Synthesis of Metal-doped $LiFePO_4$ from Nickel Laterite Lixivium

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Nickel laterite lixivium is purified by fast phosphate coprecipitation. ICP analysis confirms that Ni, Co, Mn recovery rates are 88.83, 92.66, 93.48%, respectively, and all iron is removed as $FePO_4{\cdot}xH_2O$ precursor with trace Al, Mg, Ni, and Mn elements. To evaluate the structure and electrochemical performance of $FePO_4{\cdot}xH_2O$, metal-doped $LiFePO_4$ is prepared from the as-prepared precursor. It is noted that the metal-doped $LiFePO_4$ exhibits well-crystallized structure, homogeneous distribution, and excellent electrochemical properties.

It is reported that around 70% of global land-based nickel resources is contained in laterite ores. Nevertheless, due to the difficulty in refining oxides, only about 40% of nickel product is extracted from such ores, with the balance as sulfides.[1] Along with the decline of global nickel sulfide reserves and increasing demand for nickel, at an average of 4% pa;[2] there is, therefore, a need for a new processing route to recover the value from laterite ores.

Currently, acid leaching has become the primary technology for processing laterite ores, due to rapid high extractions coupled with high plant throughputs. However, one drawback is that iron is removed as hematite during pyrohydrolysis or hydrolysis, which are not only energy-intensive but also requires high capital expenditure, inhibiting its industrialization.[3] Recently, some studies have focused on decreasing the cost of iron removal, how to keep the amount of iron in lixivium to a minimum and removing iron by ion exchange have been proposed.[4,5] However, these technologies still have some problems, such as lower Ni and Co recovery rate caused by limited iron content, and complicated routes and vast consumption of ion exchanger. Additionally, the value of iron in laterite ores is less utilized in those technologies, which causes not only severe environmental problems but also the waste of iron resources. Hence, considering the 30% or greater of total iron content in laterite ores, more efficient and economical ways to remove and utilize the iron in such ores should be studied.

In this work, through a fast coprecipitation method, all iron in laterite lixivium is removed as iron(III) phosphate, which is the precursor of $LiFePO_4$, a promising cathode material for lithium ion batteries. The valuable elements in laterite lixivium, Ni, Co, and Mn, on the other hand, remain in the filtrate. The attained by-product $FePO_4{\cdot}xH_2O$ requires no further purification because some of the impurities remaining in the material (such as Al, Mg, Ni, Co, etc.) improve the electrochemical performance of $LiFePO_4$.[6–9] It is noted that the metal-doped $LiFePO_4$, prepared from the laterite lixivium, exhibits excellent electrochemical properties.

Metal-doped $FePO_4{\cdot}xH_2O$ was synthesized by the following procedure: (1) laterite lixivium (Table 1) was attained by leaching nickel laterite ores (from Yuanjiang, China) with an atmospheric hydrochloric acid process, at 80 °C and 3 h; the weight ratio between nickel laterite ores and hydrochloric acid (35 wt %) is 1:2.7. (2) H_3PO_4 (85 wt %) was added to laterite lixivium in a molar ratio for $Fe:PO_4 = 1:1$. (3) concentrated hydrogen peroxide (30 wt %) was added to the solution to ensure all Fe^{2+} oxidizing to Fe^{3+}. (4) then $NH_3{\cdot}H_2O$ (2 M) was added dropwise into the solution to control the pH 2.0 ± 0.1, subsequently a yellow precipitate formed immediately. (5) after being stirred for 20 min, the precipitate was filtered, washed several times with deionized water, and dried in an oven at 80 °C. Thus, metal-doped $FePO_4{\cdot}xH_2O$ powders were obtained. (6) the filtrate was collected to analyse element contents. Crystalline metal-doped $LiFePO_4$ was prepared by ball milling with Li_2CO_3, oxalic acid, and precursor powder via ambient temperature reduction. Element contents, structure, image, and electrochemical properties of sample were tested by ICP, XRD, EDS, and battery test system, respectively, further experimental details can be found in our previous work.[10,11]

Table 1. Chemical composite of laterite lixivium and corresponding recovery of filtrate

	Fe	Al	Mg	Ni	Co	Mn	Cu	Ca
Concentration/$g\,L^{-1}$	28.04	0.7	33.02	2.149	0.0749	0.511	0.0065	0.05
Recovery/%	0	16.4	61.69	88.83	92.66	93.48		

Table 2. The molar ratio of Fe, Mg, Ni, Co, Mn, Al, Cu, and Ca in raw material (laterite lixivium) and product (metal-doped $LiFePO_4$)

Samples	Fe	Al	Mg	Ni	Co	Mn	Cu	Ca
Lixivium	100	5.15	270.6	7.29	0.25	1.85	0.02	0.24
$LiFePO_4$	100	1.99	0.147	0.075	0.001	≈0	≈0	0.001

Table 1 lists chemical composite of laterite lixivium and corresponding recovery of filtrate, which was obtained from ICP results. It is obvious that the recovery rates of Mn, Co, and Ni in filtrate are 93.48, 92.66, and 88.83, respectively, and all Fe is removed successfully. Besides Fe, the contents of other impurities, such as Al and Mg also decrease to 16.4 and 61.69%, partly due to some of them precipitating in precursor and partly due to some of them losting in the wash process.

The molar ratios of different elements in laterite lixivium and metal-doped $LiFePO_4$ are compared in Table 2. As shown, about 2 atom % Al, Mg, Ni, Co, and Ca mixture is doped in the precursor. It is reported that supervalent substitutions, such as Al^{3+}, Mg^{2+}, Ni^{2+}, and Co^{2+}, will be conducive to the electrochemical performance of $LiFePO_4$,[6–9] the influence of Ca^{2+} doping was seldom reported but could be ignored in this paper, because of the low quantity.

X-ray diffraction patterns of the synthesized $FePO_4{\cdot}xH_2O$ and metal-doped $LiFePO_4$ are shown in Figure 1. It can be seen that there is no evidence of diffraction peaks in precursor, indicating the synthesized $FePO_4{\cdot}xH_2O$ is amorphous. Previously, Chiang et al. found that aliovalent cations tend to substitute at

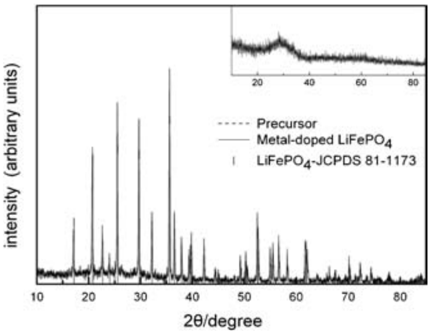

Figure 1. XRD pattern of $FePO_4 \cdot xH_2O$, metal-doped $LiFePO_4$ powder, and standard $LiFePO_4$.

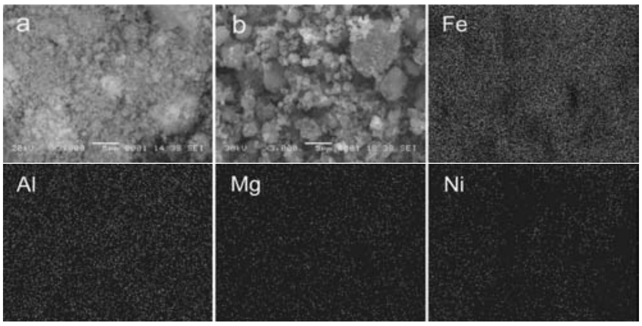

Figure 2. SEM images of amorphous $FePO_4 \cdot xH_2O$ (a) and metal-doped $LiFePO_4$ (b), with corresponding EDS maps of image b (the scale in Figures 2a and 2b is 5 μm).

Li^+ sites to form solid solutions without any impurities, because the sixfold ionic radii of Al^{3+} and Mg^{2+} (0.054 and 0.072 nm respectively) are close to the radius of Li^+.[7] As seen in $LiFePO_4$ XRD patterns, all diffraction lines are indexed to the orthorhombic *Pnmb* space group and no impurity is detected, this demonstrates cations (Al^{3+}, Mg^{2+}, etc.) had doped into Li^+ sites and also indicates that well-crystallized $LiFePO_4$ could be attained from laterite lixivium via this fast coprecipitation method. The crystal lattice parameters calculated by Rietveld refinement are $a = 10.3149$, $b = 6.0012$, $c = 4.691$ Å, and $V = 290.38$ Å^3, which are quite consistent with the Al-doped $LiFePO_4$ data reported by Chiang et al.[7]

Figure 2 shows the SEM images of amorphous $FePO_4 \cdot xH_2O$ (a) and metal-doped $LiFePO_4$ (b), and corresponding EDS maps of Figure 2b. It is noted that both $FePO_4 \cdot xH_2O$ and metal-doped $LiFePO_4$ exhibit a uniform sphere-like microstructure and little agglomeration. The particle size of $LiFePO_4$ is 200–500 nm interconnected with a porous network, which is conducive to the lithium diffusion. Furthermore, the element (Fe, Al, Mg, and Ni) distribution areas are homogeneous, partly due to the fact that laterite lixivium is molecular level mixed solution and partly due to the fast coprecipitation method leading to small and well-dispersed product.

Figure 3 shows the electrochemical performance of metal-doped $LiFePO_4$. The cell was cycled 20 times at 0.1C firstly and then cycled 100 times at 1C, 2C, 5C in turn, testing in the voltage range of 2.5–4.1 V at room temperature. The wavy curves can be ascribed to room temperature change. The initial discharge capacity values of sample at the rate of 0.1C, 1C, 2C, and 5C are 157.3, 140, 132.2, and 110 mA h g^{-1}, respectively. It is obvious that the cycle efficiency is almost 100% from the first cycle to the 20th cycle at 0.1C, 21th cycle to 120th cycle at 1C and 121th cycle to 220th cycle at 2C. After the 220th cycle, the discharge capacity decreases a little, 106.4 mA h g^{-1} is attained until 320th cycles (96.7%). The excellent rate ability and cycle performance of $LiFePO_4$ should be ascribed to metal-doping and fast coprecipitation, the former intrinsically improves the electronic conductivity of $LiFePO_4$ material and the latter contributes to small particle size and homogeneous distribution of all elements.

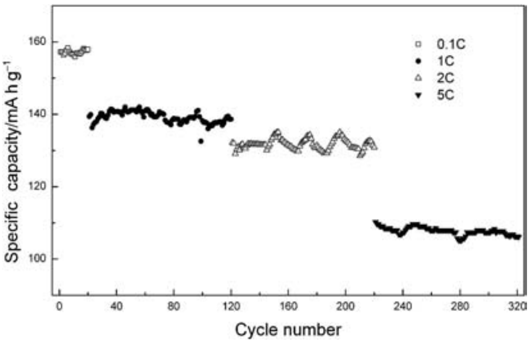

Figure 3. Discharge cycling performance of metal-doped $LiFePO_4$ at different C rates of 0.1C, 1C, 2C, and 5C.

In sum, nickel laterite lixivium is successfully purified by fast phosphate coprecipitation. ICP analysis confirms that Ni, Co, Mn recovery rates are 88.83, 92.66, 93.48%, respectively, and all iron is removed as $FePO_4 \cdot xH_2O$ precursor with trace Al, Mg, Ni, and Mn elements. Electrochemical studies further confirm that the metal-doped $LiFePO_4$ prepared from laterite lixivium exhibits excellent rate and life cycle properties.

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