PREPARATION OF LIFEPO4 CATHODE MATERIALS BY HYDROTHERMAL METHOD

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Abstract- In this study, ferrous sulfate, phosphoric acid, and lithium hydroxide, were used as raw materials to synthesize lithium iron phosphate/carbon ($LiFePO_4$/C) cathode materials by using the hydrothermal method under the addition of 5-6wt% glucose as a carbon source and Li: Fe: P molar ratio of 1: 1: 3. The carbon coating procedure was carried out by calcining at 650°C with 95% argon/5% hydrogen atmosphere for 10 hours. The effect of the operating conditions for synthesis on the properties of lithium iron phosphate cathode material was tested by adding ascorbic acid (vitamin C), removing impurity by washing/filtering, controlling pH value. SEM images showed that adding carbon sources during the preparation of $LiFePO_4$/C could reduce the particle size and improve the electrochemical performance. In addition, properly controlling pH and carefully washing/filtration steps could also improve the electrochemical performance of $LiFePO_4$/C cathode material due to the better chemical purity. The results showed that the discharge capacity at different C-rates for $LiFePO_4$/C prepared under the addition of 1g ascorbic acid and pH=6.0 were 127 mAh/g at 0.1C/0.1C; 100 mAh/g at 0.2C/0.2C, 40mAh/g at 0.2C/10C, respectively.

Index Terms- Lithium iron phosphate, Hydrothermal method, Cathode material, Lithium ion battery

I. INTRODUCTION

Lithium ion batteries are widely used in potential power sources not only for portable electronic devices such as cellular telephones, lap-top computers and cameras, but also for the electrical vehicles (EVs) and hybrid electric vehicles (HEVs). Conventionally, $LiCoO_2$ with a capacity of 140 mAh/g has been used as a cathode material in commercial Li-ion batteries. However, $LiCoO_2$ has its own drawbacks such as the limited abundance in nature, the toxicity issue and the high cost. lithium iron phosphate ($LiFePO_4$) has been suggested as a promising candidate to replace $LiCoO_2$ as a cathode material for the next generation Li-ion batteries. $LiFePO_4$ has distinctive features of high theoretical capacity (170 mAh/g), high discharge potential (~3.45 V vs Li+/Li), excellent thermal stability, low cost and being environmentally friendly. Thus, $LiFePO_4$ olivine is regarded as one of the most promising cathode materials for power batteries used in electric and hybrid electric vehicles. However, pristine LiFePO4 suffers from its poor ion diffusion coefficient (10^{-14} cm^2 s^{-1}) and low electrical conductivity (10^{-9} S cm^{-1}), limiting its application in large devices. To solve these drawbacks, various strategies have been employed in the literature such as coating particles with a conductive carbon layer [1, 2], reducing the particle sizes [3, 4], and doping with guest elements. Among these strategies, particle size reduction and carbon coating have proven to be effective methods for improving the electrochemical performance of $LiFePO_4$ material, due to their contribution to decreasing the diffusion path length with a larger surface area for more reaction and the enhancement of electronic conductivity of surface of $LiFePO_4$ material. In addition, it is also known that by using the ascorbic acid ($C_6H_8O_6$) as reducing and morphology control agent could effectively prevent oxidation of iron ions [5, 10].

In this study, ferrous sulfate, phosphoric acid, and lithium hydroxide, were used as raw materials to synthesize lithium iron phosphate/carbon ($LiFePO_4$/C) cathode materials by using the hydrothermal method. The effect of some important parameters for preparing cathode materials, including the addition of vitamin C, washing and filtration, control of pH value, and addition of manganese metal elements, on the electrochemical properties of lithium iron phosphate cathode material was investigated.

II. EXPERIMENTAL

A. Preparation of $LiFePO_4$/C cathode materials

The detailed procedures are described as follows. LiOH, H_3PO_4, and $FeSO_4$ with a molar ratio of 3:1:1 were dissolved in 100 ml deionized water under stirring, and then 0.8g ascorbic acids were added.The pH value of the suspension was controlled in the range of 6.0~8.5 (pH=6.0, 6.5, 7.0, 7.5, 8.5) by adding CH_3COOH or NH_4OH. After 10 min vigorous stirring, the suspension was transferred into a 600 ml Teflon-lined stainless steel autoclave followed by a hydrothermal treatment at 180°C for 10 h. The obtained gray precipitate was filtered, washed several times with ethanol and distilled water, and dried in the vacuum oven at 80°C for 8h. For the LIFEPO4/C synthesis, glucose and LFP powders with a weight

ratio of 0.17:1 were blended using a high-energy ball-milling machine at 350 rpm for 30min, then the mixture was dried and ground. The as-prepared powders were annealed in a tubular furnace at 350°C for 4h, and then heated at 700°C for 10h in Ar/H_2 atmosphere ($Ar:H_2$=95:5) flow to obtain the carbon-coated LFP samples. For preparing $LiFePO_4$/C materials from different level of solution pH, the pH values were controlled by the amount of $NH_3 \cdot H_2O$ or CH_3COOH and were measured to be 6.5, 7.5, 8.5, and 6.0. After 10 min vigorous stirring, the suspension was transferred into a 500 ml Teflon-lined stainless steel autoclave followed by a solvothermal treatment at 180°C for 10 h. The obtained gray precipitate was filtered, washed several times with ethanol and distilled water, and dried in the vacuum oven at 80°C for 8h. For the $LiFePO_4$/C synthesis, glucose and LFP powders with a weight ratio of 0.17:1 were blended using a high-energy ball-milling machine at 350 rpm for 30min, then the mixture was dried and ground. The as-prepared powders were annealed in a tubular furnace at 350°C for 4h, and then heated at 700°C for 10h in Ar/H_2 atmosphere ($Ar:H_2$=95:5) flow to obtain the carbon-coated LFP samples.

B. Characterization of LiPePO4/C cathode materials

The crystal structures of the $LiFePO_4$/C composite samples were examined using an X-ray diffraction (XRD) spectrometer (Philip, X'pert Pro System). Surface morphology was revealed using a scanning electron microscope (SEM, Hitachi). Micro Raman spectra were recorded on a confocal micro-Renishaw with a 632-nm He/Ne laser excitation. The electrochemical performance of the $LiFePO_4$/C composite battery was measured using a 2-electrode system (CR2032 coin cell assembled in an argon-filled glove box). The $LiFePO_4$/C composite electrodes were prepared by mixing active $LiFePO_4$/C materials, Super P, and poly (vinyl fluoride) (PVDF) binder at a weight ratio of 80:10:10. The mixture was pasted onto aluminum foil (Aldrich), and then dried in a vacuum oven at 120°C for 12 h. Lithium foil (Aldrich) was used as the counter and reference electrode. Microporous PE film was used as the separator. The electrolyte was 1 M LiPF6 in a mixture of EC and DEC (1:1, v/v, Merck). The $LiFePO_4$/C composite batteries were charged by a constant current at a constant voltage protocol, and discharged by a constant current profile, over a potential range of 2.0-3.8 V at various C-rates, which were determined using a battery tester (Arbin BT2000). All tests were performed at room temperature.

III. RESULTS AND DISCUSSION

Figure 1 illustrates the XRD patterns of as-prepared $LiFePO_4$ synthesized with different amount of ascorbic acid. It shows that the well-resolved diffraction peaks indexed to olivine structure. It is found that the diffraction peaks located at 2θ = 17.9°, 30.7°are characteristic, which can be identified as the $FePO_4$ phases. The peaks around at 17.1°, 29.6° as well as 35.6° are characterized as $LiFePO_4$ phase. The main diffraction peaks of the sample are consistent with the diffraction peaks of the literature, indicating that the prepared $LiFePO_4$ have a high purity and crystallinity. It is noticed that the intensity of diffraction peaks located at 2θ = 33.3° for $LiFePO_4$ obtained with the addition of 1 g ascorbic acid (as shown in fig. 1(b)) is stronger than that synthesized from the addition of 10 g ascorbic acid (as shown in fig. 1(a)). This result indicates the LFP synthesized with proper amount of ascorbic acid can have a higher purity and crystallinity and thus higher discharge capacity. In addition, XRD patterns shows that all samples exhibit a single phase of $LiFePO_4$ with an ordered olivine structure indexed to the orthorhombic pnma space group.

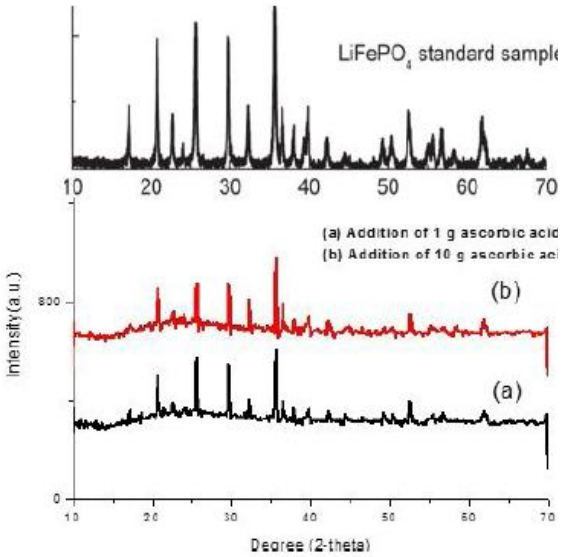


Fig. 1. XRD patterns of LiFePO4 synthesized with different amount of ascorbic acid

The morphology and particle size of $LiFePO_4$/C cathode materials have great influence on their electrochemical performance. Figure 2 illustrates the SEM images of $LiFePO_4$/C powders synthesized with different amount of ascorbic acid. It shows that the $LiFePO_4$/C synthesized with addition of 1 g ascorbic acid not only has a smaller particle size (as shown in figs. 2(c) and (d)), but also has a more uniform carbon coverage. Therefore, the LIFEPO4/C cathode material synthesized with addition of 1 g ascorbic acid has a better electrochemical performance. The result is consisting with that obtained from the charge/discharge analysis. It is found that the $LiFePO_4$/C microspheres are composed of carbon-coated nanoparticles with size of 50-100 nm. On the other hand, the morphology of $LiFePO_4$/C synthesized from different solution pH is shown

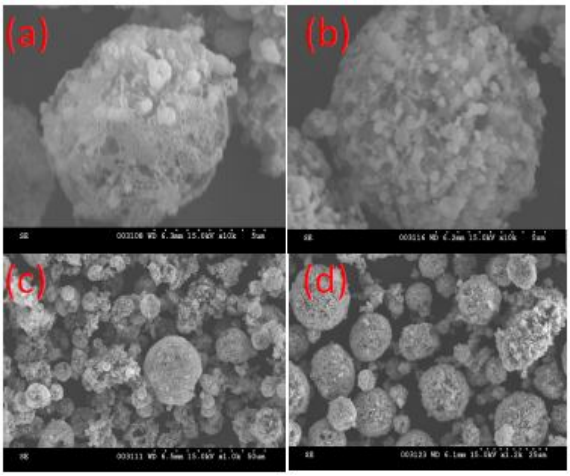


Fig. 2 SEM images of (a),(c) addition of 1 g ascorbic acid in $LiFePO_4$/C microspheres and (b),(d) addition of 10 g ascorbic acid in $LiFePO_4$/C microspheres

in figure 3. It is found that the prepared $LiFePO_4$/C materials at pH = 6 and pH = 8.5 have an obvious impurity phase and poor electrochemical performance. On the other hand, the $LiFePO_4$/C prepared at pH=6.5 pH = 7.5 have more uniform particle size and thus the better electrochemical performance.

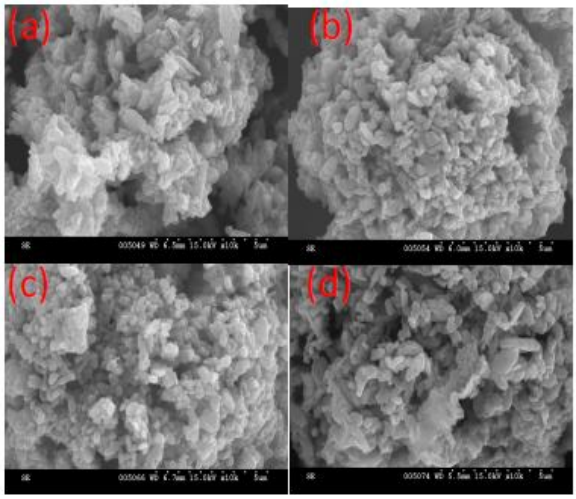


Fig. 3 SEM images of the LIFEPO4/C synthesized from different pH: (a) pH=6.0, (b) pH=6.5, (c) pH=7.5, and (d) pH =8.5

Figure 4 illustrates the Raman spectra of $LiFePO_4$/C cathode materials synthesized with different solution pH. The related data have been listed in Table 1. As shown in fig. 4 and Table 1, There are three bands in the Raman spectrum of $LiFePO_4$ are observed between 900 and 1600 cm^{-1}. The band at 945 cm^{-1} is contributed by phosphate ions PO_4^{3-}, and the other two bands is related to disorder carbon (D-band at 1340 cm^{-1}) and graphitic carbon (G-band at 1580 cm^{-1}), respectively. The formation of graphitic carbon can enhance the conductivity of the $LiFePO_4$/C cathode materials. On the other hand, no observation of PO_4^{3-} band means the complete carbon coverage on the

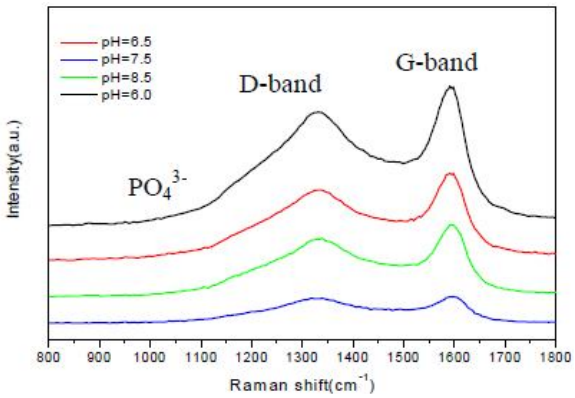


Fig. 4 Raman spectra of $LiFePO_4$/C materials prepared at different solution pH values

$LiFePO_4$/C surface. The peak intensity ratio (I_D/I_G) between 1358 and 1600 cm^{-1} in Raman shifts was calculated to be an index of the degree of disordering. An increase in the ID/IG ratio reflects more disorder. From Table 1, it is found that the $LiFePO_4$ cathode material has the best carbon graphitization and surface carbon coverage at pH=8.5. However, the $LiFePO_4$ prepared at pH=8.5 has not the best electrochemical performance. It suggests that the chemical purity has the more important influence on the electrochemical properties for the lithium iron phosphate cathode materials.

pH values	PO_4^{3-}	D bands	G bands	$R=(I_D/I_G)$	$(D+G)/PO_4^{3-}$
	Intensity(a.u.)	Intensity(a.u.)	Intensity(a.u.)		
6.5	801.23	4125.78	4910.98	0.840113	11.27861
7.5	275.48	1373.17	1423.52	0.96463	10.15206
8.5	714.36	4393.69	5359.98	0.819721	13.65372
6	1484.31	8066.18	9580.01	0.84198	11.88848

Table 1 The peak intensity of D band, G band, and PO_4^{3-} in Raman spectra for LIFEPO4/C obtained from different pH values.

The charge/discharge measurements were used to evaluate the electrochemical performance of $LiFePO_4$/C cathode materials. Figure 5 shows the initial charge/discharge curves of $LiFePO_4$/C prepared from different adding amount of ascorbic acid. It indicates that the $LiFePO_4$/C prepared with addition of 1g ascorbic acid has an initial discharge capacities of 55 mAh/g at 0.1C that is obviously higher than that obtained from $LiFePO_4$/C with addition of 10 g ascorbic acid. Figure 6 exhibits the best first charge/discharge profiles of the $LiFePO_4$/C at 0.1 C in the voltage window of 2.0-3.8 V. The charge/discharge capacity at 0.1C rate was about 154 mA h/g. Figure 7 shows the charge–discharge curves of the $LiFePO_4$/C with various high C-rates from 0.2 to 10 C between 2.0 and 3.8 V. It indicates that the charge/discharge capacity at different C-rate are 100 mAh/g at 0.2C, 95 mAh/g at 1C, 80 mAh/g at 3C, 78 mAh/g at 5C, and 43 mAh/g at 10C, respectively.

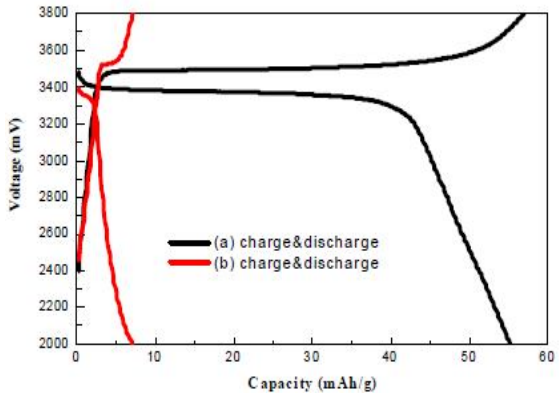


Fig. 5 The initial charge/discharge capacity curves of $LiFePO_4$ at 0.1 C: (a) addition of 1 g ascorbic acid and (b) addition of 10 g ascorbic acid

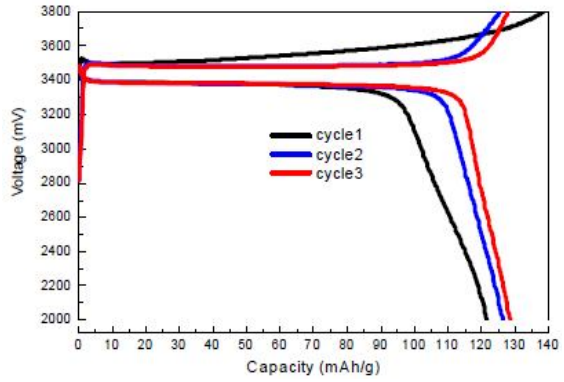


Fig. 6 The first charge/discharge profiles of the $LiFePO_4$/C at 0.1 C in the voltage window of 2.0-3.8 V.

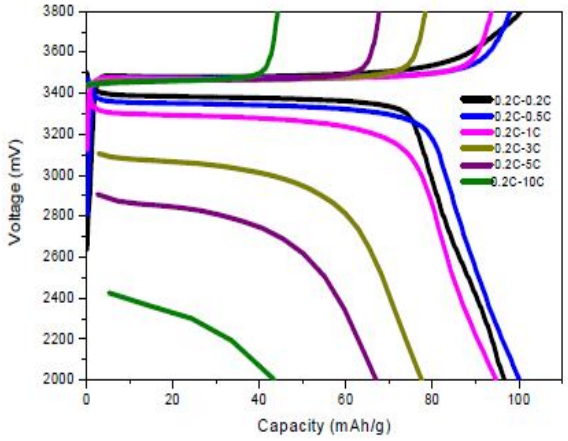


Fig. 7 The initial charge–discharge capacity curves of LiFePO4/C at 0.2C/0.2C-10 C in the voltage window of 2.0-3.8 V

The constant-current charge/discharge curves of $LiFePO_4$/C synthesized from different values of pH are shown in Figure 8. As shown in fig. 8, the discharge capacity of $LiFePO_4$/C cathode obtained from various pH values are 130mAh/g for pH=6.5, 108mAh/g for pH=7.5, 82 mAh/g for pH=8.5, 65 mAh/g for pH=6.0, respectively. It indicates the $LiFePO_4$/C synthesized at pH=6.5 exhibits the highest discharge capacity. To sum up, pH value has a great influence on the performance of $LiFePO_4$/C cathode materials.

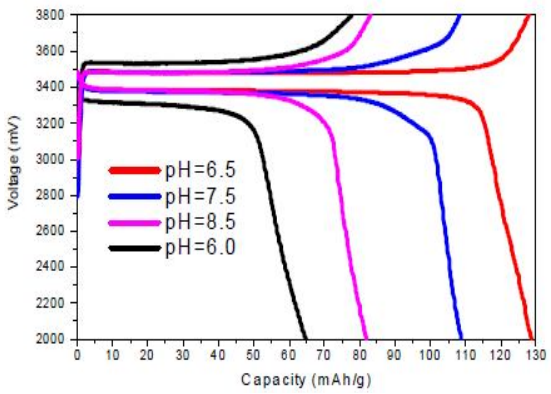


Fig. 8 The charge/discharge curves of $LiFePO_4$/C synthesized from different pH values

CONCLUSIONS

Well-crystalline $LiFePO_4$ particles were successfully synthesized by the hydrothermal reaction in the present study. The particle size of the $LiFePO_4$ samples thus obtained was almost of submicron. The XRD patterns show well-resolved diffraction peaks indexed to olivine structure. addition of proper amount of ascorbic acid does not affect the crystal structure. SEM images indicate that the particle morphology and size are markedly influenced by the adding amount of ascorbic acid in $LiFePO_4$/C. In addition, the cathode materials synthesized at pH = 6.5 exhibit the highest discharge capacity. In the electrochemical performance, the $LiFePO_4$/C cathode materials have a high discharge capacity of 130mAh/g, which corresponds to about 76% of the theoretical capacity. In conclusion, by simply adjusting the content of ascorbic acid, removing the impurity from precursor and control of solution pH during the preparation, $LiFePO_4$/C can show a good electrochemical performance as the cathode materials for application in the lithium ion batteries.

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