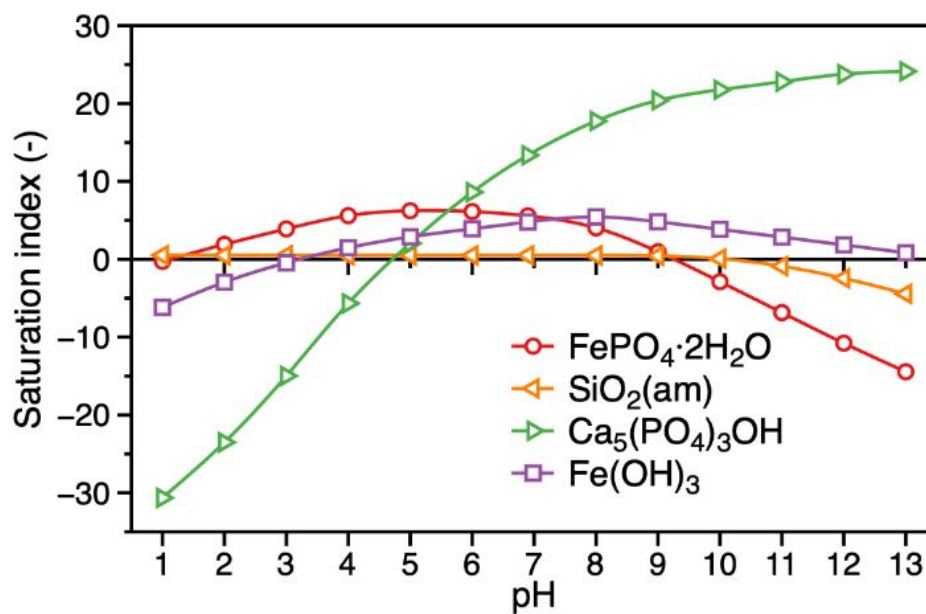


Figure 1. Saturation index of the possible precipitation in steelmaking slag leachate by simulation.

(online version in color)

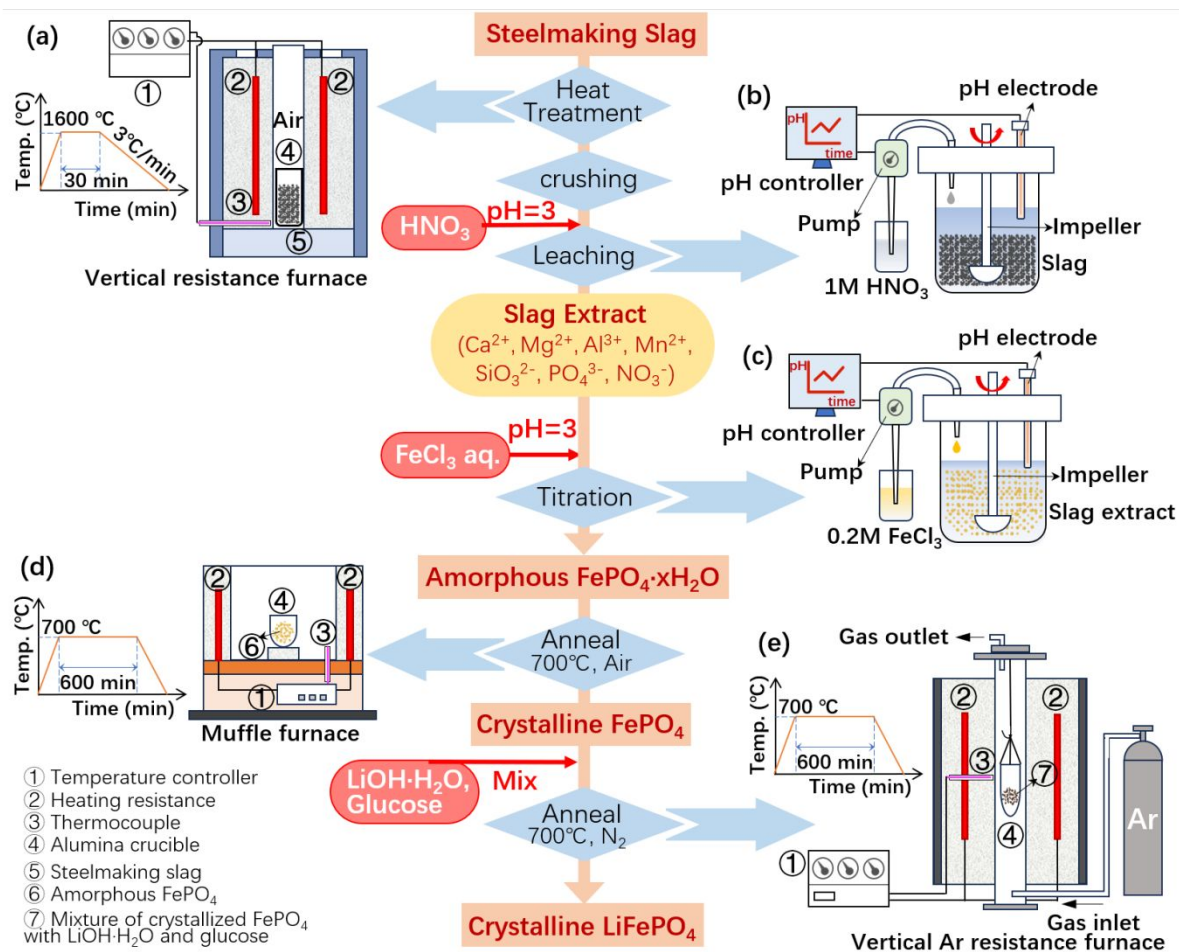


Figure 2. The experimental flow of synthesis on LFP using steelmaking slag through (a) the heat treatment of the slag, (b) the selective leaching of the slag, (c) FeCl₃ titration for precipitation of FePO₄, (d) heating treatment of amorphous FePO₄ and (e) synthesis of LFP using the vertical resistance furnace. (online version in color)

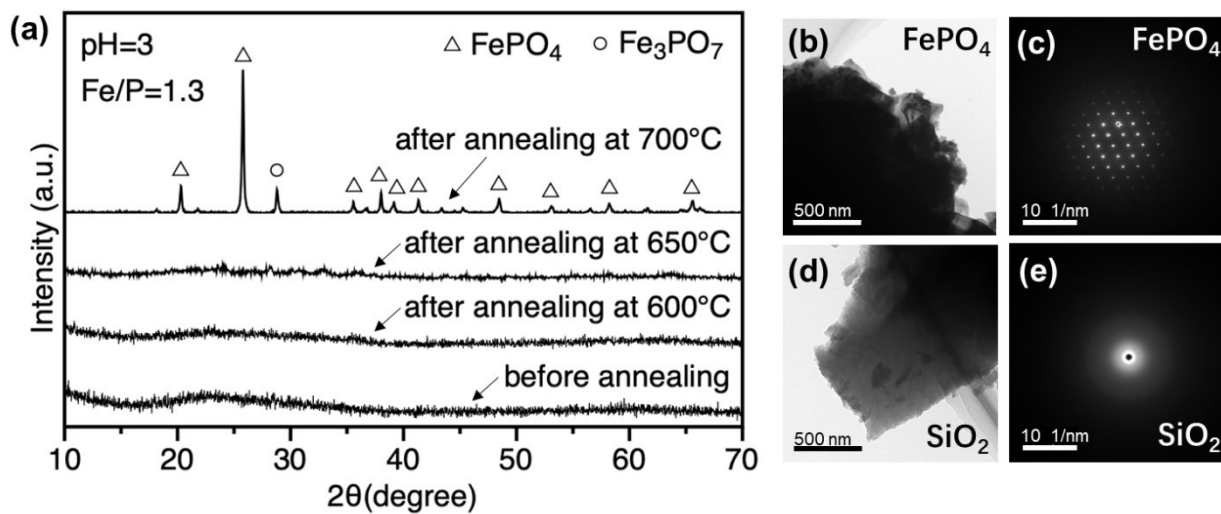


Figure 3. (a) The XRD results of the precipitation before and after the annealing at 600°C, 650°C and 700°C. (b) (c) TEM result of the major part of the precipitation as crystallized FePO_4 phase, and (d) (e) the minor part of the detection on amorphous SiO_2 .

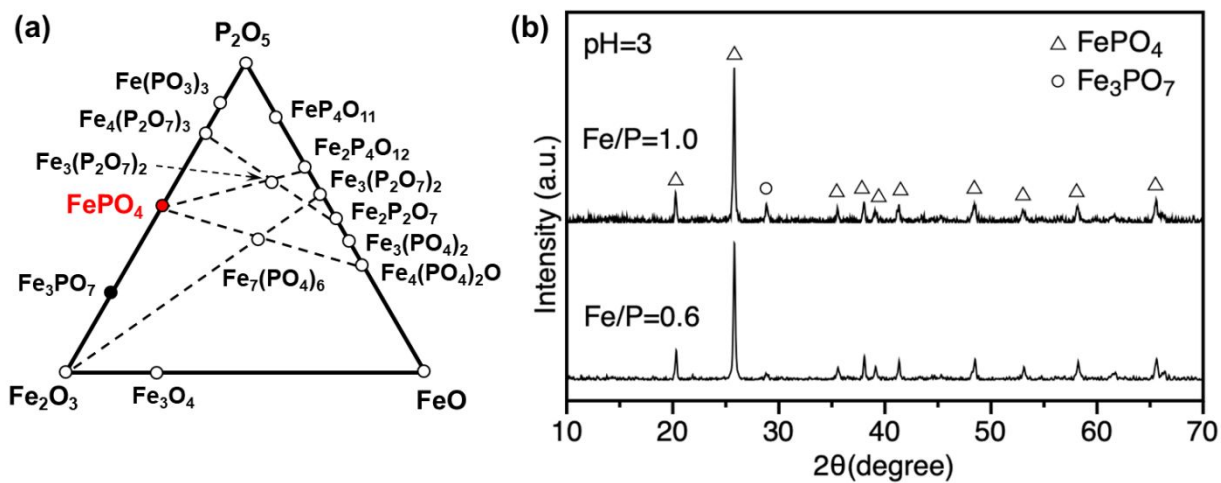


Figure 4. (a) The phase diagram of the P_2O_5 - Fe_2O_3 - FeO system⁴²⁾ and (b) The XRD results of the precipitation with titration amount of Fe^{3+} at Fe/P mole ratio of 0.6 and 1.0 in the simulated slag extract. (online version in color)

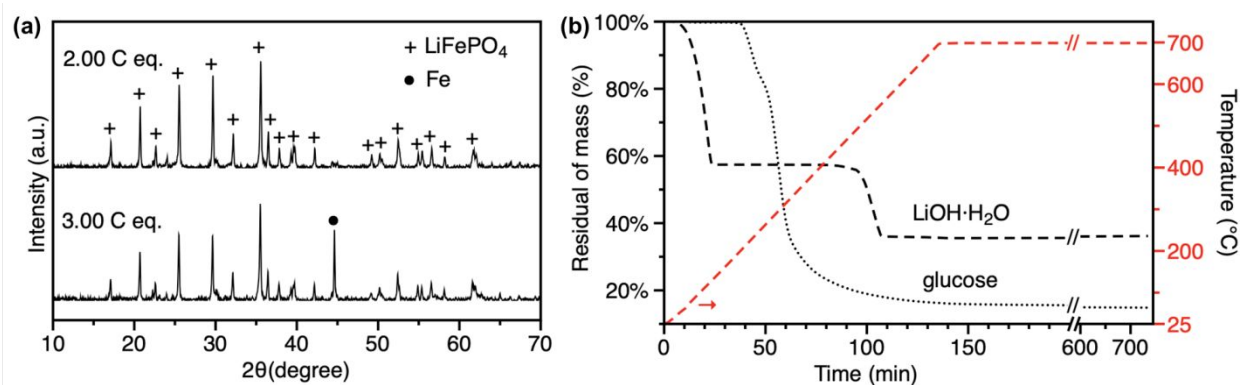


Figure 5. (a) The XRD results of the synthesized LFP using FePO_4 prepared from the slag extract. (b) The thermogravimetry (TG) of $\text{LiOH}\cdot\text{H}_2\text{O}$, and glucose. (online version in color)

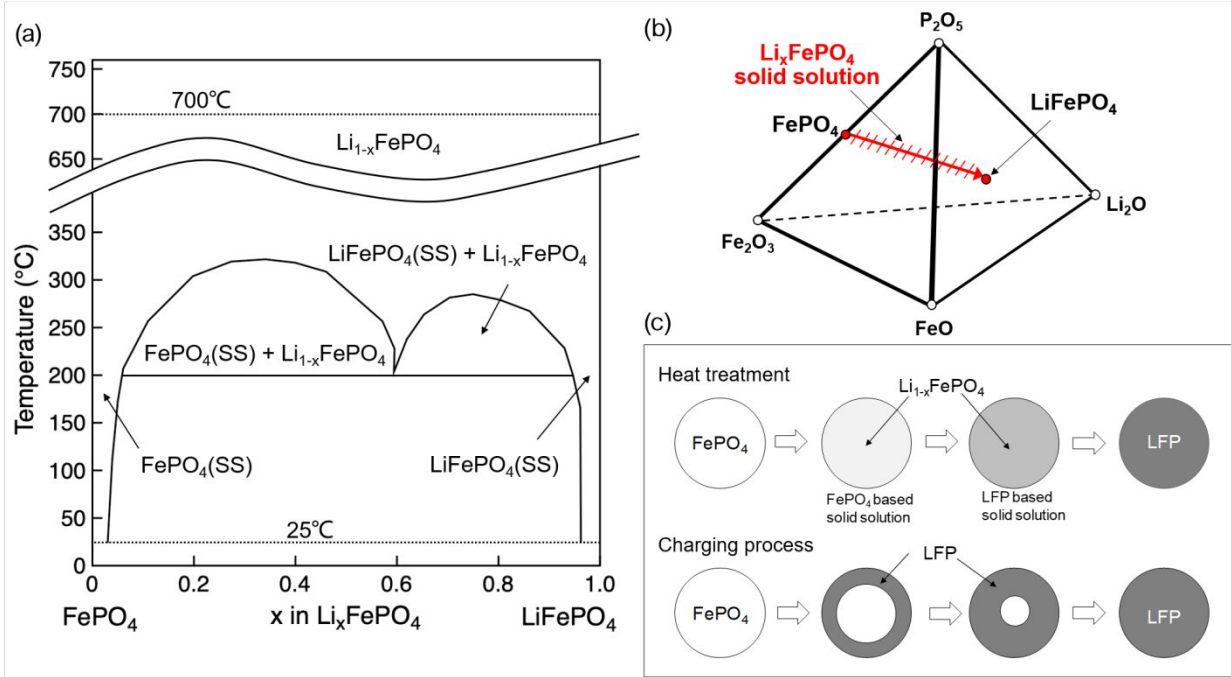


Figure 6. (a) The FePO_4 - LiFePO_4 system⁴⁴⁾. (b) The FeO - Fe_2O_3 - Li_2O - P_2O_5 system. In Figure 6 (b), $\text{Li}_{1-x}\text{FePO}_4$ means the solid solution of FePO_4 and LiFePO_4 , where $0 \leq x \leq 1$. (c) The phase development from FePO_4 to LFP during heat treatment at 700°C and the phase development during charging of the FePO_4 cathode in the battery at room temperature. (online version in color)

Supporting Information

Production of LiFePO_4 by using steelmaking slag as a phosphorus source

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Table S1. The components of the steelmaking slag (1) before and (2) after the heat treatment (mass %)

No.	CaO	SiO ₂	T-Fe	FeO	Fe ₂ O ₃	M-Fe
(1)	31.3	19.0	22.1	19.2	7.3	2.1
(2)	30.3	25.3	-	-	25.6	-
No.	Al ₂ O ₃	MnO	MgO	P ₂ O ₅	f-CaO	f-MgO
(1)	3.4	5.4	6.3	3.2	2.1	0.004
(2)	3.6	4.0	8.5	2.7	-	-

Table S2. The composition of the simulated slag leachate in 1L distilled water

$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	Na_2SiO_3	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	2M H_3PO_4	1M HNO_3
12.96g	3.44g	1.67g	1.45mL	26.00mL

Table S3. The ICP-AES results of the simulated steelmaking slag leachate and solution after filtration by titration of FeCl₃ at pH=3 with Fe/P mole ratios at 0.6, 1.0, and 1.3 (ppm)

	Fe	Ca	Si	Mg	P
Synthesized extract	0	2200	340	200	90
After filtration of precipitation of Fe/P=0.6	0	2200	313	200	30
After filtration of precipitation of Fe/P=1.0	5	2160	307	191	2
After filtration of precipitation of Fe/P=1.3	27	2155	340	200	7

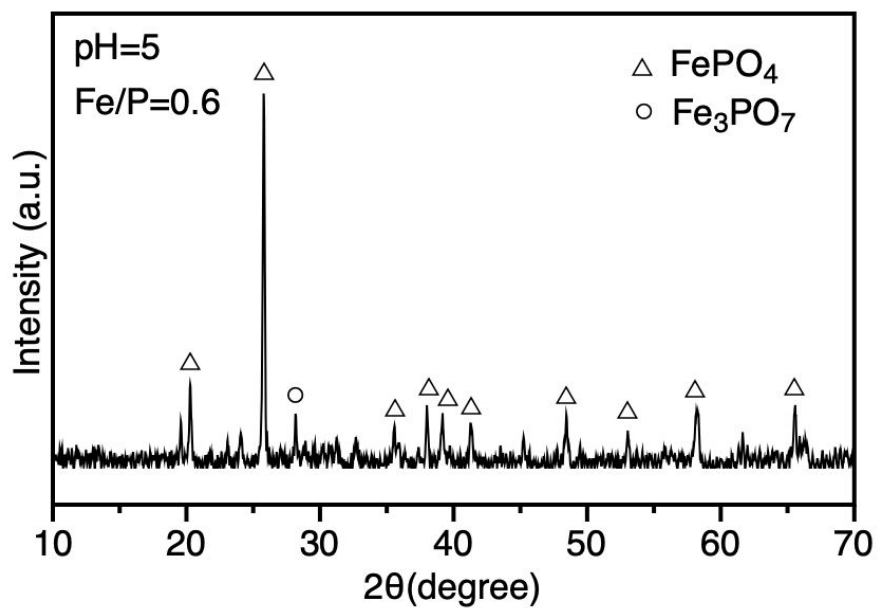


Figure S1. The XRD results of the precipitation at pH=5 with titration amount of Fe^{3+} at Fe/P mole ratio of 0.6 in the slag extract.