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MICROWAVE-ASSISTED PROCESSING FOR THE SYNTHESIS OF $LiFePO_4$/C COMPOSITE POWDERS FROM THE STEEL SLAGS

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Abstract

In this paper, the steel slags were reduced by microwave-assisted processing and the heating-up characteristics of steel slags, the influence of reduction agent content and the annealing temperature as well as the removal of Ca impurities on the synthesis of $LiFePO_4$ were discussed. The results indicated that with the addition of glucose reduction agent, and the recovery of elemental Fe can reach as high as 87.77wt%. With the removal of Ca and the addition of Li_2CO_3 and glucose, $LiFePO_4$/C composite powders could be obtained by microwave-assisted annealing. Electrochemical measurements showed that the initial discharge capacities of the $LiFePO_4$ lithium batteries were around 136.1~138.0 mAh/g, which remained as high as 132.4~134.39mAh/g after 10 cycles charge and discharge measurements.

Introduction

The steel slags usually have great content of main elements, such as Ca, Si, Mg, P, Fe, O *etc*. and also contain some other useful elements, such as Mn, V, Cr, Ni, Nb, *etc*. These useful elements can be recovered by reduction and magnetic separations. By adding some additives to the steel slags, $LiFePO_4$, which is an important cathode material for lithium-ion batteries, can be prepared. Furthermore, previous studies suggest that $LiFePO_4$ conductivity can be improved by doping with specific metal ions, such as Mn^{2+}, Cr^{3+}, Ti^{4+}, Zr^{4+}, Nb^{5+}, V^{5+}, W^{6+}, Mo^{6+} [1,2]. In this work, we report a novel processes to synthesise $LiFePO_4$/C composite powders by using steel slags, Li_2CO_3 and glucose as the raw materials. This investigation has two advantages, on one hand the cost of raw materials for lithium battery can be reduced, while the electrochemical performance of $LiFePO_4$ can be improved; on the other hand it offers the possibility to recycle wastes, practice in line with the industrial policy of circular economy.

Experiments

Raw materials and equipment

Steel slags were obtained from Baotou Steels Ltd. All chemical regents such as H_2SO_4, H_3PO_4, H_2O_2, NaOH, glucose, lithium carbonate were used as purchased.

Microwave-assisted process was performed with a DLGR-05S microwave oven (Delangneng Company). The power is 6 KW and the frequency is 2450 ± 50MHz.

Experimental process

Steel slags were crushed into particles with the size of less than 0.2 mm. A certain amount of glucose was added to the crushed slags and uniform mixture was obtained. The mixture was reduced at different temperatures by microwave. The slag extracts were obtained by magnetic separation. Further the slag extracts were added into diluted sulphuric acid solution, and were kept at 80°C for 3 hours under continuous stirring. After ageing and pumping filtration, the filtrate was collected. Hydrogen peroxide and phosphoric acid were added into the filtrate. The temperature was kept at 40°C and the pH value was adjusted to 3-5. After filtration and washing, Fe-P extract powders were obtained with Ca removal.

Synthesis of $LiFePO_4$/C composite powders was carried out as follows: lithium carbonate, glucose (reducing agent) and citric acid water solution were added under stirring into the Fe-P extract powers without Ca, and a slurry was formed. The slurry was placed in a crucible, left it for aging for 24 hours and placed into the microwave oven. After 20 min of microwave irradiation at 600°C the $LiFePO_4$/C samples were obtained. To test the electrochemical performance $LiFePO_4$/C samples were used as cathode materials. The charge/discharge cycles were performed within a voltage range of 2.5–4.1V at different rates by Land Battery Testers.

Results and discussion

Extract of Fe and P

To determine the microwave absorbing properties of the steel slags, the temperature rising characteristics were tested, results appear in Figure 1 (left). It is revealed that the steel slag can be well heated by microwave. When the temperature is around 780-950°C, the heating rate increased rapidly, which indicates the reduction of Fe (III) and the formation of iron phosphide.

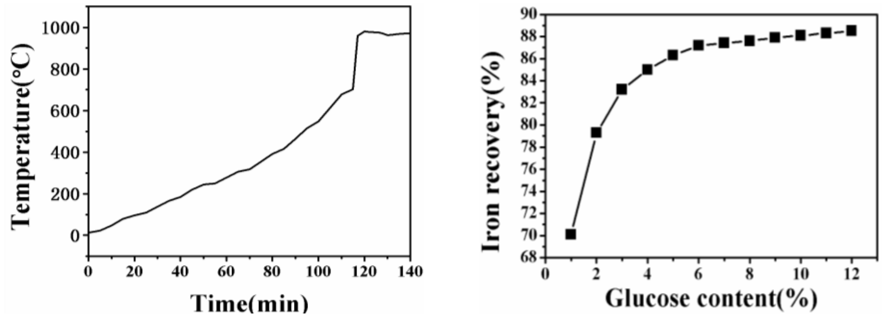

Figure 1: The heating-up characteristics of the steel slag in microwave fields (left); the Influence of glucose content on the iron recovery (right)

Figure 1 (right) reveals the influence of glucose content on the iron recovery. Fe recovery increases drastically with glucose increase. However, when the content of glucose was too high, the recovery of Fe was limited. This was because only magnetism-responsive Fe components (mostly in the Fe_3O_4 form) can be recovered during the magnetic separation process. When the amount of glucose is too high, large proportions of significantly reduced Fe (II) are formed, and the recovery of Fe is being hindered. The optimised content of glucose was 6 wt%.

When the steel slags were annealed at 550°C for 10 min with 6 wt% of glucose, Fe and P recovery reached 87.77 wt% and respectively 82.32 wt%. This high percentage recovery allows the resulted Fe_3O_4 to be easily concentrated by magnetic separation treatments.

As shown in Figure 2 (left), the resulted steel slags contain large amounts of CaP. The extra Ca element should be excluded. Table 1 shows the composition of the steel slags after the extraction of Ca at pH 3.0, measured by XRF. The major elements are Fe, P and other target elements (such as, Mn, Cr, Mg, Al, Ti), and the content of impurities (such as Ca and Si) were quite low. After further annealing at 700°C, $Fe_7(PO_4)_6$ phase could be obtained, which can be seen from the XRD results of Figure 2 (right figure). All the recorded diffraction peaks can be assigned to pure $Fe_7(PO_4)_6$.

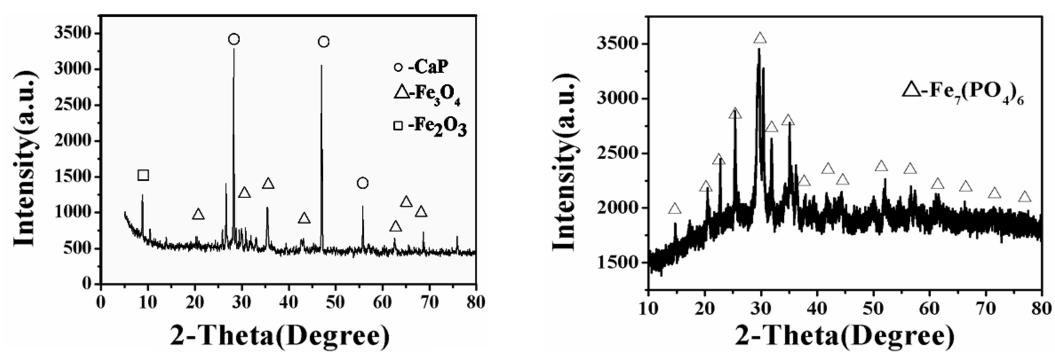

Figure 2: XRD pattern for the steel slag powders after magnetic separation (left); XRD patterns of the extracted powders annealed at 700°C (right)

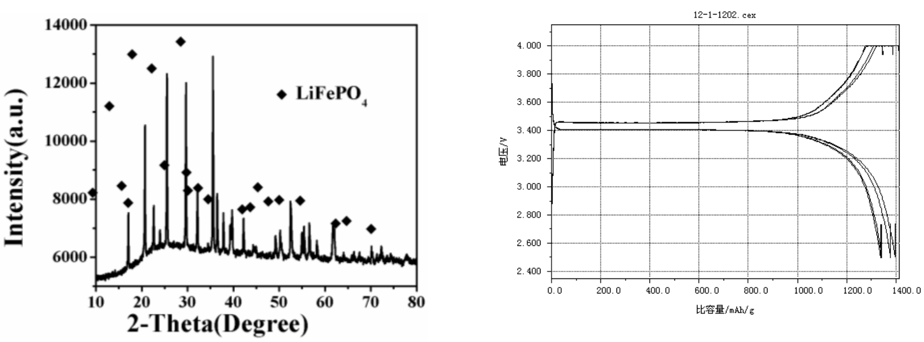

Figure 3: XRD patterns of the as-synthesised $LiFePO_4$/C composite powders (left); charge and discharge curves of the as-obtained $LiFePO_4$/C composite powders (right)

Table 1: The chemical composition of steel slags (in wt%)

Composition	CaO	FeO	Al_2O_3	SiO_2	MgO	MnO	P_2O_5
Content	30-60	15-26	3-8	8-23	4-9	5-10	0.5-2

Electrochemical properties of the as-synthesised $LiFePO_4$/C composite powders

XRD results of the powders (Figure 3) revealed the formation of $LiFePO_4$ phase, while Raman spectra (not shown) further confirmed the existence of carbon (with two peaks located at around 1400-1600 cm^{-1}), indicating the powders were mainly $LiFePO_4$/C composites. The electrochemical properties of the battery are shown in Figure 3 (right). The initial discharge capacities of the cells were 136.1~138.0 mAh/g, and after 10 cycles of charge and discharge measurements, as high as 132.4~134.39 mAh/g of capacities can also be retained, indicating the current processing were of great benefits for synthesising high performance $LiFePO_4$/C composite powders.

Conclusion

The microwave-assisted annealing process has great advantages for the synthesis of $LiFePO_4$/C composite powders from steel slags. The initial discharge capacity of the $LiFePO_4$ lithium batteries was 136.1~138.0 mAh/g, and after 10 cycles charge and discharge measurements, capacity of 132.4~134.39 mAh/g can also be retained.

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