

Synthesis of LiFePO_4 *in situ* vapor-grown carbon fiber (VGCF) composite cathode material via microwave pyrolysis chemical vapor deposition

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One of the most important factors that limits the use of LiFePO_4 as cathode material for lithium ion batteries is its low electronic conductivity. In order to solve this problem, LiFePO_4 *in situ* vapor-grown carbon fiber (VGCF) composite cathode material has been prepared in a single step through microwave pyrolysis chemical vapor deposition. The phase, microstructure, and electrochemical performance of the composites were investigated. Compared with the cathodes without *in situ* VGCF, the initial discharge capacity of the composite electrode increases from 109 to 144 mA h g^{-1} at a 0.5-C rate, and the total electric resistance decreases from 538 to 66 Ω . The possible reasons for these effects are proposed.

vapor-grown carbon fiber, LiFePO_4 , microwave, chemical vapor deposition, lithium ion batteries

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LiFePO_4 (LFP) can be used as cathode material for lithium ion batteries [1]. It has a relatively large theoretical capacity of 170 mA h g^{-1} , good thermal stability in fully charged states and exhibits little hygroscopic behavior. In addition, this material is inexpensive, nontoxic, and environmentally benign [2,3]. However, the electronic conductivity of pure LFP (10^{-10} to 10^{-9} S cm^{-1} [4]) is several orders of magnitude lower than that of other important cathode materials ($\sim 10^{-3}$ S cm^{-1} for LiCoO_2 [5] or 10^{-4} S cm^{-1} for LiMn_2O_4 [6]). Therefore, lattice doping [4] or surface coating methods [7–10] have been attempted to overcome this weakness.

Vapor-grown carbon fiber (VGCF) has been reported as ideal conductive filler in electrodes, because of their excellent mechanical properties and high electrical and thermal conductivity [11–13]. The first discharge capacity of VGCF enhanced LFP composites was more than two times of those without VGCF [14]. Nevertheless, ball milling, the most widely used

method to introduce conductive additives in the mixing process, could inevitably damage their initial structure and increase the contact resistance between additives [14–16].

Higuchi et al. were the first to apply microwave in the preparation of LFP [17]. Microwave can ensure uniform and fast heating through a self-heating process based on direct microwave energy absorption by the materials [18]. Microwave pyrolysis chemical vapor deposition (MCVD) has ever been used to obtain VGCF in our previous work [19]. In this paper, MCVD technology was developed to synthesize *in situ* network-like VGCF-improved LFP cathode with enhanced electronic conductivity.

1 Experimental

1.1 Synthesis

$\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$, and $\text{LiOH} \cdot \text{H}_2\text{O}$ in a 1 : 1 : 1 molar

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ratio were dispersed into 75 wt% (compared to the raw materials) alcohol, and then 5.4 wt% carbon black (SuperP Erachem, Maryland, USA) was added to the mixture. The mixture was mixed with a ball mill at 300 r min^{-1} for 6 h. After being dried under vacuum at 120°C for 12 h, the samples were placed in a home-made quartz reactor installed in the MCVD equipment [20] (Figure 1). After the chamber was with argon, the MCVD equipment was operated at 2.45 GHz, with an output power of 800 W. One kind of samples, designated as “VC/LFP”, was prepared at a temperature range of $550\text{--}800^\circ\text{C}$. When the temperature reached the setting value, the quartz reactor was exposed to a propylene flow of 90 sccm for 10 min, and then the MCVD equipment was closed. For comparison, another test sample, “C/LFP”, was also obtained at the same conditions, but there was no propylene used in the synthesis process.

1.2 Characterization

X-ray powder diffraction (XRD, D8 ADVANCE, Bruker AXS) with $\text{Cu K}\alpha$ radiation was used to identify the phases. An integrated Raman spectroscopy system (inVia Reflex, Renishaw) was used to analyze the structure and composition. The excitation wavelength was supplied by an internal Ar (514.5 nm) 20 mW laser. A field emission scanning electron microscope (FESEM, S-4800, HITACHI) and energy dispersive X-ray spectroscopy (EDS, EDAX, New Jersey, USA) were used to analyze the morphology and elementary components, respectively.

1.3 Electrochemical properties

The cathodes containing 95 wt% active materials and 5 wt% polyvinylidene fluoride (PVDF) were prepared by spreading a slurry in N-methylpyrrolidone (NMP) onto aluminum foil current collectors and allowing them to dry. 2032-size coin cells were assembled in an argon-filled glove box, using lithium as a counter electrode and 1 M LiPF_6 in 1:2 ethylene carbonate/dimethyl carbonate (EC/DMC) as the electrolyte

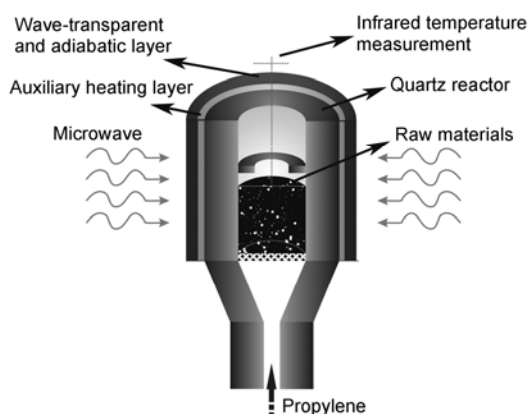


Figure 1 Sketch of the MCVD reactor.

solution. Charge–discharge tests were performed using an Arbin Instruments’ BT2000 (Texas, USA) at 25°C . Electron impedance spectroscopy (EIS) was measured with a frequency response analyzer (Solatron 1260, California, USA) interfaced with a potentiogalvanostat (Solatron 1287).

2 Results and discussion

The XRD spectrum shown in Figure 2(a) of VC/LFP can be attributed to a major phase of orthorhombic LFP (JCPDS: 83-2092) and a minor phase of rhombohedral graphite-3R (JCPDS: 26-1079), except for several weak diffraction peaks of orthorhombic Li_3PO_4 (JCPDS: 15-0760). The mean crystallite size of LFP is $\sim 72 \text{ nm}$, which was calculated from the widths of the major diffraction peaks of (200), (101), and (311) using Scherrer’s formula. The diffraction peaks of graphite result from the carbon black mixed in the raw materials. The phase content of LFP, C, and Li_3PO_4 , are calculated using the semiquantitative method of relative intensity to a reference and are $\sim 84 \text{ wt}\%$, $\sim 14.5 \text{ wt}\%$, and $\sim 1.5 \text{ wt}\%$, respectively. The Raman spectra of the VC/LFP and carbon black used in the raw materials are shown in Figure 2(b) and (c). The bands at $500\text{--}100 \text{ cm}^{-1}$ and $1120\text{--}520 \text{ cm}^{-1}$ correspond to the Raman vibrations of Fe–O and PO_4^{3-} in LFP, respectively [21], but

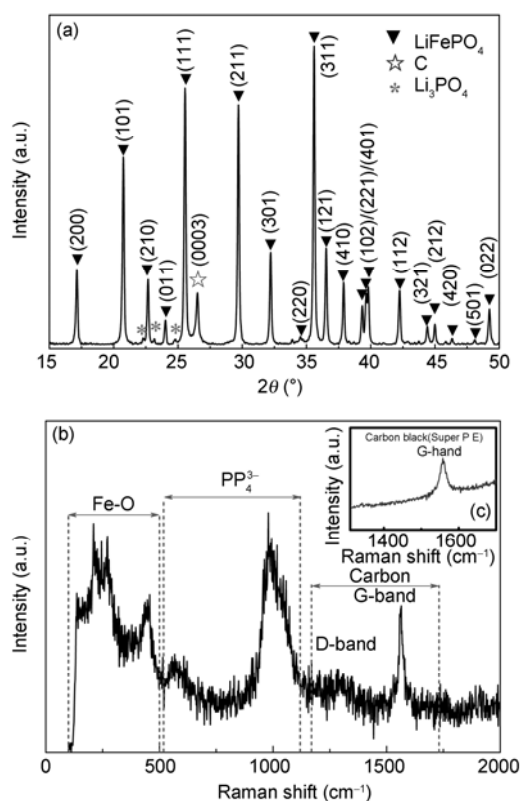


Figure 2 (a) XRD spectrum and (b) Raman spectrum of VC/LFP synthesized via MCVD at 650°C ; (c) Raman spectrum of the carbon black used as a raw material.

the bands in the range of 1460–1170 cm^{-1} and 1730–1470 cm^{-1} can be assigned to the D-band (disorder-induced phonon mode) and G-band (graphite band) of carbon, respectively. Compared with the Raman spectrum of the pure carbon black used as a raw material, the ratio of the D/G integrated peak intensities much greater.

The typical FESEM morphology shown in Figure 3(a) and EDS analyses (not shown here) of the VC/LFP indicate that the VC/LFP is composed of sphere-like LFP, flaky graphite, and network-like fibers. From Figure 3(b), it can be seen that most VGCF grows on the surface of the graphite particles, and from further magnified image shown

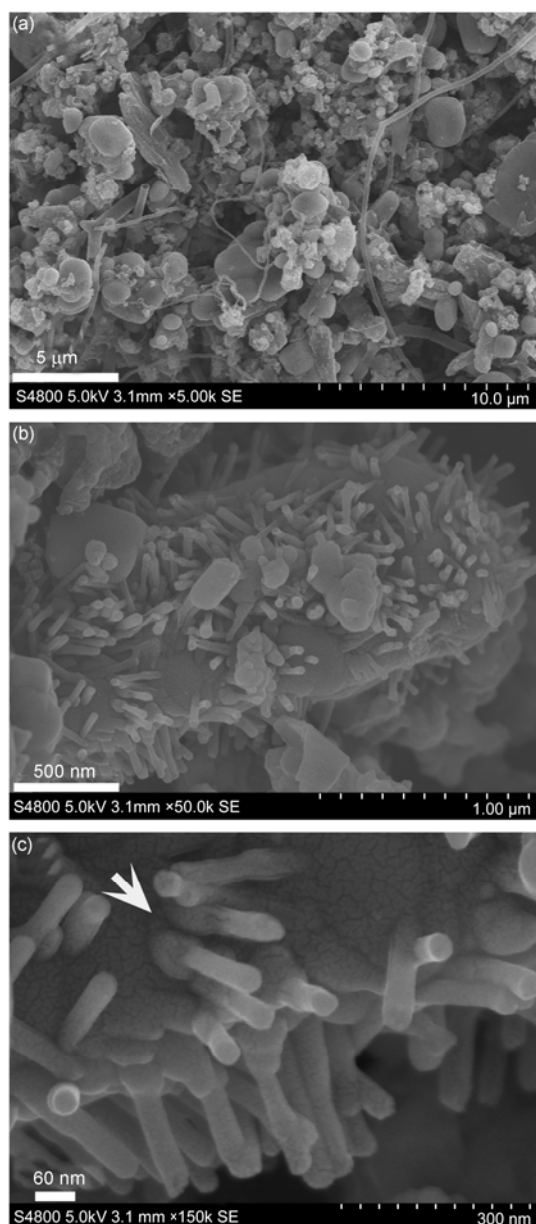


Figure 3 (a) FESEM image of VC/LFP synthesized via MCVD at 700°C; (b) the FESEM morphology of VGCF observed on the surface of graphite particles in VC/LFP obtained via MCVD at 600°C; (c) higher magnification.

in Figure 3(c), an *in situ* growth mode can be seen. The *in situ* formation of VGCF can be attributed to the pyrolysis and deposition of propylene under the effects of microwave heating and/or the self-catalytic action of the raw materials (e.g. $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$). In addition, the turbostratic graphite formed near the surface of the VGCF [13] may give some clues to the proper interpretation of the weak D-band in the Raman spectrum (see Figure 2(b)).

The electrochemical performance of the VC/LFP cathodes, which is shown in Figure 4, is better than that of C/LFP cathodes. The initial discharge capacity of the VC/LFP cathodes are 148 mA h g^{-1} and 144 mA h g^{-1} at a 0.1-C rate and a 0.5-C rate, respectively, which are slightly better than those of some other materials [14]. Furthermore, the cycling capacity fading in VC/LFP cathodes is negligible.

The impedance spectra of C/LFP and VC/LFP cathodes, which are shown in Figure 5, are both combinations of a depressed semicircle at high frequencies and a straight line at low frequencies. In the high-frequency region, the intercepts with the real impedance [Z'_{re}] axis, which correspond to electron jumping, vary from 538 to 66 Ω . The decrease in total electric resistance could be ascribed to the *in situ* formation of VGCF networks in the cathodes. In the low-frequency area, the slope of the impedance of VC/LFP is greater than that of C/LFP, indicating that the network-like VGCF improves the electrochemical activity of LFP effectively.

3 Conclusions

In situ network-like VGCF-improved LiFePO_4 composite cathode material for lithium ion batteries has been synthesized using a MCVD method in the temperature range between 550°C and 800°C. As a result of the *in situ* growth mode of the network-like VGCF formed on the graphite particles, the composite cathodes show satisfactory rate behavior

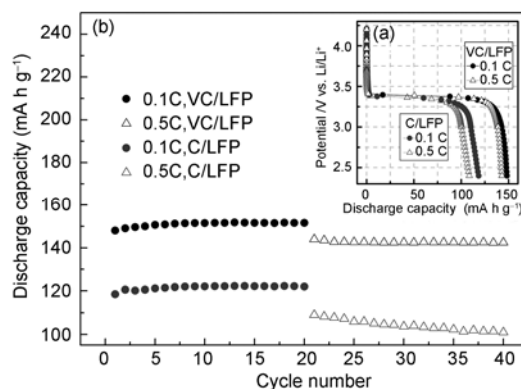


Figure 4 (a) Discharge curves and (b) cycling performance of VC/LFP and C/LFP (both obtained via MCVD at 650°C). The cathode's performance was measured at different rates at 25°C.

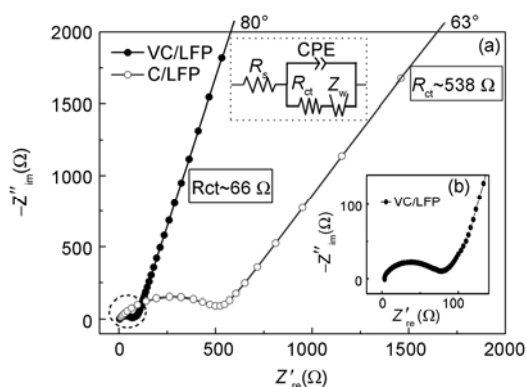


Figure 5 (a) EIS traces for VC/LFP and C/LFP (both obtained via MCVD at 650°C) composite cathodes and (b) enlarged EIS trace for VC/LFP of the elliptic dashed zone shown in (a); the symbols R_s , R_{ct} , Z_w , and CPE denote the solution resistance, the charge-transfer resistance, the Warburg impedance, and the constant phase angle element, respectively.

and cycling life. This study shows that it is possible to synthesize high-performance VGCF-improved LiFePO_4 cathode material through a simple low-cost high-efficiency process.

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- 1 Padhi A K, Najundaswamy K S, Goodenough J B. Phospho-olivines as positive-electrode materials for rechargeable lithium batteries. *J Electrochem Soc*, 1997, 144: 1188–1194
- 2 Padhi A K, Najundaswamy K S, Masquelier C, et al. Effect of structure on the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple in iron phosphates. *J Electrochem Soc*, 1997, 144: 1609–1613
- 3 Padhi A K, Najundaswamy K S, Masquelier C, et al. Mapping of transition metal redox energies in phosphates with NASICON structure by lithium intercalation. *J Electrochem Soc*, 1997, 144: 2581–2586
- 4 Chung S Y, Bloking J T, Chiang Y M. Electronically conductive phospho-olivines as lithium storage electrodes. *Nat Mater*, 2002, 1: 123–128
- 5 Molenda J, Stoklosa A, Bak T. Modifications in the electronic structure of cobalt bronze Li_xCoO_2 and the resulting electrochemical properties. *Solid State Ionics*, 1989, 36: 53–58
- 6 Guan J, Liu M. Transport properties of LiMn_2O_4 electrode materials

for lithium-ion batteries. *Solid State Ionics* 1998, 110: 21–28

- 7 Huang H, Yin S C, Nazar L F. Approaching theoretical capacity of LiFePO_4 at room temperature at high rates. *Electrochem Solid-State Lett*, 2001, 4: A170–A172
- 8 Ravet N, Goodenough J B, Besner S, et al. Improved iron based cathode material. In: 196th Meeting Abstract of the Electrochemical Society, 1999, Oct 17–22, Hawaii. Meeting Abstracts, 1999. 127
- 9 Belharouak I, Johnson C, Amine K. Synthesis and electrochemical analysis of vapor-deposited carbon-coated LiFePO_4 . *Electrochem Commun*, 2005, 7: 983–988
- 10 Croce F, Epifanio A D, Hassoun J, et al. A novel concept for the synthesis of an improved LiFePO_4 lithium battery cathode. *Electrochem Solid-State Lett*, 2002, 5: A47–A50
- 11 Tatsumi K, Zaghbi K, Sawada Y, et al. Anode performance of vapor-grown carbon fibers in secondary lithium-ion batteries. *J Electrochem Soc*, 1995, 142: 1090–1096
- 12 Endo M, Nishimura Y, Takahashi T, et al. Lithium storage behavior for various kinds of carbon anodes in ion secondary battery. *J Phys Chem Solids*, 1996, 57: 725–728
- 13 Endo M, Kim Y A, Hayashi T, et al. Vapor-grown carbon fibers basic properties and their battery applications. *Carbon*, 2001, 39: 1287–1297
- 14 Chen C C, Liu M H, Chen J M. Influence of addition of VGCF on LiFePO_4 cathode materials in Li-ion batteries. In: 206th Meeting of the Electrochemical Society, 2004, Oct 3–8, Hawaii. Meeting Abstracts, 2004. 413
- 15 Li X L, Kang F Y, Bai X D, et al. A novel network composite cathode of LiFePO_4 /multiwalled carbon nanotubes with high rate capability for lithium ion batteries. *Electrochem Commun*, 2007, 9: 663–666
- 16 Jin B, Jin E M, Park K H, et al. Electrochemical properties of LiFePO_4 -multiwalled carbon nanotubes composite cathode materials for lithium polymer battery. *Electrochem Commun*, 2008, 10: 1537–1540
- 17 Higuchi M, Katayama K, Azuma Y, et al. Synthesis of LiFePO_4 cathode material by microwave processing. *J Power Sources*, 2003, 119–121: 258–261
- 18 Park K S, Son J T, Chung H T, et al. Synthesis of LiFePO_4 by co-precipitation and microwave heating. *Electrochem Commun*, 2003, 5: 839–842
- 19 Zou J Z, Zeng X R, Xiong X B, et al. Preparation of vapor grown carbon fibers by microwave pyrolysis chemical vapor deposition. *Carbon*, 2007, 45: 828–832
- 20 Zeng X R, Deng F, Zou J Z, et al. Preparation of carbon-coated LiFePO_4 by microwave heating method. PRC Patent, CN101714634A, 2010-05-26
- 21 Burba C M, Frech R. Raman and FTIR spectroscopic study of Li_xFePO_4 ($0 \leq x \leq 1$). *J Electrochem Soc*, 2004, 151: A1032–A1038

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