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## DMSO-Assisted Liquid-Phase Synthesis of $\text{LiFePO}_4/\text{C}$ Nanocomposites with High-Rate Cycling as Cathode Materials for Lithium Ion Batteries

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Nanometer-sized  $\text{LiFePO}_4$  was synthesized by a liquid-phase method, using dimethyl sulfoxide (DMSO) as a boiling point raiser and crystal growth inhibitor under ambient pressure, then mixed with a certain amount of glucose and sintered at  $600^\circ\text{C}$  under inert atmosphere for 3 h to obtain  $\text{LiFePO}_4/\text{C}$  nanocomposites, which had a well developed olivine-type structure, small crystals, and a narrow size distribution. Tests showed that the special capacity of  $\text{LiFePO}_4/\text{C}$  at discharge rates of 0.2 and 1 C was 157.7 and 142.5 mAh/g, respectively. A capacity of 126 mAh/g at 5 C and 104 mAh/g at 10 C was even achievable, with no significant capacity fading after 200 cycles.

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Since Goodenough and his co-workers reported in 1997 that  $\text{LiFePO}_4$  could be used as a cathode material in lithium rechargeable batteries,  $\text{LiFePO}_4$  has been regarded as a promising cathode material for lithium ion batteries due to its relatively low cost, excellent heat stability, lower toxicity, fewer safety issues, and good structural stability.<sup>1-3</sup> However,  $\text{LiFePO}_4$  has low electronic conductivity and low lithium diffusivity, which prevent its large-scale application in electric vehicles (EVs) and hybrid electric vehicles (HEVs). To enhance the electronic conductivity and electrochemical properties of  $\text{LiFePO}_4$  cathode materials, many researchers have suggested using carbon coating, metallic ion doping, and particle fining.<sup>4-6</sup> Recent studies show that the particle size and morphology of  $\text{LiFePO}_4$  have significant influences on electrochemical performance, especially on high-rate discharge capability, so the synthesis of  $\text{LiFePO}_4$  with fine, uniform particles has become a research hotspot.<sup>7-9</sup>

To date, many different methods have been developed to prepare  $\text{LiFePO}_4$ , such as solid-state reactions, co-precipitation, hydrothermal/solvothermal processes, sol-gel routes, and microwave methods.<sup>10-15</sup> Among these, while the high-temperature solid-phase method is simple and easy for industrial production, the resulting particle sizes are large and unevenly distributed and the process is lengthy, wasting time and energy. Although particle size can be controlled by hydrothermal means, which shortens the reaction time, the process needs to start at high temperature and pressure, which is challenging for industrial production. Products with uniform size can be gained by the sol-gel route, but the process of drying the precursor is complicated and the product still requires a long time for final annealing.

Herein, we use a liquid-phase method to obtain  $\text{LiFePO}_4$  nanoparticles, using dimethyl sulfoxide (DMSO) as a boiling point raiser and crystal growth inhibitor at  $108^\circ\text{C}$  and ambient pressure for a short time; then we mix the as-prepared  $\text{LiFePO}_4$  powder with a certain amount of glucose, obtaining  $\text{LiFePO}_4/\text{C}$  nanocomposites with uniform particle size after sintering at  $600^\circ\text{C}$  under a 5%  $\text{H}_2$ -95%  $\text{N}_2$  atmosphere for 3 h. High-rate discharge properties are investigated, using the material as the cathode in lithium ion batteries.

### Experimental

The  $\text{LiFePO}_4$  preparation process was as follows. DMSO was added to 1 M  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and 1 M  $\text{H}_3\text{PO}_4$ . After the solution cooled to room temperature, 3 M  $\text{LiOH} \cdot \text{H}_2\text{O}$  was added. To obtain a mixture pH of 7, the molar ratio of  $\text{Li}:\text{Fe}:\text{P}$  added was about 3:1:1. The mixture was heated at  $108^\circ\text{C}$  for 2 h in a nitrogen atmosphere, then cooled to room temperature and filtered; the precipitate was washed with distilled water several times and dried in a vacuum drying oven at  $120^\circ\text{C}$  for 4 h, then sieved to obtain  $\text{LiFePO}_4$  (sample A).

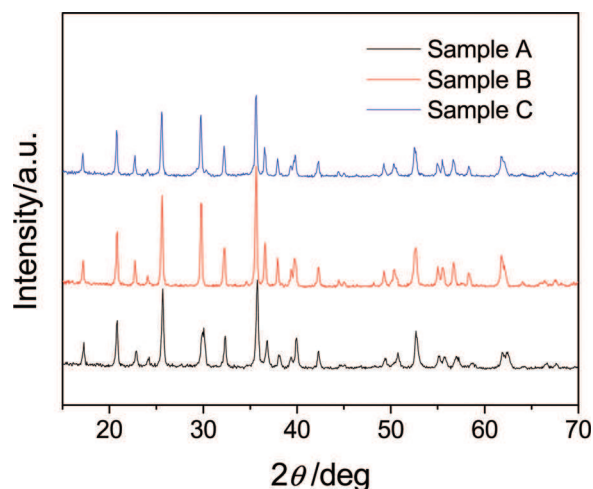
The  $\text{LiFePO}_4$  (sample B) was obtained by sintering sample A in a pipe furnace at  $600^\circ\text{C}$  for 3 h under a 5%  $\text{H}_2$ -95%  $\text{N}_2$  atmosphere.

The  $\text{LiFePO}_4/\text{C}$  nanocomposites (sample C) could be obtained by sintering the mixture of Sample A and glucose with a weight ratio of 100 to 3 at  $600^\circ\text{C}$  for 3 h under a 5%  $\text{H}_2$ -95%  $\text{N}_2$  atmosphere.

Electrochemical characterization was performed on electrodes prepared as follows. A mixture of  $\text{LiFePO}_4/\text{C}$ , carbon black, and polyvinylidene fluoride (PVDF; Chemical grade) in a given ratio (85:10:5) was ground in an agate mortar, then *N*-methyl-2-pyrrolidone (NMP; Analytical grade) was added to the mixture under continuous stirring. The obtained slurry was spread on an aluminum current collector with 14 mm in diameter and 0.02 mm in thickness, dried at  $120^\circ\text{C}$  for 12 h under a vacuum atmosphere ( $-0.1\text{MPa}$ ), and then pressed to form a cathode electrode with an active material loading of  $1.50\text{ mg cm}^{-2}$ . CR2016 coin cells were assembled in an argon-filled glove box in which oxygen and water were kept below 2 ppm. Lithium metal was used as the anode and a 1 M solution of  $\text{LiPF}_6$  in EC:DEC (1:1, v/v) was used as the electrolyte. The cells were tested on a Land CT2001A battery tester at room temperature.

### Results and Discussion

**XRD analysis.**—Figure 1 presents the XRD patterns obtained for bare  $\text{LiFePO}_4$  and for the samples synthesized through the chosen methods. In each case, the diffraction peaks are in full accord with the ordered  $\text{LiFePO}_4$  olivine structure (JCPDS Card No. 40-1499)

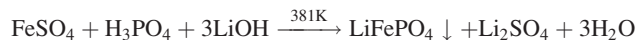


**Figure 1.** (Color online) XRD patterns of (A) bare  $\text{LiFePO}_4$ ; (B) bare  $\text{LiFePO}_4$  by sintering; (C)  $\text{LiFePO}_4/\text{C}$  nanocomposites by sintering.

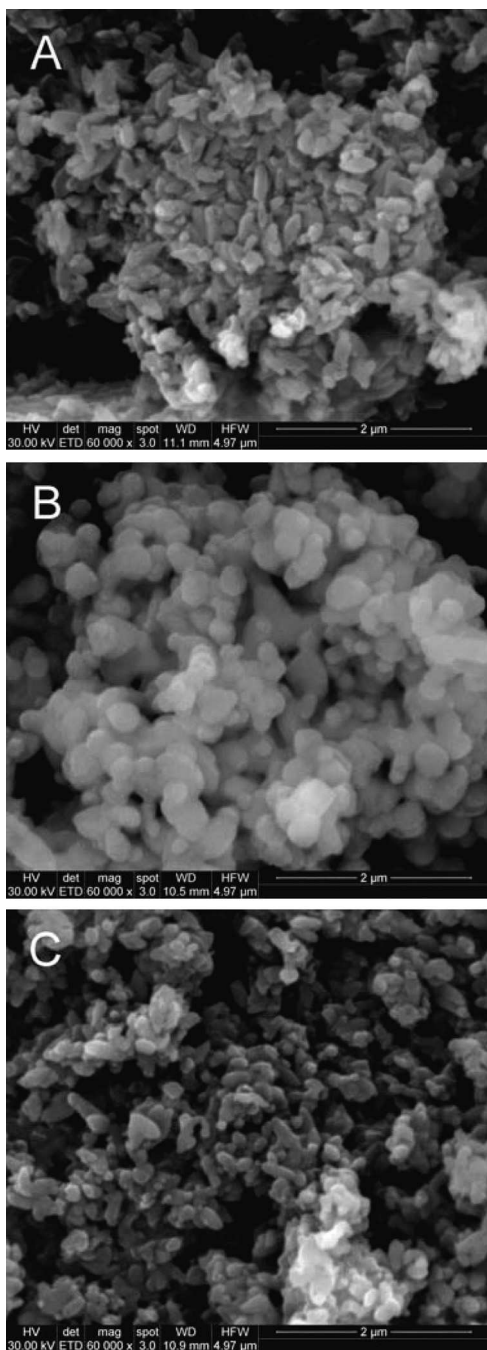
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indexed in the orthorhombic  $Pnma$  space group and show no evidence of impurity phases. No diffraction response was detected for the carbon coating due to its low content and amorphous state. It can be concluded that olivine-structured  $\text{LiFePO}_4$  can be synthesized in a mixture of DMSO and water at  $108^\circ\text{C}$  in only 2 h, which is far less than the 16 h reported in Ref. 16. This process can be expressed by the following equation



The factor of the formation of  $\text{LiFePO}_4$  through this system is the boiling point raise by DMSO, which can reduce the surface tension of the initial  $\text{LiFePO}_4$  crystalline nucleus and impel the reaction towards the formation of  $\text{LiFePO}_4$ .



**Figure 2.** SEM images of samples, (A) bare  $\text{LiFePO}_4$ ; (B) bare  $\text{LiFePO}_4$  by sintering; (C)  $\text{LiFePO}_4/\text{C}$  nanocomposites by sintering.

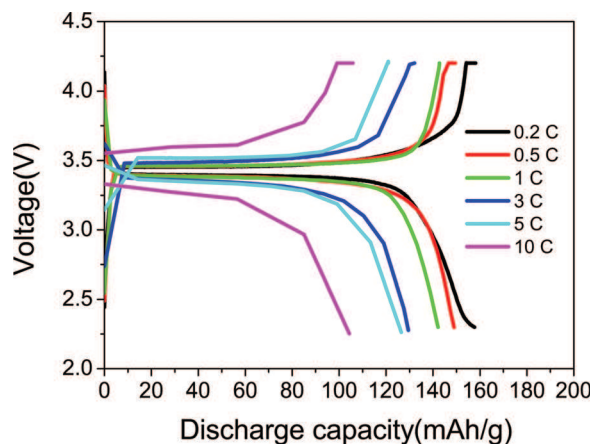
In addition, as shown in Fig. 1, the diffraction peak intensity of sample B is significantly stronger than that of sample A, which indicates that the crystal lattice of sample A formed by the liquid-phase method can be further improved in an atmosphere of high temperature and inert gas. However, when glucose is added to sample A and the mixture is then sintered under the same conditions (forming sample C), all the diffraction peak intensities decrease, becoming even weaker than those of sample A. One possible reason is that the surface of crystalline  $\text{LiFePO}_4$  is coated with amorphous carbon formed by glucose at high temperature, which inhibits grain growth.

**SEM analysis.**—Figure 2 shows SEM images of three samples. The olivine-structured  $\text{LiFePO}_4$  created through the chosen method is clearly made of grains approximately 100–200 nm. The formation of nanograins is attributable to the inhibitory effect of DMSO in the solution. After sintering at  $600^\circ\text{C}$  for 3 h, the  $\text{LiFePO}_4$  grains show spherical uniformity in the range of 150–250 nm, which indicates that heat treatment over a short time has a significant spheroidizing effect. It is noteworthy that sample C, formed by the addition of glucose, not only exhibits a sphere-like structure but also has a smaller grain size than samples A and B, in the approximate range of 100–150 nm. This result is obviously attributable to the amorphous carbon coating that inhibits grain growth, results that are consistent with the XRD analysis.

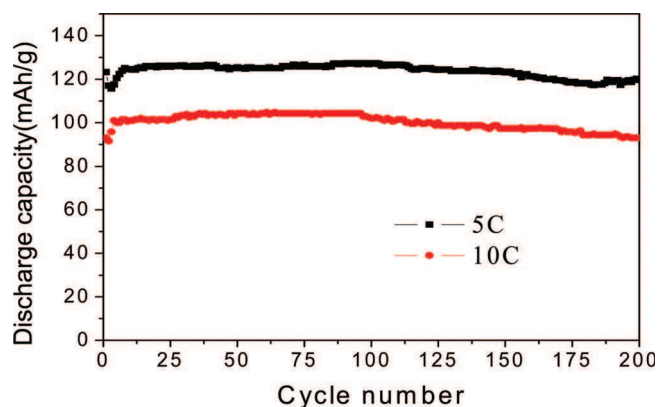
**Electrochemical properties.**—Figure 3 shows the initial charge-discharge curves of  $\text{LiFePO}_4/\text{C}$  nanocomposites between 2.3 and 4.2 V at different rates. It can be seen that the first discharge capacity is 157.7 mAh/g at 0.2 C, which is close to 93% of the theoretical capacity (170 mAh/g). Good discharge platforms are still maintained even at charge-discharge rates of 0.5, 1, 3, and 5 C, with first discharge capacities of 149, 142.5, 129.5, and 126.5 mAh/g, respectively. Even at 10 C, the discharge specific capacity of the product reaches 104 mAh/g, demonstrating a good high-rate discharge property. The results indicate significant potential for meeting the requirements of EVs and HEVs.

Figure 4 presents the cycling behavior of  $\text{LiFePO}_4/\text{C}$  nanocomposites at room temperature. It can be seen that the capacity retention rate remains above 90% of the initial rate after 200 cycles at 5 and 10 C. These results demonstrate that the  $\text{LiFePO}_4/\text{C}$  nanoparticle cathode materials prepared by the liquid-phase method in this study not only exhibit an excellent discharge capability but also demonstrate good high-rate cycling. Thus, the excellent electrical properties of the materials first derive from the small, uniform  $\text{LiFePO}_4/\text{C}$  nanoparticles obtained by the liquid-phase method, then from carbon-encapsulation and spheroidization.<sup>17,18</sup>

The above experiments show that the particle size of  $\text{LiFePO}_4$  has a great effect on its charge-discharge capacity, especially its rate capability.<sup>19</sup> When the grains are smaller, their surfaces can be



**Figure 3.** (Color online) Charge-discharge curves of  $\text{LiFePO}_4/\text{C}$  nanocomposites at different rates.



**Figure 4.** (Color online) Cycling behavior of LiFePO<sub>4</sub>/C nanocomposites tested at room temperature.

effectively improved to increase their contact area with the electrolyte and shorten the lithium ion diffusion channel, which is beneficial for the intercalation and exfoliation of lithium ions.<sup>20</sup> Meanwhile, the presence of a small amount of carbon can also increase the material's conductivity.

### Conclusion

In summary, we prepared LiFePO<sub>4</sub> nanoparticles by a liquid-phase method, using DMSO as a boiling point raiser and crystal growth inhibitor under ambient pressure. By mixing prepared LiFePO<sub>4</sub> nanoparticles with a certain amount of glucose and then sintering the mixture at 600°C under a 5% H<sub>2</sub>–95% N<sub>2</sub> atmosphere for 3 h, LiFePO<sub>4</sub>/C nanocomposites were obtained. Compared with the traditional preparation method, uniform LiFePO<sub>4</sub> nanoparticles can be obtained without high pressure; additional advantages include short reaction time, simple equipment, and low energy consumption. The materials obtained by this method have an integrated olivine structure and uniformly smaller grain size. Electrochemical tests show that the special capacity of spherical LiFePO<sub>4</sub>/C is 157.7 mAh/g at a 0.2 C discharge rate, which is close to 93% of the theoretical capacity (170 mAh/g). A special capacity of 126 and 104 mAh/g can be achieved even at 5 and 10 C discharge, and the mate-

rial has no significant capacity fading after 200 cycles. The results show that LiFePO<sub>4</sub>/C nanocomposites have a good high-rate discharge property and excellent cycling performance. We also found that if no DMSO was added to the reaction system, LiFePO<sub>4</sub> could only be obtained above 150°C using hydrothermal means, indicating that DMSO played an important role under conditions of ambient pressure and low temperature. The specific efficiency of DMSO will be the focus of further investigation.

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### References

1. A. K. Padhi, K. S. Nanjundaswamy, and J. B. Goodenough, *J. Electrochem. Soc.*, **144**, 1188 (1997).
2. B. F. Wang, Y. L. Qiu, and L. Yang, *Electrochem. Commun.*, **8**, 1801 (2006).
3. H. Liu, Q. Cao, L. J. Fu, C. Li, Y. P. Wu, and H. Q. Wu, *Electrochem. Commun.*, **8**, 1553 (2006).
4. M. Konarova and I. Taniguchi, *J. Power Sources*, **195**, 3661 (2010).
5. Y. D. Choa, G. T. K. Feya, and H. M. Kao, *J. Power Sources*, **189**, 256 (2009).
6. G. T. K. Fey and T. L. Lu, *J. Power Sources*, **178**, 807 (2008).
7. K. F. Hsu, S. Y. Tsaya, and B. J. Hwang, *J. Mater. Chem.*, **14**, 2690 (2004).
8. C. Y. Lai, Q. J. Xu, H. H. Ge, G. D. Zhou, and J. Y. Xie, *Solid State Ionics*, **179**, 1736 (2008).
9. S. B. Lee, S. H. Cho, S. J. Cho, G. J. Park, S. H. Park, and Y. S. Lee, *Electrochem. Commun.*, **10**, 1219 (2008).
10. X. H. Liu and Z. W. Zhao, *Powder Technol.*, **197**, 309 (2010).
11. M. Konarova and I. Taniguchi, *Powder Technol.*, **191**, 111 (2009).
12. J. F. Ni, M. Morishita, Y. Kawabe, M. Watada, N. Takeichi, and T. Sakai, *J. Power Sources*, **195**, 2877 (2010).
13. S. A. Needham, A. Calka, G. X. Wang, A. Mosbah, and H. K. Liu, *Electrochem. Commun.*, **8**, 434 (2006).
14. D. Rangappa, K. Sone, T. Kudo, and I. Honma, *J. Power Sources*, **195**, 6167 (2010).
15. M. Higuchia, K. Katayamaa, Y. Azumaa, M. Yukawab, and M. Suhara, *J. Power Sources*, **119–121**, 258 (2003).
16. C. Delacourt, P. Poizot, S. Levasseur, and C. Masquelier, *Electrochem. Solid-State Lett.*, **9**, A351 (2006).
17. W. J. Zhang, *J. Electrochem. Soc.*, **157**, A 1040 (2010).
18. S. W. Oh, S. T. Myung, S. M. Oh, K. H. Oh, K. Amine, B. Scrosati, and Y. K. Sun, *Adv. Mater.*, **22**, 4842 (2010).
19. M. Gaberscek, R. Dominko, and J. Jamnik, *Electrochem. Commun.*, **9**, 2778 (2007).
20. Z. R. Chang, H. J. Lv, H. W. Tang, H. J. Li, X. Z. Yuan, and H. J. Wang, *Electrochim. Acta*, **54**, 4595 (2009).