Nanosized spherical LiFePO$_4$/C composite was synthesized from nanosized spherical FePO$_4$$\cdot$H$_2$O, Li$_2$C$_2$O$_4$, aluminum oxide, titanium oxide, oxalic acid, and sucrose by binary sintering process. The phases and morphologies of LiFePO$_4$/C were characterized using SEM, TEM, CV, EIS, EDS, and EDX as well as charging and discharging measurements. The results showed that the as-prepared LiFePO$_4$/C composite with good conductive webs from nanosized spherical FePO$_4$$\cdot$H$_2$O exhibits excellent electrochemical performances, delivering an initial discharge capacity of 161.7 mAh g$^{-1}$ at a 0.1 C rate, 152.4 mAh g$^{-1}$ at a 1 C rate and 131.7 mAh g$^{-1}$ at a 5 C rate, and the capacity retention of 99.1%, 98.7%, and 95.8%, respectively, after 50 cycles. Meanwhile, the high and low temperature performance is excellent for 18650 battery, maintaining capacity retention of 101.7%, 95.0%, 88.3%, and 79.3% at 55$^\circ$C, 0$^\circ$C, −10$^\circ$C, and −20$^\circ$C by comparison with that of room temperature (25$^\circ$C) at the 0.5 C rate over a voltage range of 2.2 V to 3.6 V, respectively.

1. Introduction

Clean and rechargeable secondary energy sources are urgently needed for the development of modern technology and widespread application of portable electrical equipment. Among secondary energy sources, rechargeable lithium-(Li) ion battery is the most attractive and promising. In 1997, Padhi et al. [1] proved that olivine LiFePO$_4$ has an excellent performance in Li-ion intercalation and deintercalation. Its theoretical capacity is 170 mAh g$^{-1}$ with a flat discharge voltage at 3.4 V. Among polyanion cathodes, LiFePO$_4$ has the advantages of excellent cycle ability, good thermal stability, inexpensive raw materials, and environmental friendliness. LiFePO$_4$ is also attractive for use as a next generation cathode material for Li-ion batteries. However, the low electronic conductivity of LiFePO$_4$ leads to a poor charge-discharge performance at a high current rate. Therefore, modifications to LiFePO$_4$ to improve its properties have been developed. Such modifications include coating with nanocarbon [2–9], encapsulation with a conductive polymer [10, 11], and doping with suitable metals [12–18].

FePO$_4$$\cdot$xH$_2$O is a promising precursor for preparing the Li-ion battery cathode material LiFePO$_4$. The advantages of this precursor include innocuity, low cost, similar structure with LiFePO$_4$, and oxidation avoidance of ferrous iron [19–21]. Traditional methods for the synthesis of FePO$_4$$\cdot$xH$_2$O and LiFePO$_4$ include solid phase synthesis [22, 23], sonochemistry [24], coprecipitations [25–29], and hydrothermal synthesis [30–32]. These methods usually involve the use of expensive metal-organic compounds. In the solid-state synthetic process, high-energy consumption is generated and particles are relatively unevenly distributed. The sonochemistry process has some advantages in preparing iron phosphate, including nonrequirement of oxidant, less reaction time, and controllable particle size. However, the large-scale production of iron phosphate is difficult to be realized [33, 34]. Lee and Teja [35] Xu et al. [36] prepared LiFePO$_4$ nanoparticles in subcritical and superheated water. Yu et al. [37] investigated the rapid and continuous production of LiFePO$_4$/C nanoparticles in superheated water. Chen et al. [38] reported the influences of carbon sources on the electrochemical performances of LiFePO$_4$/C composites.

In this work, nanosized spherical LiFePO$_4$/C composite was prepared from nanosized spherical FePO$_4$$\cdot$2H$_2$O, Li$_2$C$_2$O$_4$, aluminum oxide, titanium oxide, oxalic acid, and
2. Experimental

2.1. Preparation of Materials. The LiFePO$_4$/C composite was prepared by mixing stoichiometric amounts of nanosized spherical FePO$_4$·2H$_2$O, Li$_2$C$_2$O$_4$, aluminum oxide, and titanium oxide dispersed in ethylene glycol with oxalic acid and sucrose, followed by grinding via ball milling. After evaporating the ethylene glycol, the mixture was firstly sintered in a horizontal quartz tube at 400°C for 6 h in an argon atmosphere. As the presintered product cooled to room temperature, the LiFePO$_4$/C composites were obtained after being calcined at 650°C for 8 h.

2.2. Material Characterization. The LiFePO$_4$/C sample was characterized by X-ray diffraction (XRD; Rigaka D/MAX 2500 V) using CuKα radiation (λ = 0.154 nm) to identify the crystalline phase. Data were collected between 10° and 90° in steps of 8°/min. The surface morphologies of the samples were observed by a scanning electron microscopy (SEM) system (JSM-6380LV). The details of carbon coating were observed with transmission electron microscopy (TEM) (Hitachi, H-8100). A three-electrode system was used to characterize the electrochemical performances of the as-deposited LiFePO$_4$/C composites. LiFePO$_4$/C freshly deposited under the same experimental parameters were used in cyclic voltammetry (CV) analysis and normal charging and discharging experiments, as well as high rate charge and discharge characterizations. Electrochemical impedance spectroscopy (EIS) measurements were performed over a frequency range of 0.001 Hz to 1 MHz at a 50% discharge stage.
with a perturbation signal of 5 mV over a Chi 660c setup. All electrochemical measurements were conducted at room temperature (25°C).

2.3. Electrode Fabrication and Electrochemical Measurements.

The as-prepared cathode was mixed with acetylene black and polyvinylidene difluoride at a mass ratio of 80:10:10. LiFePO₄/C cathode was prepared by spreading the above mixture on an aluminum foil and drying in a vacuum oven at 120°C. Charge-discharge tests on LiFePO₄/C were performed in coin cells using LiFePO₄/C cathodes and Li anodes. A porous membrane (Celgard 2300) was used as a separator, and the electrolyte was 1 mol L⁻¹ LiPF₆ dissolved in a mixture of ethylene carbonate, dimethyl carbonate, and methyl-ethyl carbonate at a volume ratio of 1:1:1. Coin cells (CR 2025) were assembled in an argon-filled glove box. The cells were charged and discharged at the rates of 0.1 C, 1 C and 5 C over a voltage range of 2.5 V to 4.2 V, respectively, versus the Li/Li⁺ electrode at ambient temperature using a battery testing system (Neware BTS-2000). The high and low temperature performance of LiFePO₄/C was tested via fabricating 18650 battery at the rate of 0.5 C over a voltage range of 2.2 V to 3.6 V.

3. Results and Discussion

3.1. Morphology of LiFePO₄/C Prepared with Nanosized Spherical FePO₄·2H₂O.

Nanosized spherical FePO₄·2H₂O has been used to prepare LiFePO₄/C. As seen in Figure 1, the SEM images of LiFePO₄/C from nanosized spherical FePO₄·2H₂O were shown. The products had diverse morphology. The as-prepared LiFePO₄/C composite was spherical and the particles’ size close to 100 nm in size was uniformly distributed. The shapes of particles were traced back, following each step of preparation (Figure 2(a) for mixture, Figure 2(b) for presintering product, and Figure 2(c) for sintered product). Oxalic acid as reductant was ultimately decomposed into CO₂ and H₂O. Sucrose as carbon source was used for coating nanosized LiFePO₄ particles.

Figure 3 showed the TEM images of LiFePO₄/C. As shown in the image, LiFePO₄ particles were well surrounded by a thin surface layer of carbon. The thickness of the carbon-coated layer was about 4 nm. There was a layer of carbon web, providing good electronic contact between LiFePO₄ particles.

As seen from Figure 4, the EDS and EDX results showed that as-prepared sample had the elements, such as Fe, P, O, C, Ti, and Al, and all of the elements were distributed uniformly, indicating that C, Ti, and Al dispersed in LiFePO₄ evenly.
3.2. Electrochemical Performance of LiFePO₄/C Prepared with Nanosized Spherical FePO₄·2H₂O

3.2.1. Initial Charge/Discharge Curves and Cycling Performance. The theoretical capacity of stoichiometric LiFePO₄ is 170 mAh·g⁻¹. Figure 5 showed the initial charge-discharge capacity and cycling performance of the LiFePO₄/C composite cathodes at three different rates of 0.1C, 1C, and 5C. The discharge capacity of LiFePO₄/C composite synthesized with nanosized spherical FePO₄·2H₂O was 161.7, 152.4 and 131.7 mAh/g at 0.1C, 1C and 5C, respectively. Noticeably, the long and flat voltage plateaus were at 3.44 and 3.40 V at the rate of 0.1C for Li extraction and insertion, respectively. It implied the excellent two-phase redox reaction between FePO₄ and LiFePO₄, as well as the typical electrochemical features of olivine-type LiFePO₄. The small voltage difference between the charge and discharge plateaus at about 0.04 V was representative of good kinetics, especially considering the poor electronic conductivity and low electrochemical diffusion rate of Li ions in a solid phase.

The cycle life of LiFePO₄/C composite synthesized from nanosized spherical FePO₄·2H₂O at the rates of 0.1C, 1C, and 5C was shown. After 50 cycles, the capacity retention obtained 99.1%, 98.7%, and 95.8%, respectively.

3.2.2. High and Low Temperature Performance. The fatal disadvantage of commercial LiFePO₄ is that it is poor at low temperature performance. The general low temperature was referred to −20°C. Over a voltage range of 2.0V to 3.65V, commercial LiFePO₄ had a capacity retention ratio of 60%~70% at 0.5C at −20°C by comparison with that of room temperature (25°C). Therefore, to resolve the problem plays an important role in industrialized application. The performance of LiFePO₄ can be characterized by 18650 battery with designed capacity of 1000 mAh. As illustrated in Figure 6, the high and low temperature performance of the LiFePO₄/C composite cathodes delivered the outstanding progress to the rate of 0.5C over a voltage range of 2.2 V to 3.6 V for 18650 battery. Meanwhile, it was found that the battery exhibited a discharge of 1028.3 mAh, 1010.9 mAh, 960.4 mAh, 892.9 mAh, and 801.5 mAh at 55°C, 25°C, 0°C, −10°C, and −20°C, respectively. Compared with discharge performance at room temperature (25°C), the capacity retention maintained 101.7%, 95.0%, 88.3%, and 79.3% at 55°C, 0°C, −10°C, and −20°C, respectively. Moreover, the high discharge voltage plateaus at various temperatures demonstrated the as-prepared sample to be the excellent material for industrialized application.

3.2.3. CV and EIS. Freshly deposited LiFePO₄/C composite has been examined by CV at a scan rate of 0.1 mV·s⁻¹, as shown in Figure 7. Figure 7(a) showed that the first CV curve of the LiFePO₄/C composite synthesized with nanosized spherical FePO₄·2H₂O was described. The voltage difference was 0.19 V. The voltage observed at 3.55 V in the anodic sweep and at 3.33 V in the cathodic sweep characterized
the extraction and insertion of Li⁺ in the LiFePO₄ olivine structure, respectively.

Meanwhile, as we can see from Figure 7(b), the electrochemical impedance of LiFePO₄/C synthesized from nanosized spherical FePO₄·H₂O was shown. The curve was formed by a depressed semicircle in the high- to middle-frequency region and a straight line in the low-frequency range. According to the literature [39], the depressed semicircle represented the charge-transfer reaction between the active materials and the electrolyte (Rct). From the result, Rct had the charge-transfer reaction resistance of 82 Ω, indicating the excellent electrical conductivity and Li-ion diffusion of LiFePO₄/C composites.

4. Conclusions
LiFePO₄/C composites were then prepared from nanosized spherical FePO₄·2H₂O, Li₃C₂O₄, aluminum oxide, titanium oxide, oxalic acid, and sucrose by binary sintering process. The EDS and EDX showed that Ti and Al were distributed in LiFePO₄/C uniformly. And the composites had good conductive carbon webs and delivered an initial discharge capacity of 161.7 mAh·g⁻¹ at a 0.1 C rate, 152.4 mAh·g⁻¹ at a 1 C rate, and 131.7 mAh·g⁻¹ at a 5 C rate. And the capacity retention obtained 99.1%, 98.7%, and 95.8%, respectively, after 50 cycles. Meanwhile, the high and low temperature performance is excellent for 18650 battery, exhibiting a discharge of 1028.3 mAh, 1010.9 mAh, 960.4 mAh, 892.9 mAh, and 801.5 mAh at 55°C, 25°C, 0°C, −10°C, and −20°C, respectively.

In summary, the as-prepared LiFePO₄/C materials had favorable properties for their commercial applications.

Conflict of Interests
The authors declare that there is no conflict of interests regarding the publication of this paper.

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References
[1] A. K. Padhi, K. S. Nanjundaswamy, and J. B. Goodenough, "Phospho-olivines as positive-electrode materials for rechargeable lithium batteries," Journal of the Electrochemical Society, vol. 144, no. 4, pp. 1188–1194, 1997.
[2] R. Dominko, J. M. Goupil, M. Bele et al., "Impact of LiFePO₄/C composites porosity on their electrochemical performance," Journal of the Electrochemical Society, vol. 152, no. 5, pp. A858–A863, 2005.
[3] B. F. Wang, Y. L. Qiu, and L. Yang, "Structural and electrochemical characterization of LiFePO₄ synthesized by an HEDP-based soft-chemistry route," Electrochemistry Communications, vol. 8, no. 11, pp. 1801–1805, 2006.
[4] K. Zaghib, A. Mauger, F. Gendron, and C. M. Julien, "Surface effects on the physical and electrochemical properties of thin LiFePO₄ particles," Chemistry of Materials, vol. 20, no. 2, pp. 462–469, 2008.
[5] M. Maccario, L. Croguennec, F. le Cras, and C. Delmas, "Electrochemical performances in temperature for a C-containing LiFePO₄ composite synthesized at high temperature," Journal of Power Sources, vol. 183, no. 1, pp. 411–417, 2008.
[6] Y. Huang, H. Ren, Z. Peng, and Y. Zhou, “Synthesis of LiFePO₄/carbon composite from nano-FePO₄ by a novel stearic acid assisted rheological phase method,” Electrochimica Acta, vol. 55, no. 1, pp. 311–315, 2009.
[7] F. Sauvage, E. Baudrin, L. Laffont, and J.-M. Tarascon, “Origin of electrochemical reactivity enhancement of post-annealed LiFePO₄ thin films: preparation of heterosite-type FePO₄,” Solid State Ionics, vol. 178, no. 1-2, pp. 145–152, 2007.
[8] L. N. Wang, Z. G. Zhang, and K. L. Zhang, “A simple, cheap soft synthesis routine for LiFePO4 using iron(III) raw material,” Journal of Power Sources, vol. 167, no. 1, pp. 200–205, 2007.

[9] S. Scaccia, M. Carewski, P. Wisniewski, and P. P. Prosini, “Origin of electrochemical reactivity enhancement of post-annealed LiFePO4 thin films: preparation of heterosite-type FePO4,” Solid State Ionics, vol. 178, no. 1-2, pp. 145–152, 2007.

[10] G. X. Wang, L. Yang, J. Z. Wang, S. Bewlay, and H. K. Liu, “An investigation of polypryrole-LiFePO4 composite cathode materials for lithium-ion batteries,” Electrochimica Acta, vol. 50, no. 24, pp. 4649–4654, 2005.

[11] A. Vadivel Murugan, T. Muraligand, and A. Manthiram, “Rapid microwave-solvothermal synthesis of phospho-olivine nanorods and their coating with a mixed conducting polymer for lithium ion batteries,” Electrochemistry Communications, vol. 10, no. 6, pp. 903–906, 2008.

[12] C. Delmas, M. Maccario, L. Croguennec, F. Le Cras, and F. Weill, “Lithium deintercalation in LiFePO4 nanoparticles via a domino-cascade model,” Nature Materials, vol. 7, no. 8, pp. 665–671, 2008.

[13] T. G. Xu, L. B. Wang, C. Li, and C. N. Ma, “Synthesis and properties of low cost LiFePO4/C cathode material for li-ion battery,” Acta Chimica Sinica, vol. 67, p. 2275, 2009.

[14] S. W. Oh, S.-T. Myung, S.-M. Oh et al., “Double carbon coating of LiFePO4 as high rate electrode for rechargeable lithium batteries,” Advanced Materials, vol. 22, no. 43, pp. 4842–4845, 2010.

[15] F.-Y. Kang, J. Ma, and B.-H. Li, “Effect of carbonaceous materials on the physical and electrochemical performance of a LiFePO4 cathode for lithium-ion batteries,” New Carbon Materials, vol. 26, no. 3, pp. 161–170, 2011.

[16] Y.-D. Li, S.-X. Zhao, C.-W. Nan, and B.-H. Li, “Electrochemical performance of SiO2-coated LiFePO4 cathode materials for lithium ion battery,” Journal of Alloys and Compounds, vol. 509, no. 3, pp. 957–960, 2011.

[17] J. Ma, B. Li, H. Du, C. Xu, and F. Kang, “The effect of vanadium on physicochemical and electrochemical performances of LiFePO4 cathode for lithium battery,” Journal of the Electrochemical Society, vol. 158, no. 1, pp. A26–A32, 2011.

[18] J. Ma, B. Li, H. Du, C. Xu, and F. Kang, “Effects of tin doping on physicochemical and electrochemical performances of LiFe1−xSnxPO4/C (0 ≤ x ≤ 0.07) composite cathode materials,” Electrochimica Acta, vol. 56, no. 21, pp. 7385–7391, 2011.

[19] S. Scaccia, M. Carewski, P. Wisniewski, and P. P. Prosini, “Morphological investigation of sub-micron FePO4 and LiFePO4 particles for rechargeable lithium batteries,” Materials Research Bulletin, vol. 38, no. 7, pp. 1155–1163, 2003.

[20] S. Okada, T. Yamamoto, Y. Okazaki, J.-I. Yamaki, M. Tokunaga, and T. Nishida, “Cathode properties of amorphous and crystalline FePO4,” Journal of Power Sources, vol. 146, no. 1-2, pp. 570–574, 2005.

[21] F. Sauvage, E. Baudrin, L. Laffont, and J.-M. Tarascon, “Origin of electrochemical reactivity enhancement of post-annealed LiFePO4 thin films: preparation of heterosite-type FePO4,” Solid State Ionics, vol. 178, no. 1-2, pp. 145–152, 2007.

[22] Z. C. Shi, A. Attia, W. L. Ye, Q. Wang, Y. X. Li, and Y. Yang, “Synthesis, characterization and electrochemical performance of mesoporous FePO4 as cathode material for rechargeable lithium batteries,” Electrochimica Acta, vol. 53, no. 6, pp. 2665–2673, 2008.

[23] P. P. Prosini, D. Zane, and M. Pasquali, “Improved electrochemical performance of a LiFePO4-based composite cathode,” Electrochimica Acta, vol. 46, no. 23, pp. 3517–3523, 2001.

[24] H. Okawa, J. Yabuki, Y. Kawamura, I. Arise, and M. Sato, “Synthesis of FePO4 cathode material for lithium ion batteries by a sonochemical method,” Materials Research Bulletin, vol. 43, no. 5, pp. 1203–1208, 2008.

[25] Y. Xu, Y. Lu, P. Yin, L. Yan, Z. Yang, and R. Yang, “A versatile method for preparing FePO4 and study on its electrode performance in lithium ion batteries,” Journal of Materials Processing Technology, vol. 204, no. 1–3, pp. 513–519, 2008.

[26] G. R. Hu, Y. L. Zhou, Z. D. Peng, and X. G. Gao, “Preparation and performance of FePO4 precursor for LiFePO4,” Battery Bimonthly, vol. 37, no. 5, pp. 339–341, 2007 (Chinese).

[27] G. Arnold, J. Garche, R. Hemmer, S. Stroèbele, C. Vogler, and M. Wohlfahrt-Mehrens, “Fine-particle lithium iron phosphate LiFePO4 synthesized by a new low-cost aqueous precipitation technique,” Journal of Power Sources, vol. 119–121, pp. 247–251, 2003.

[28] Z. X. Wang, L. Wu, X. H. Li et al., “Preparation of precursor and performance of LiFePO4,” Journal of Functional Materials, vol. 39, p. 614, 2008 (Chinese).

[29] G. Arnold, J. Garche, R. Hemmer, S. Stroèbele, C. Vogler, and M. Wohlfahrt-Mehrens, “Fine-particle lithium iron phosphate LiFePO4 synthesized by a new low-cost aqueous precipitation technique,” Journal of Power Sources, vol. 119–121, pp. 247–251, 2003.

[30] K. Zaghib and C. M. Julien, “Structure and electrochemistry of FePO4·2H2O hydrate,” Journal of Power Sources, vol. 142, no. 1-2, pp. 279–284, 2005.

[31] S. Yang, Y. Song, P. Y. Zavalij, and M. S. Whittingha, “Hydrothermal synthesis of lithium iron phosphate cathodes,” Electrochemistry Communications, vol. 3, no. 9, pp. 505–508, 2001.

[32] H. Gong, Y. Yu, T. Li et al., “Solvothermal synthesis of LiFePO4/C nanopolyhedrons and microellipsoids and their performance in lithium-ion batteries,” Materials Letters, vol. 66, no. 1, pp. 374–376, 2012.

[33] Y. Huang, H. Ren, Z. Peng, and Y. Zhou, “Synthesis of LiFePO4/C carbon composite from nano-FepO by a novel stearic acid assisted rheological phase method,” Electrochimica Acta, vol. 55, no. 1, pp. 311–315, 2009.

[34] Y. Huang, H. Ren, S. Yin, Y. Wang, Z. Peng, and Y. Zhou, “Synthesis of LiFePO4/C composite with high-rate performance by starch sol assisted rheological phase method,” Journal of Power Sources, vol. 185, no. 2, pp. 610–613, 2010.

[35] J. Lee and A. S. Teja, “Synthesis of LiFePO4 micro and nanoparticles in supercritical water,” Materials Letters, vol. 60, no. 17–18, pp. 2105–2109, 2006.

[36] C. Xu, J. Lee, and A. S. Teja, “Continuous hydrothermal synthesis of lithium iron phosphate particles in subcritical and supercritical water,” Journal of Supercritical Fluids, vol. 44, no. 1, pp. 92–97, 2008.

[37] W. Yu, Y. Zhao, and Q. Rao, “Rapid and continuous production of LiFePO4/C nanoparticles in super heated water,” Chinese Journal of Chemical Engineering, vol. 17, no. 1, pp. 171–174, 2009.

[38] Z.-Y. Chen, H.-L. Zhu, S. Ji, R. Fakir, and V. Linkov, “Influence of carbon sources on electrochemical performances of LiFePO4/C composites,” Solid State Ionics, vol. 179, no. 27–32, pp. 1810–1815, 2008.

[39] Z. G. Lu, M. F. Lo, and C. Y. Chung, “Pulse laser deposition and electrochemical characterization of LiFePO4–C composite thin films,” The Journal of Physical Chemistry C, vol. 112, no. 17, pp. 7069–7078, 2008.