

Synthesis and Electrochemical Characteristics of LiFePO₄/C Cathode Materials from Different Precursors

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Synthetic conditions and electrochemical characters of electrode materials mainly depend on the precursor. LiFePO₄/C cathode materials are synthesized by solid-state reaction, using α -Fe₂O₃, Fe₃O₄, FePO₄ and NH₄FePO₄ as precursors, respectively. The influences of precursor on structure and electrochemical performance of LiFePO₄/C are investigated. The composition, structure, morphology, and physicochemical properties of the LiFePO₄/C products from each precursor are characterized in detail by XRD, SEM, BET and electrochemical performance measurements. LiFePO₄/C obtained from FePO₄ precursor has the excellent electrochemical performances. LiFePO₄/C prepared from α -Fe₂O₃ or Fe₃O₄ precursor also have good electrochemical properties, and the cost is much low because of the cheap precursors. For NH₄FePO₄ precursor, LiFePO₄/C is most easy to be synthesized because the ratio of Fe²⁺ to PO₄³⁻ is 1:1 and the carbothermal reduction is not necessary.

Keywords: lithium-ion battery, cathode material, LiFePO₄, precursor, synthesis

1. INTRODUCTION

Lithium-ion batteries are widely used in portable equipment, such as mobile phone, notebook computer, electron instrument, and so on. But in high-power and high-energy field, lithium-ion batteries are rarely used, such as electric vehicles (EVs), hybrid electric vehicles (HEVs), dispersed energy storage systems and space batteries. The cost, safety, environmental friendliness and long operational life of the electrode materials are of major concern for the application of large-scale powerful and energy storage lithium-ion batteries [1].

Olivine-structured LiFePO₄ proposed by Goodenough [2] is gaining particular interest as a promising candidate cathode material for lithium-ion batteries. Comparing to the commercial LiCoO₂, LiNiO₂, LiMn₂O₄ and their derivatives, LiFePO₄ cathode material almost has the same outstanding

advantages of abundant available resource and low cost, excellent thermal stability, excellent cycling performance, satisfactory safety, environmentally benign and low toxicity, etc. However, the primary disadvantage of LiFePO_4 is the low conductivity, which unfortunately prevents it from being used in high power applications [3-9].

Synthetic conditions and electrochemical characters of electrode materials mainly depend on the precursor. A perfect precursor can permit lower sintering temperature and shorter sintering time, furthermore, which can provide better electrochemical performance of the product. In this presentation, we have introduced several precursors of $\alpha\text{-Fe}_2\text{O}_3$, Fe_3O_4 , FePO_4 and NH_4FePO_4 to prepare LiFePO_4 . For precursors of Fe_2O_3 and Fe_3O_4 , $[\text{Fe}]$ and $[\text{PO}_4]$ are not in one compound and it is hard to mix two resources at atomic level. If Fe_2O_3 or Fe_3O_4 is chosen as the precursor material, multistage mixing and sintering processes are needed because the diffusion of Fe^{2+} and PO_4^{3-} is difficult. If FePO_4 or NH_4FePO_4 is chosen as the precursor material, the $[\text{Fe}]$ and $[\text{PO}_4]$ are in one compound and the ratio of $[\text{Fe}]$ to $[\text{PO}_4]$ is 1:1, so the LiFePO_4 is easy to be synthesized and the coherence of product's performance is very good. Moreover, In NH_4FePO_4 precursor, the ratio of $[\text{Fe}]$ to $[\text{PO}_4]$ is 1:1 and the value of $[\text{Fe}]$ is +2, so the carbothermal reduction is not necessary and the LiFePO_4 is easily synthesized at low sintering temperature and short sintering time [10, 11]. Sucrose is the good carbon source according the former studies [12-15].

In this work, the composition, structure, morphology, and physicochemical properties of the LiFePO_4 products from each precursor are characterized in detail by XRD, SEM, BET and electrochemical performance measurements.

2. EXPERIMENTAL

LiFePO_4/C materials are synthesized by solid-state reaction. If the precursor is $\alpha\text{-Fe}_2\text{O}_3$ or Fe_3O_4 , the precursor, LiH_2PO_4 , and sucrose, in a molar ratio of Li: Fe: P: C=1:1:1:1.2, are mixed. The mixture is ground by ball milling (with a rotation speed of 500r/min, agate balls) for 2 hours in water. After being dried at 80°C , the mixture is calcined at 520°C for 6 h initially. Then the presintered mixture is reground for 2 hours. The LiFePO_4/C products are synthesized by sintering the mixture at 800°C for 16h in N_2 . It is tested that the content of carbon is 2.9% and 3.1% in products from $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 , which are named LFPO-1 and LFPO-2, respectively.

When FePO_4 is the precursor, FePO_4 , Li_2CO_3 and sucrose (molar ratio of Li: Fe: P: C=1:1:1:1.2) are mixed by ball milling for 2 hours. The LiFePO_4/C is synthesized by sintering the mixture at 700°C for 16h in N_2 , which is named LFPO-3 and contains 3.3% carbon.

If the precursor is NH_4FePO_4 , NH_4FePO_4 , Li_2CO_3 and sucrose (molar ratio of Li: Fe: P: C=1:1:1:1) are mixed by ball milling for 2 hours. Finally, the mixture is maintained at 600°C for 12 h in N_2 and the final product named LFPO-4 is obtained. The content of carbon is 3.2%.

Powder X-ray diffraction (XRD, D/max-rB) using $\text{Cu K}\alpha$ radiation is used to identify the crystalline phase and crystal lattice parameters of the powders. The particle morphology of the powders is observed using a scanning electron microscopy (SEM, JSM6301F). The BET specific surface area is measured by N_2 absorption-desorption method at liquid nitrogen temperature on SSA-

4000. The tap density of the powders is tested as the following method. A certain quality of powders is added into a dry measuring cylinder, and then the measuring cylinder is taped until the volume of the powders does not change anymore. The ratio of the quality and the volume is the tap-density of the powders.

Experimental cells for measurements use the cathode with the composition of 80 wt.% active material, 10 wt.% carbon black, and 10 wt.% PTFE. The diameter of the cathode roundel is 8 mm and the thickness is 0.2 mm. The separator is a Celguard 2400 microporous polyethylene membrane. The electrolyte is 1 M LiPF₆ EC+DEC (1:1 by volume). A lithium metal anode is used in this study. The cells are assembled in a glove box filled with argon gas. The discharge-charge cycling is galvanostatically performed at 0.1C and 1.0C rates with cut-off voltages of 2.5—4.2 V (versus Li/Li⁺) at room temperature.

3. RESULTS AND DISCUSSION

Fig.1 shows the TG–DSC curves of the mixture of precursor powders, lithium source and sucrose with a heating rate of 10°C·min⁻¹ from room temperature to 1000°C in argon.

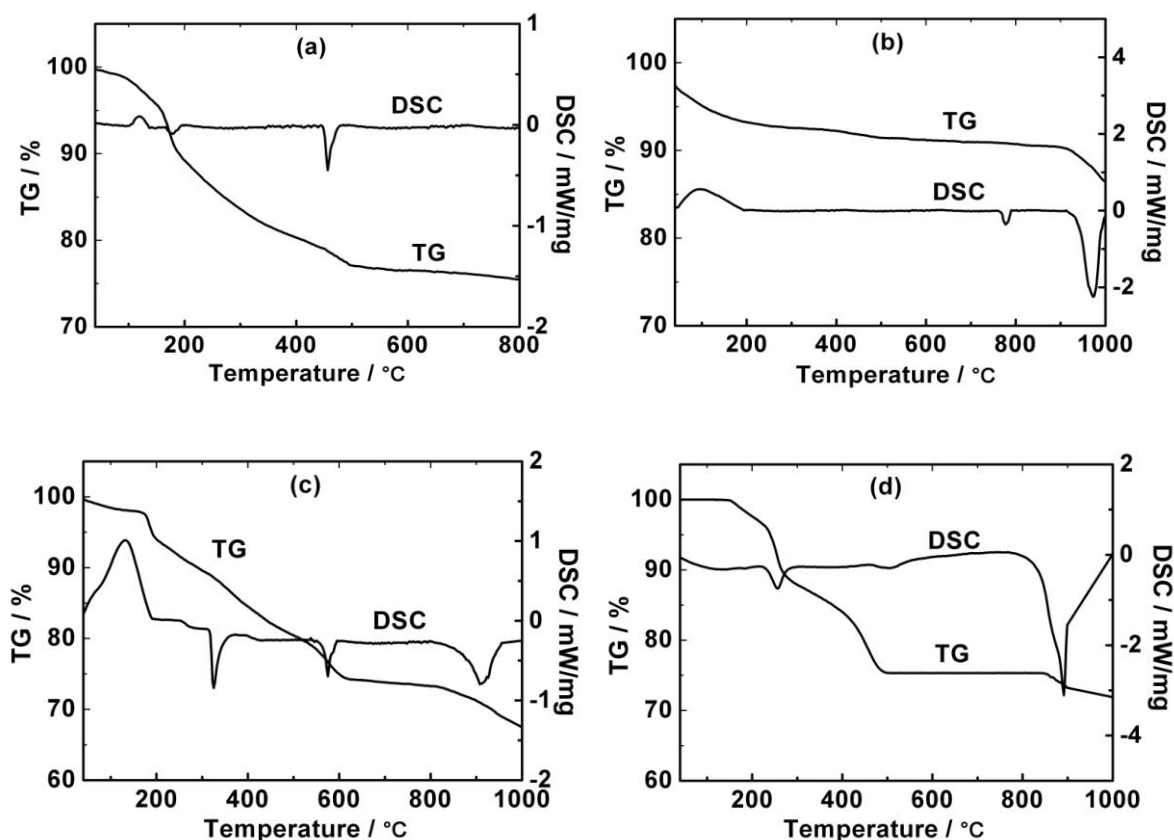


Figure 1. TG/DSC curves of the mixture of precursor powders, lithium source and sucrose (a) α -Fe₂O₃ or Fe₃O₄ and LiH₂PO₄; (b) presintered and regrounded mixture of (a); (c) FePO₄ and Li₂CO₃; (d) NH₄FePO₄ and Li₂CO₃

As shown in Fig.1(a), on the DSC curve near 120 and 180°C, there is an obvious endothermic peak and an exothermic peak, associating with the weight loss on the TG curve, which are related to the dehydration of mixture and decomposition of sucrose, respectively. On the DSC curve near 470°C, there is an obvious exothermic peak, which is related to the preparation of LiFePO_4 and the loss of H_2O and CO_2 . When the temperature is high than 500°C, the weight remains constant according to the TG curve. Since the $[\text{Fe}]$ and $[\text{PO}_4]$ are hard to be mixed at atomic level, the synthesis reaction of LiFePO_4 is not accomplished through once mixing and calcination. It is necessary that the mixture is calcined at 520°C for 6 h initially. As shown in Fig.1(b), after regrinding the mixture, there is an obvious endothermic peak and an exothermic peak on the DSC curve near 100 and 790°C. We can primarily conclude that the synthesis reaction of LiFePO_4 will finish when the heat treating temperature is higher than 790°C. As shown in Fig.1(c), if the precursor is FePO_4 , there is one endothermic peak and three exothermic peaks on the DSC curve near 100, 320, 580 and 910°C, which are related to the evaporation of water, decomposition of sucrose, preparation reaction of LiFePO_4 and compounds of LiFePO_4 , respectively. For the mixture of NH_4FePO_4 , Li_2CO_3 and sucrose, the synthesis reaction of LiFePO_4 maybe finish when the sintering temperature is higher than 550°C, as shown in Fig.1(d). For four samples, the compound of LiFePO_4 will decompose over 900°C

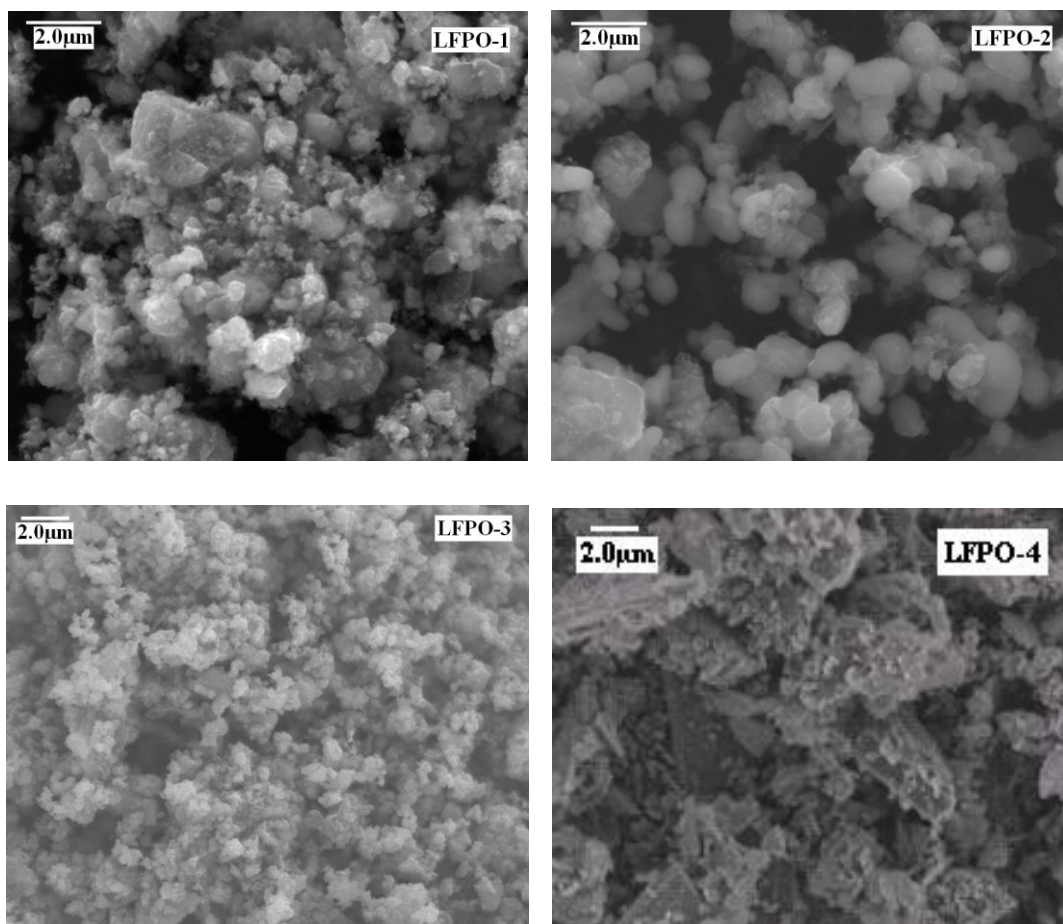


Figure 2. SEM images of the LiFePO_4/C samples

Based on the above analysis, if Fe_2O_3 or Fe_3O_4 is chosen as precursor, multistage mixing and sintering processes are adopted. For FePO_4 precursor, 700°C is an appropriate sintering temperature. The LiFePO_4/C can be synthesized at 600°C from NH_4FePO_4 precursor.

Fig.2 shows the morphology of the LiFePO_4/C powders obtained from the four precursors. As shown in images of LFPO-1, LFPO-2 and LFPO-3, the LiFePO_4/C samples are composed of many dispersed particles. The particle size is around $1\mu\text{m}$ and dissociative carbon is hardly observed. But, from the LFPO-4, the flake-like crystal structure is observed and the particle size is around $4\mu\text{m}$. The particles in LFPO-1 LFPO-2 and LFPO-4 are lightly agglomerated and can be easily distinguished from each other. The particles in LFPO-3 are well dispersed. So it is certain that the carbon from sucrose can prevent the agglomeration of crystal particles and the product can reserve the morphology of the precursor. The specific surface area of four samples is determined by the BET (Brunauer-Emmett-Teller) method, which is 36.13 , 33.15 , 32.37 and $17.82\text{m}^2\cdot\text{g}^{-1}$ for LFPO-1, LFPO-2, LFPO-3 and LFPO-4, respectively. Bigger BET can augment the interface of electrode material and electrolyte, which also benefits to the diffusion of Li^+ .

Fig.3 shows the X-ray diffraction patterns of the samples. The products are all identified as crystal type LiFePO_4 according to the comparison with PDF card. But the relative intensity of the peaks is different among the samples.

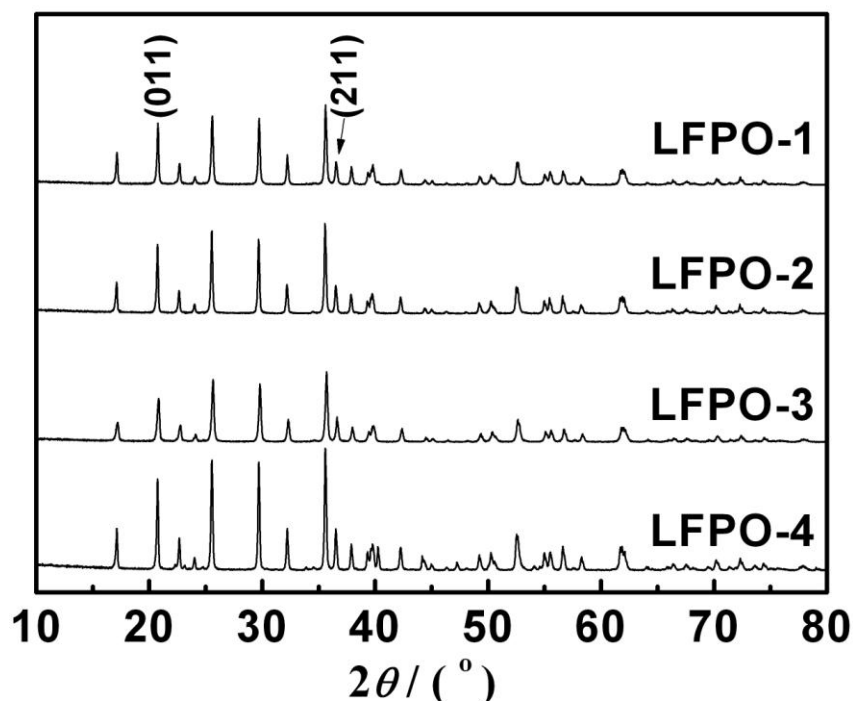


Figure 3. X-ray diffraction patterns of the LiFePO_4/C samples

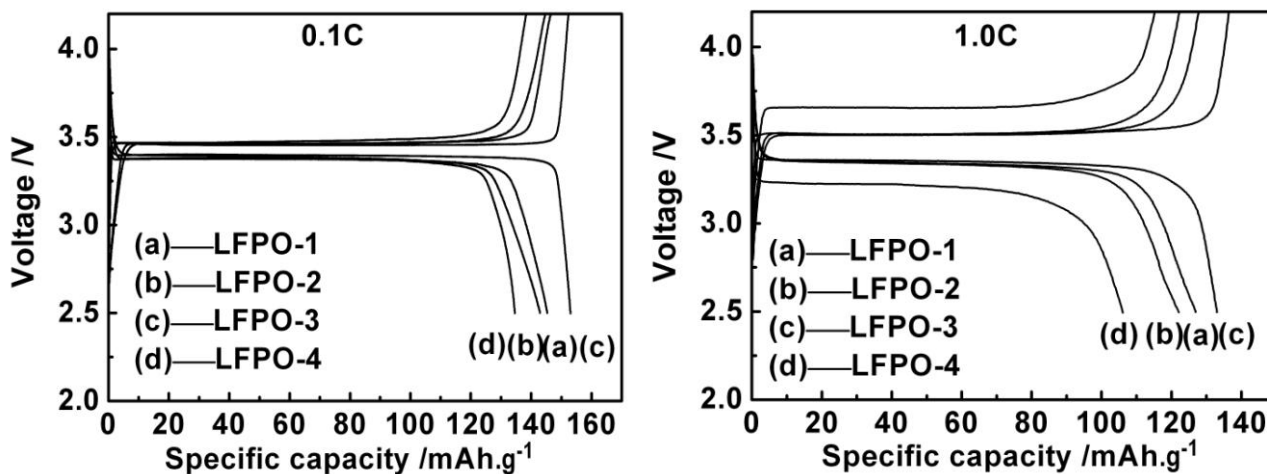
As known, Li^+ diffuses in one-dimensional (1D) and hardly crosses between two 1D channels in LiFePO_4 in charge/discharge process. If the 1D channel is much long or blocked, the diffusion of Li^+ in this channel will be difficult. Short 1D channel is helpful for the lithium ions to reach the

boundaries easily and can reduce the odds of blocking. So, small particle and crystal grain size are in favor of the diffusion of Li^+ and perfect electrochemical performance at high rate. The crystal grain size is calculated by Scherrer formula. According to the foregoing report [10], the thickness of (011) and (211) plane, which are marked as D(011) and D(211), stand for the length of 1D channels and the electrons diffusion approximatively. The grain sizes in the direction of plane (011) and (211) of four samples are listed in table 1. It is observed that the grain sizes of LFPO-3 in two planes are the smallest and those of LFPO-4 sample are the largest.

Table 1. The grain size of four samples in the direction of plane (211) and (011)

Sample name of the LiFePO_4/C	LFPO-1	LFPO-2	LFPO-3	LFPO-4
D (011) /nm	49.9	51.2	33.4	52.2
D (211) /nm	38.0	40.6	37.8	42.2

The samples having different grain size and particle size have different electrochemical performance. As Fig.4 illustrates, the discharge voltage plateaus of the samples are around 3.4 V in all the curves and the polarization of charge/discharge for four samples is almost same at 0.1C rate. The initial discharge capacities of LFPO-1, LFPO-2, LFPO-3 and LFPO-4 samples are 145.3, 142.9, 153 and 134.6mAh/g at 0.1C rate, respectively. The difference of capacity is mainly caused by the different grain sizes at low charge/discharge rate. However, along with the increase of charge/discharge rate, the polarization and the capacities of four samples are quite different. The initial discharge capacities of LFPO-1, LFPO-2, LFPO-3 and LFPO-4 samples are 126.9, 122.1, 133.2 and 106.1mAh/g at 1.0C rate, respectively, which are 109.4, 98.3, 117.6 and 76.4mAh/g at 2.0C rate. The polarization of sample LFPO-4 is the most obvious at high rate because of the large particles and grain size. The higher capacity and slight polarization of sample LFPO-3 are contributed to the smaller particles and grain size.



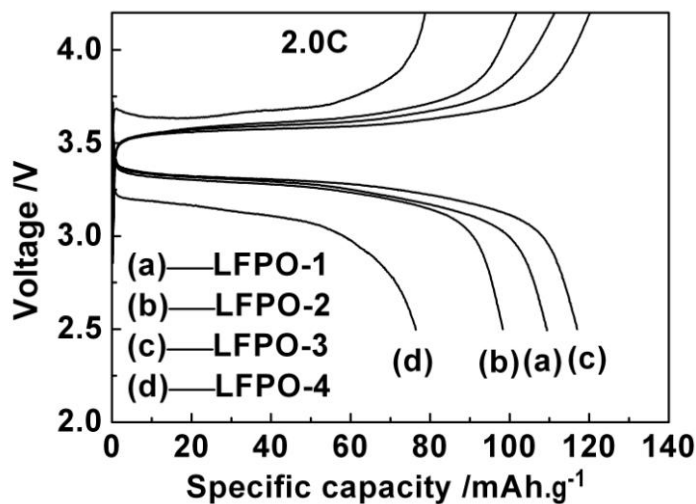


Figure 4. Discharge curves of the initial cycle of the LiFePO_4/C samples at 0.1C, 1.0C and 2.0C rates

Cycling performance of the samples at different charge/discharge rates is shown in Fig.5. The four samples all have perfect cycling stabilities, especially for sample LFPO-3.

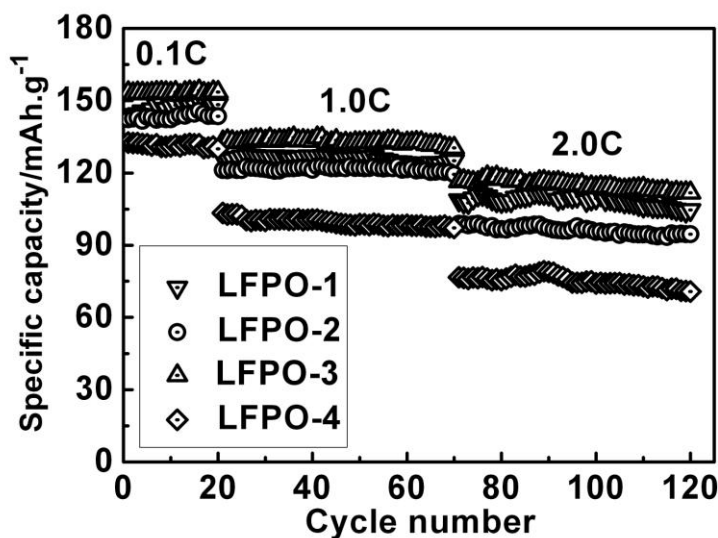


Figure 5. Cycle performance curves of the LiFePO_4/C samples at 0.1C, 1.0C and 2.0C rates

4. CONCLUSION

Four kinds of precursors, $\alpha\text{-Fe}_2\text{O}_3$, Fe_3O_4 , FePO_4 and NH_4FePO_4 , are presented in the synthesis of LiFePO_4/C . The synthesis conditions are different for different precursors. The LiFePO_4/C obtained from FePO_4 precursor has the excellent electrochemical performances. The precursors of $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 are cheap. LiFePO_4/C with good electrochemical properties is hard to be prepared from $\alpha\text{-Fe}_2\text{O}_3$

and Fe_3O_4 because $[\text{Fe}]$ and $[\text{PO}_4]$ are not in one compound. The LiFePO_4/C is much easy to be synthesized from NH_4FePO_4 precursor because the carbothermal reduction is not necessary. It is a pity that LiFePO_4/C obtained from NH_4FePO_4 precursor has unsatisfactory electrochemical performance, which is because the LiFePO_4/C particles and grain size are large and hard to be controlled.

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