

A carbon–LiFePO₄ nanocomposite as high-performance cathode material for lithium-ion batteries

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Abstract A cathode material of an electrically conducting carbon–LiFePO₄ nanocomposite is synthesized by wet ball milling and spray drying of precursor powders prior to a solid-state reaction. The structural characterization shows that the composite is composed of LiFePO₄ crystals and 4.8 wt.% amorphous carbon. Galvanostatic charge/discharge measurements indicate that the composite exhibits a superior high energy and high cycling stability. This composite delivers a discharge capacity of 159.1 mAh g^{−1} at 0.1 C, 150.8 mAh g^{−1} at 1 C, and 140.1 mAh g^{−1} at 2 C rate. The capacity retention of 99% is achieved after 200 cycles at 2 C. The 18,650 cylindrical batteries are assembled using the composite as cathode materials and demonstrate the capacity of 1,400 mAh and the capacity retention of 97% after 100 cycles at 1 C. These results reveal that the as-prepared LiFePO₄–carbon composite is one of the promising cathode materials for high-performance, advanced lithium-ion batteries directed to the hybrid electric vehicle and pure electric vehicle markets.

Keywords Lithium iron phosphate · Carbon · Nanocomposite · Li-ion battery · Spray drying

Introduction

Olivine structure LiFePO₄ was first studied by Padhi et al. [1] and has attracted much attention as a promising cathode material for lithium-ion batteries due to high theoretical capacity (170 mAh g^{−1}), good cycle stability, excellent thermal safety, low cost, and environmental friendliness [2, 3]. Nevertheless, LiFePO₄ still requires further modifications to overcome limitations such as poor electronic conductivity and slow lithium-ion diffusion [4]. Decreasing particle size and surface coating or mixing with electrically conductive materials, especially carbon, have been extensively studied to overcome the ionic and electronic transport limitations [5–10].

Currently solid-state synthesis has been adopted for the commercial scaled-up production of LiFePO₄ powders [11]. In general, in the case of solid-state synthesis, the starting material consists of a stoichiometric amount of iron salt (Fe (II) acetate, Fe(II) oxalate), a lithium compound (Li₂CO₃ or LiOH), and a phosphorous source (NH₄H₂PO₄ or (NH₄)₂HPO₄) [2, 12–15]. The starting material firstly decomposes at a low temperature of 300–400 °C to release the gases, and then some carbon-containing material is added to the precursor. After being reground, the precursor is calcined at a high temperature ranging from 400 to 800 °C to form LiFePO₄–carbon composite. The major disadvantage of solid-state synthesis is uncontrollable particle growth and agglomeration. Furthermore, inhomogeneous distribution of carbon can make it difficult to realize full utilization of active LiFePO₄ materials. For example, in the literature [16], LiFePO₄–carbon composite was prepared by a solid-state method using the glycolic

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acid as a reducing agent and also as a carbon source. The as-prepared composite presented an irregular particle shape and a wide range of size distribution. A low capacity of 119.0 mAh g^{-1} , accompanied with large overpotential, was obtained when cycled at 2 C rate.

Wet chemistry approach has an obvious advantage over solid-state synthesis in achieving better homogeneity and mixing of the starting compounds on molecular level [2]. Water-soluble carbon-included compounds, e.g., sucrose [17, 18], glucose [19], or citrate [20], are generally used as carbon source in wet chemical synthesis of $\text{LiFePO}_4\text{-C}$ composite. A great challenge in wet chemical route is the component segregation, especially for carbon-included compounds in drying process due to density differences among multiple starting materials. Spray drying is a well-known continuous method for the preparation of multi-component powders. Since the solvent can be heated and evaporate in a very short time by hot carrier gas, as-prepared powder by spray drying has a uniform component distribution [21]. In this study, we report the synthesis and electrochemical performance of a $\text{LiFePO}_4\text{-carbon}$ nanocomposite prepared by wet ball milling and spray drying of precursor powders prior to a solid-state reaction. It is because of the uniform carbon distribution that the $\text{LiFePO}_4\text{-C}$ composite shows a superior high energy and high stability when used as cathode material in lithium-ion batteries.

Experimental section

Synthesis of $\text{LiFePO}_4\text{-C}$ composite The $\text{LiFePO}_4\text{-C}$ composite was synthesized using a wet ball milling procedure followed by a spray drying and a solid-state calcination synthesis route. Typically, the precursor $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ (Shenzhen SheK Tin, China) was firstly dehydrated by calcination at 500°C for 6 h in air atmosphere. The anhydrous FePO_4 was mixed with Li_2CO_3 and sucrose by a wet ball milling process in a basket-type mill equipped with zirconia balls. Water was used as a ball milling medium. The rotating speed was fixed at 450 rpm, and the milling time was 2 h. The molar ratio of $\text{Li}_2\text{CO}_3/\text{FePO}_4/\text{sucrose}$ was 0.51:1:0.1. After the ball milling, the resulting stable suspension was dried to form a mixed dry spherical precursor by a high-speed centrifugal spray dryer. The suspension was centrifuged in a round disk with some special shape pores at a high rotating speed of 30,000 rpm to form small drops, and was immediately dried in the spray dryer by hot air. The inlet air temperature was 200°C , and the exit air temperature was 120°C . The spray-dried precursor powders were then placed into a tube furnace

and heated to 700°C at a heating rate of 3°C min^{-1} for 10 h under an argon atmosphere.

Structural characterization A TG/DSC analysis using a NETZSCH STA 409 PC/PG instrument was used to determine the water content in hydrated iron phosphate precursor. XRD measurements were carried out using a powder X-ray diffraction (D/max-RB) with a filtered $\text{Cu K}\alpha$ radiation ($1.5406 \text{ \AA}$). Raman measurements were performed using an RM 2000 microscopic confocal Raman spectrometer (Renishaw PLC, England) employing a 514-nm laser beam. A carbon and sulfur analyzer was used to determine the carbon content in the final $\text{LiFePO}_4\text{-C}$ composite. The element content in the final composite was detected by an ICP analyzer (IRIS Intrepid II XSP). Scanning electron microscopy (SEM; FEI Quanta 200 FEG) was used to investigate the morphology and size of the $\text{LiFePO}_4\text{-C}$ composite. The specific surface areas of the powders were measured by a NOVA 4000 high-speed surface area and pore size analyzer. The particle size distribution was measured in a laser particle size analyzer (Malvern Mastersizer 2000).

Electrochemical characterization Electrochemical measurements were performed using CR2032 coin cells assembled in an argon-filled glove box. For preparing the working electrode, a mixture of $\text{LiFePO}_4\text{-C}$ composite, carbon black, and polyvinylidene fluoride at a weight ratio of 8:1:1 was pasted on a pure Al foil. Pure lithium foil was used as a counter electrode. A Celgard 2325 PP/PE/PP membrane was used as separator. The electrolyte consisted of a solution of $1 \text{ mol L}^{-1} \text{ LiPF}_6$ in ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate. Galvanostatic cycling of the assembled cells was carried out using a LAND system in the voltage range of 2.5–4.2 V (vs. Li)

Results and discussion

As Fe/P ratio has a great impact on the electrochemical performance of LiFePO_4 product [9], iron phosphate dihydrate with a fixed Fe/P ratio (1:1) was selected as the source material of iron and phosphor. Figure 1 shows the TG–DSC curves of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ precursor when heated in air from 25 to 550°C . The first weight loss of ~5% from 25 to 150°C and the corresponding endothermic reaction peak centered at 120°C in DSC curve can be attributed to the loss of ~0.5 M crystal water in $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$. The subsequent weight loss of ~15% from 150 to 250°C and the sharp endothermic peak centered at 200°C in DSC

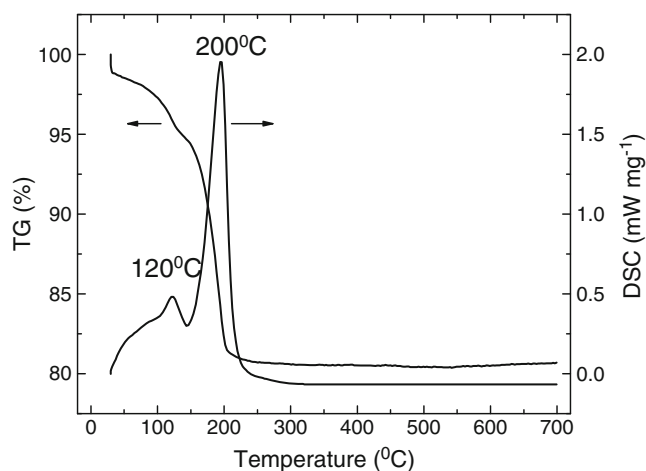


Fig. 1 TG–DSC curves of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ heated in air

curve may be ascribed to the loss of the rest ~ 1.5 M crystal water. It is concluded that the dehydration process of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ in air goes through two different stages. From TG curve, the total weight loss of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ was 19.3%, corresponding to 2 M crystal water in $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ very well. It means that $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ can be fully dehydrated in air to convert to anhydrous FePO_4 . It is also well known that FePO_4 has diversified hydrates with different water content, e.g., $\text{FePO}_4 \cdot x\text{H}_2\text{O}$ ($x=1-4, 8$). The conversion from $\text{FePO}_4 \cdot x\text{H}_2\text{O}$ to anhydrous FePO_4 by calcination in air can ensure the accuracy of Li/Fe/P ratio in the subsequent mixing process with Li_2CO_3 whatever the water content in $\text{FePO}_4 \cdot x\text{H}_2\text{O}$ precursor, which is especially important for an engineering purpose, because in that case, it is always hard to make sure the complete homogeneity of raw materials.

After dehydration, anhydrous FePO_4 was wet ball milled with the proper amount of Li_2CO_3 and sucrose as a carbon source. In the wet ball milling process, particle size of FePO_4 was decreased and simultaneously, a homogenous suspension containing Li, Fe, and P source was achieved. In order to avoid carbon component segregation in the drying process, the suspension was dried in an industrial high-speed centrifugal spray dryer to form a mixed dry spherical precursor. After a solid-state reaction in high temperature, $\text{LiFePO}_4\text{--C}$ composite was eventually obtained. Figure 2 shows the XRD patterns of the as-obtained $\text{LiFePO}_4\text{--C}$ composite and the $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ precursor. All intense peaks in the $\text{LiFePO}_4\text{--C}$ composite can be well indexed to orthorhombic LiFePO_4 (JCPDS Card No. 40–1499, space group $Pnma(62)$, $a=10.334$ Å, $b=6.010$ Å, $c=4.693$ Å, $\alpha=\beta=\gamma=90^\circ$). No obvious peaks can be assigned to graphite in the XRD pattern, indicating that the carbon in the composite was not well crystallized. The $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ precursor showed a low crystallinity and

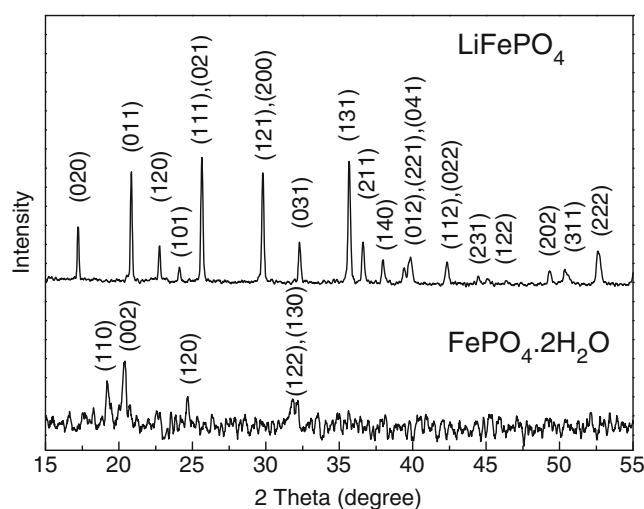


Fig. 2 XRD patterns of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ and as-prepared $\text{LiFePO}_4\text{--C}$ composite

the XRD pattern was indexed to a monoclinic $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ (JCPDS Card No. 33–666, space group $P121/n1(14)$, $a=5.32$ Å, $b=9.75$ Å, $c=8.65$ Å, $\alpha=\gamma=90^\circ$, $\beta=90.6^\circ$). Figure 3 shows the Raman spectrum of the $\text{LiFePO}_4\text{--C}$ composite. The bands in the range of $1,100\text{--}1,500$ cm^{-1} and $1,500\text{--}1,700$ cm^{-1} were attributed to the D band and G band of carbon, respectively. It is well known that the ratio of the D/G integrated peak intensity (I_D/I_G ratio) can be considered as an indicator of the amount of graphene clusters in the structure [22]. Figure 3 shows that the I_D/I_G of the composite is 1.01, meaning clearly that the majority carbon is amorphous in the composite. An industrial carbon and sulfur analyzer was used to determine the precise carbon content in the $\text{LiFePO}_4\text{--C}$ composite. And induc-

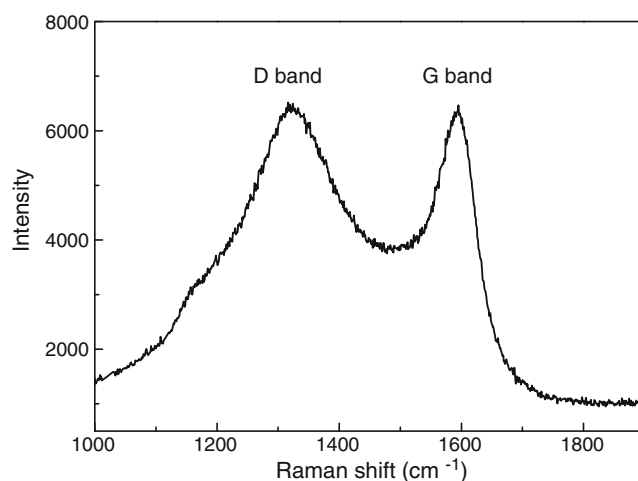


Fig. 3 Raman spectrum of the as-prepared $\text{LiFePO}_4\text{--C}$ composite

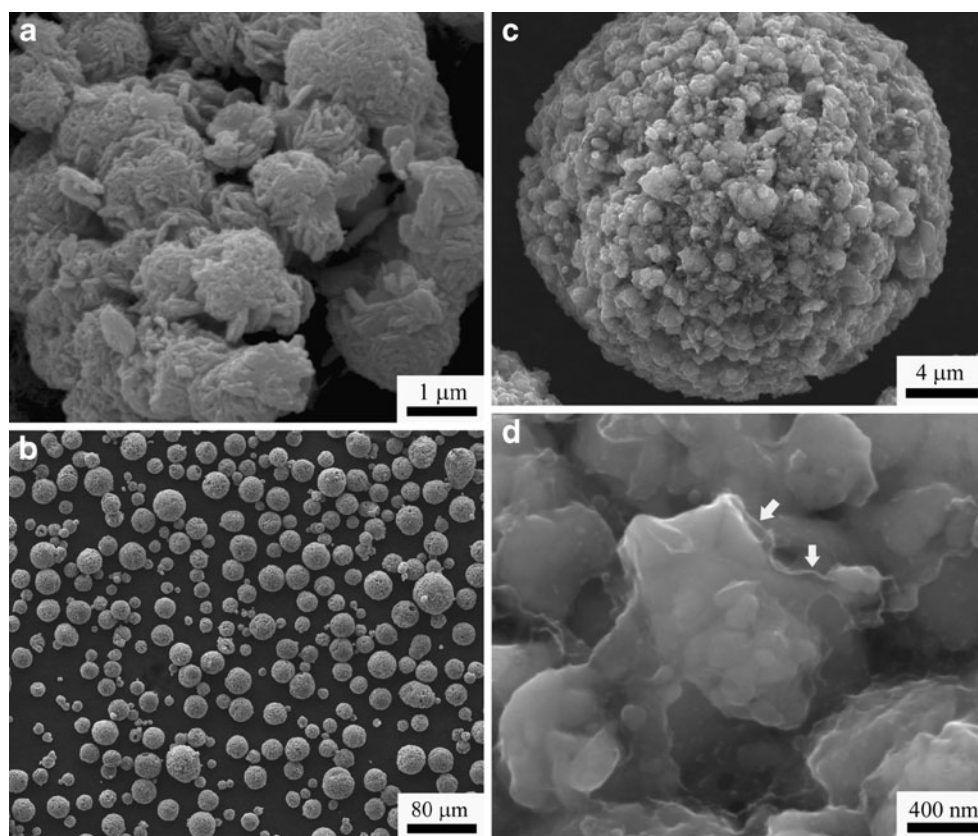
tively coupled plasma spectrum was used to detect the element content. The results showed the carbon content of 4.8 wt.% and the Li/Fe/P molar ratio of 1.01:1.01:1. All these results reveal that the composite was composed of LiFePO_4 crystals and amorphous carbon.

Figure 4 shows the SEM images of the $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ precursor and the as-prepared $\text{LiFePO}_4\text{-C}$ composite. As shown in Fig. 4a, the $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ precursor was composed of small crystals with “ribbon” or “flake”-like configuration. It is generally believed that the flake-like crystal is ideal for LiMPO_4 olivine materials ($\text{M} = \text{Fe}, \text{Mn}, \text{etc.}$) because of its 1D channels for Li^+ -ion motion [23]. As disclosed in Fig. 4b, c, the regular spherical particles consisting of LiFePO_4 sub-micrometer-sized crystals homogeneously embedded in a carbon matrix were obtained. In the high-resolution SEM image in Fig. 4d, it can be found that the particle was completely coated by a transparent surface as indicated by two white arrows. Basically, the amorphous carbon in the composite acts as “glue” to bind together the LiFePO_4 crystals to form the spherical particles. According to BET analysis, the composite has a specific surface area of $25.9 \text{ m}^2 \text{ g}^{-1}$. The particle size distribution measurement shows the D10 of 2.7 μm , D50 of 12.1 μm , and D90 of 38.0 μm . The tap

density of the composite powders was measured to be 1.1 g cm^{-3} .

The electrochemical performance of the as-prepared $\text{LiFePO}_4\text{-C}$ composite was investigated in half cells using Li foil as anode. Figure 5 shows the charge–discharge profiles of the composite at the currents of 0.1, 0.5, 1, 2, and 2 C at the 200th cycle ($1 \text{ C} = 170 \text{ mA g}^{-1}$), respectively. The specific capacity is based on the composite masses including both LiFePO_4 and carbon. The cell exhibits the typical voltage plateau along 3.5 V (vs. Li) associated with the $\text{Fe}^{2+/3+}$ redox process. The voltage profiles also show a narrow gap between charge and discharge, indicating very low electrode resistance. It is believed that the uniformly distributed carbon in the composite accounts for the electrode high electronic conductivity. The first charge and discharge capacity at 0.1 C (17 mA g^{-1}) is 166.8 and 159.1 mAh g^{-1} , resulting in a high initial efficiency of 95.4%. After 3 cycles at 0.1 C, the cells were charged and discharged at 0.5 C for 10 cycles and then at 1 C for 10 cycles, finally at 2 C for 200 cycles. The discharge capacity at the current of 0.5, 1, and 2 C is 155.8, 150.8, and 140.1 mAh g^{-1} , respectively. And in the case of 2 C, the discharge voltage plateau decreases to 3.3 V (vs. Li). The discharge profile at 2 C almost overlaps with that after 200 cycles. The residual

Fig. 4 SEM images of **a** $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ precursor and **b–d** $\text{LiFePO}_4\text{-C}$ composite



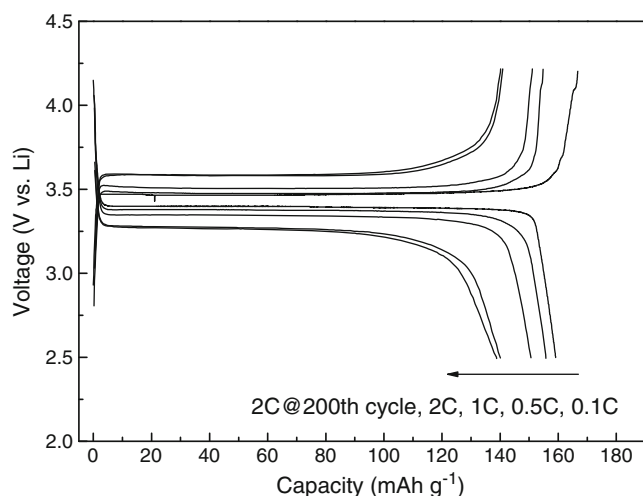


Fig. 5 Charge/discharge profiles of the LiFePO₄-C composite-based cells

capacity after 200 cycles at 2 C is 138.8 mAh g⁻¹, equal to 99% of the initial capacity at 2 C, indicating a very stable cycling performance as shown in Fig. 6.

These results demonstrate that the LiFePO₄-C composite of this work has a high specific capacity and stable cycle life. The amorphous carbon in the composite plays a very important role for the highly desirable properties. As discussed in other publications [3, 24–26], the amorphous carbon serves as a mixed conducting 3D nano-network, enabling both lithium ion and electron to migrate and reach each active LiFePO₄ crystal, hence realizing full utilization of active materials. Another important feature of the amorphous carbon is believed to be its barrier effect, preventing the LiFePO₄ crystals from the union particularly in the calcination process.

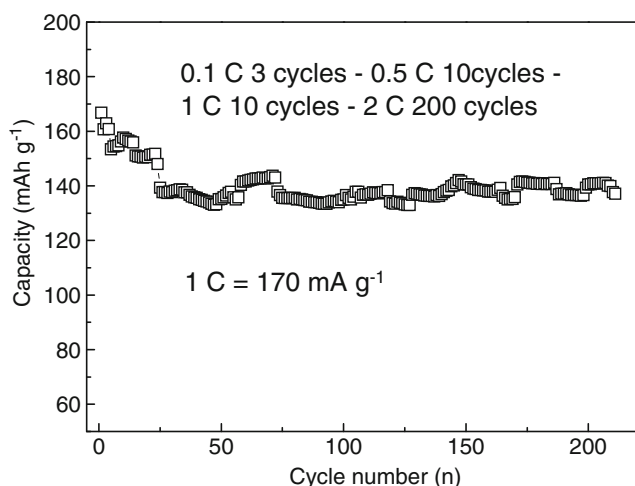


Fig. 6 Cycling performance of the LiFePO₄-C composite-based cells

An 18,650 cylindrical battery (dimension, diameter 18 mm and height 65 mm) was assembled using the as-prepared LiFePO₄-C composite as cathode and MCMB as anode. The battery demonstrates a capacity of 1,400 mAh and an internal resistance of 34.1 mΩ with the voltage of 3.2 V. The cathode electrode pressed density was measured to be 2.0 g cm⁻³. As shown in Fig. 7, a high capacity retention (97%) was delivered after 100 cycles at 1 C (1,400 mA).

Conclusion

The LiFePO₄-carbon nanocomposites were successfully prepared by wet ball milling and spray drying of precursor powders prior to a solid-state reaction. With the advantages of wet ball milling on homogeneous mixing of the starting compounds and spray drying on fast dryness and uniform component distribution, the as-prepared LiFePO₄-C composite exhibited a superior electrochemical performance, delivering discharge capacities of 159.1, 150.8, and 140.1 mAh g⁻¹ at rates of 0.1, 1, and 2 C, respectively. The capacity retention of the composite was 99% after 200 cycles at 2 C rate. The 18,650 cylindrical battery with the composite as cathode materials presented the capacity of 1,400 mAh g⁻¹ and the capacity retention of 97% after 100 cycles at 1 C. The superior properties were ascribed to the homogeneous coating of the 4.8 wt.% amorphous carbon, which prevented the union of LiFePO₄ crystals in calcination process, leading to a greatly enhanced electronic conductivity. It is hoped that this work can contribute to the development of LiFePO₄ material for high-performance, advanced lithium-ion batteries for HEV or EV.

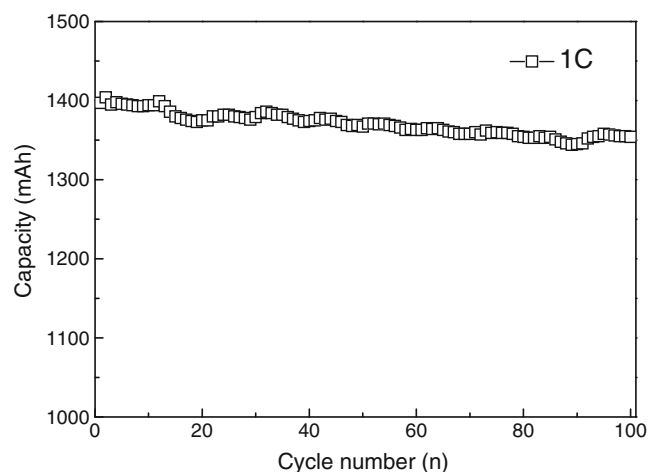


Fig. 7 Cycling performance of 18,650 cylindrical battery using as-prepared LiFePO₄-C composite as cathode material

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References

1. Padhi AK, Nanjundaswamy KS, Goodenough JB (1997) *J Electrochem Soc* 144:1188
2. Jugovic D, Uskokovic D, Power J (2009) *Sources* 190:538
3. Wu XL, Jiang LY, Cao FF, Guo YG, Wan LJ (2009) *Adv Mater* 21:2710
4. Amin R, Balaya P, Maier J (2007) *Electrochem Solid State Lett* 10:A13
5. Li H, Wang ZX, Chen LQ, Huang XJ (2009) *Adv Mater* 21:4593
6. Wang Y, Cao GZ (2008) *Adv Mater* 20:2251
7. Gibot P, Casas-Cabanas M, Laffont L, Levasseur S, Carlah P, Hamelet S, Tarascon JM, Masquelier C (2008) *Nat Mater* 7:741
8. Lee YJ, Yi H, Kim WJ, Kang K, Yun DS, Strano MS, Ceder G, Belcher AM (2009) *Science* 324:1051
9. Kang B, Ceder G (2009) *Nature* 458:190
10. Yu Y, Gu L, Zhu C, Tsukimoto S, Aken PA, Maier J (2010) *Adv Mater* 22:2247
11. Saidi MM, Huang H (2008) US Patent No. 7422823
12. Liu H, Li C, Zhang HP, Fu LJ, Wu YP, Wu HQ, Power J (2006) *Sources* 159:717
13. Kang HC, Jun DK, Jin B, Jin EM, Park KH, Gu HB, Kim KW, Power J (2008) *Sources* 179:340
14. Liu H, Cao Q, Fu LJ, Li C, Wu YP, Wu HQ (2006) *Electrochem Commun* 8:1553
15. Matsui H, Nakamura T, Kobayashi Y, Tabuchi M, Yamada Y, Power J (2010) *Sources* 195:6879
16. Kim HS, Kam DW, Kim WS, Koo HJ (2011) *Ionics* 17:293–297
17. Kim JK, Cheruvally G, Ahn JH, Solid State J (2008) *Chemistry* 12:799
18. Kadoma Y, Kim JM, Abiko K, Ohtsuki K, Ui K, Kumagai N (2010) *Electrochim Acta* 55:1034
19. Murugan AV, Muraliganth T, Manthiram A (2009) *J Electrochem Soc* 156:A79
20. Liu J, Wang JW, Yan XD, Zhang XF, Yang GL, Jalbout AF, Wang RS (2009) *Electrochim Acta* 54:5656
21. Konarova M, Taniguchi I, Power J (2009) *Sources* 194:1029
22. Guo XF, Zhan H, Zhou YH (2009) *Solid State Ionics* 180:386–391
23. Goodenough JB, Power J (2007) *Sources* 174:996
24. Oh SW, Myung ST, Oh SM, Oh KH, Amine K, Scrosati B, Sun YK (2010) *Adv Mater* 22:4842
25. Oh SM, Oh SW, Yoon CS, Scrosati B, Amine K, Sun YK (2010) *Adv Mater* 20:3260
26. Xie HM, Wang RS, Ying JR, Zhang LY, Jalbout AF, Yu HY, Yang GL, Pan XM, Su ZM (2006) *Adv Mater* 18:2609