Design and Synthesis of In-situ VGCFs Improved LiFePO$_4$ Composite Cathode Materials

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Abstract: *One of the most important factors which currently limit the application of LiFePO$_4$ cathode material in lithium-ion batteries is its low electronic conductivity. In order to enhance the electronic conductivity of LiFePO$_4$ cathode material, in situ vapor-grown carbon fibers (VGCFs) improved LiFePO$_4$ composite cathode materials were designed and synthesized in one step by microwave pyrolysis chemical vapor deposition (MCVD). The phase, microstructure and electrochemical performances of the composite cathode materials were investigated. Results show that network-like VGCFs formed during the MCVD process generally grow with an in situ growth mode on the graphite particles, which is extremely beneficial to improve the electronic conductivity of the composite cathode materials. The initial discharge capacity of the composite cathode materials, compared with the cathodes without in situ network-like VGCFs, increases from 109 mAhg^{-1} to 144 mAhg^{-1} at 0.5C rate, and the total electric resistance corresponding to the electron jumping varies from 538 Ω to 66 Ω.*

1. INTRODUCTION

The rechargeable lithium-ion cell is an advanced energy storage system. However, high cost, safety hazards, and chemical instability prohibit its use in large-scale applications. An alternative cathode material, LiFePO$_4$ (LFP)[1-3], solves these problems, but has a poor electronic conductivity (10^{-10} to 10^{-9} Scm^{-1}[4]) which is by several orders of magnitude lower than that of other important cathode materials (~10^{-3} Scm^{-1} for LiCoO$_2$[5] or 10^{-4} Scm^{-1} for LiMn$_2$O$_4$[6]). Therefore, lattice doping or surface coating methods have been conducted to overcome the weakness[4, 7-10].

Vapor-grown carbon fibers (VGCFs) have been reported as ideal conductive filler in electrodes because of their excellent mechanical properties, high electrical and thermal conductivity[11-13]. The first discharge capacity of VGCFs enhanced LFP composites was more than 2 times of those without VGCFs[14]. Nevertheless, ball milling, as the most selected way to introduce conductive additives in the mixing process, could inevitably damage their initial structure and increase the contact resistance between additives to some extent[14-16].

Higuchi et al. were the first to apply microwave in the preparation of LFP[17]. Microwave could 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 VGCFs in our previous work[19]. In this paper, a novel design of in situ network-like VGCFs for LiFePO$_4$ cathode material was achieved by MCVD process in order to improve its electrochemical performance.

2. EXPERIMENTAL

FeC$_2$O$_4$·2H$_2$O, NH$_4$H$_2$PO$_4$, and LiOH·H$_2$O with mole ratio 1:1:1 were dispersed into 75 wt% (compared to the raw materials) alcohol, and then 3.5wt% carbon black (SuperP Erachem) and 5.5 wt% table sugar were added into it. The mixture was mixed by ball-milling in a Spex-8000 ball at 300 rpm for 6h. After dried under vacuum at 120°C for 12h, the samples were placed in a home-made quartz reactor installed in the MCVD equipment[19-20]. After filled with argon, the equipment was set at a microwave output power of 800W. One kind of samples, designated as "VC/LFP", was prepared at a temperature range of 550-800 °C. When the temperature reached the setting value, propylene with a flow of 90 sccm was put into the quartz reactor for 10min, and then the MCVD equipment was closed. For comparison, another

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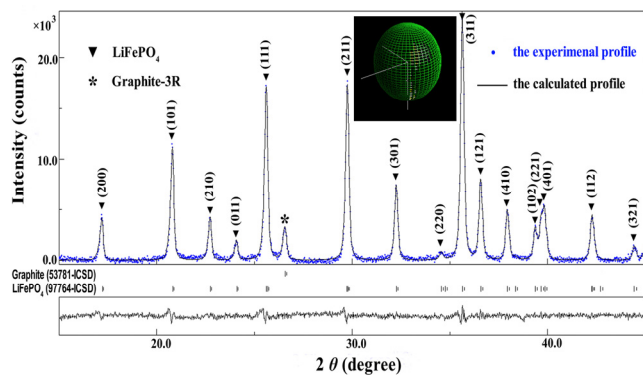Phone: +86 755 26557459; Fax: +86 755 26536239

Figure 1. Rietveld refinement of VC/LFP synthesized by MCVD at 600 °C. The experimental profile (dotted line), the calculated profile (solid line) and the difference between the observed and calculated profile (at the bottom) are shown. The inset corresponds to the simulated model of the LFP crystallites given by the MAUD program

kind of samples, designated as "C/LFP", was also obtained at the same conditions except that no propylene participated in the synthetic process.

The X-ray powder diffraction (XRD, D8 ADVANCE, Bruker AXS) with Cu K_α radiation was used to identify the phases. The X-ray diffraction data were analyzed by Rietveld refinement using the program MAUD. Field emission scanning electron microscope (FESEM, S-4800, HITACHI) and energy dispersive X-ray spectroscopy (EDS, EDAX) were used to analyze the morphology and elementary component, respectively.

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) electrolyte solution. The electronic conductivities of the samples were measured by a four-point probe method. Charge/discharge tests were performed using an Arbin Instrument (BT2000) at 25 °C. Electron impedance spectroscopy (EIS) was measured with a frequency response analyzer (Solatron 1260) interfaced with a potentio-galvanostat (Solatron 1287).

3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD diffraction pattern and the fitting result by Rietveld refinement using MAUD program (R_{wp}=1.03%). The XRD spectrum of VC/LFP prepared by MCVD at 600 °Ccan be indexed to orthorhombic LFP (JCPDS: 83-2092) and rhombohedral graphite-3R (JCPDS: 26-1079). The diffraction peaks of graphite are mainly resulted from the carbon black mixed in the raw materials. The Rietveld refinement gives a LFP to graphite-3R weight-ratio of 87:13. In addition, the shape of the LFP crystallite could be simulated to a sphere (inset in Fig. 1) by MAUD program according to the theory by Popa[21]. The diameter of the spherical LFP crystallites is ~65nm after Rietveld refinement, which approximates to ~70nm calculated from the widths of the major diffraction
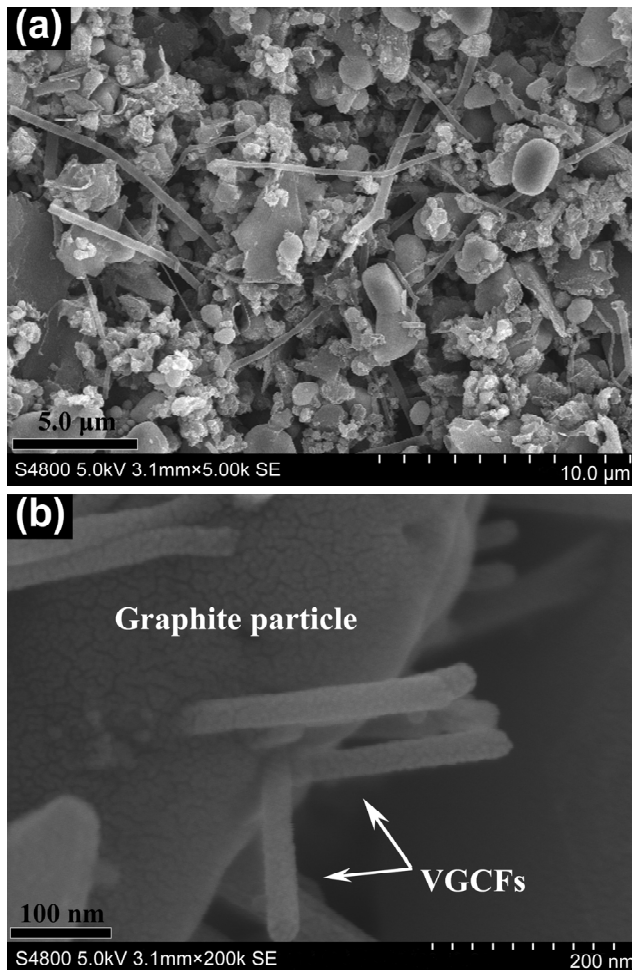

Figure 2. (a) Typical FESEM image of VC/LFP synthesized by MCVD at 700 °C, (b) VGCFs observed on the surface of graphite particles with an in situ growth mode in VC/LFP obtained by MCVD at 600 °C

peaks of (200), (101), and (311) by Scherrer's formula.

The typical FESEM morphology shown in Fig. 2a and EDS analyses (not shown here) indicate that VC/LFP is composed of sphere-like LFP, flaky graphite, and network-like VGCFs. It's important to note that VGCFs generally grow on the surface of graphite particles with an in situ growth mode (Fig. 2b), which could bridge the gap between LFP crystallites and graphite particles (Fig. 2c). The in situ formation of VGCFs may be attributed to the pyrolysis and deposition of propylene under special effect of microwave heating and/or the self-catalytic action of something (e.g. $FeC_2O_4 \cdot 2H_2O$) in the raw materials. This kind of network-like morphology formed by MCVD process, which is described visually with a schematic drawing shown in Fig. 2d, can provide pathway for the electron transference. Therefore, the electronic conductivity of VC/LFP is improved from 1.86×10^{-1} Scm^{-1} for C/LFP to 2.26×10^2 Scm^{-1} (samples were obtained at 650 °C and measured by a four-point probe method at 25 °C).
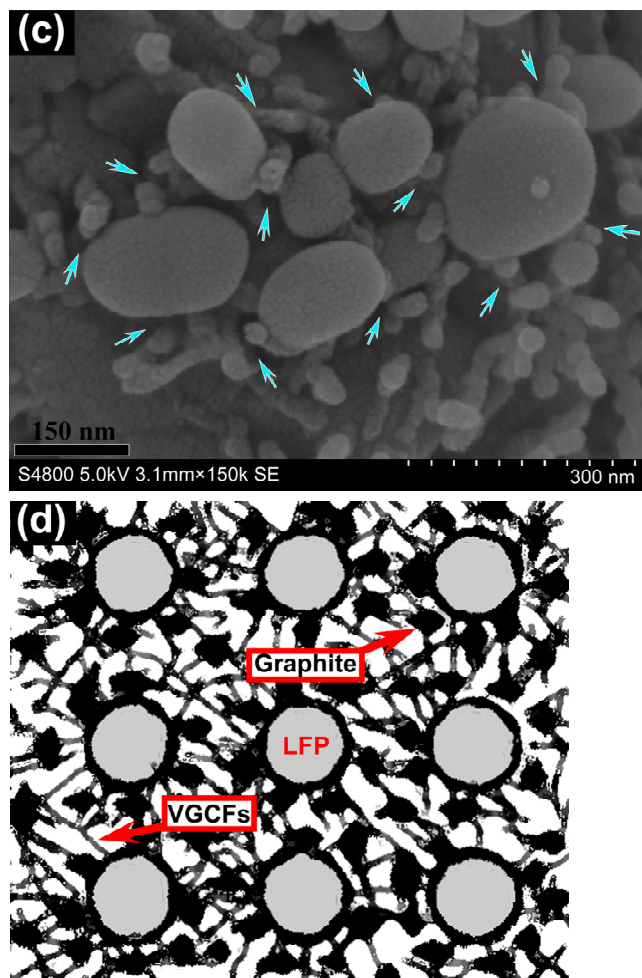
Figure 2. (c) Bridge action of VGCFs between LFP crystallites and graphite particles, (d) morphological schematic drawing of the composite cathode materials prepared by MCVD
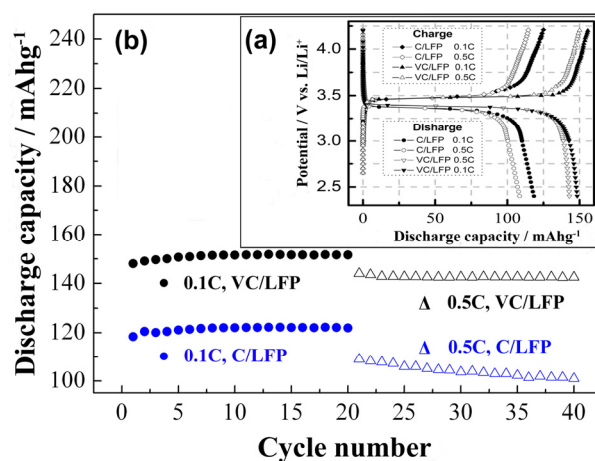

Figure 3. (a) Charge/discharge curves and (b) cycling performance of VC/LFP and C/LFP (both obtained by MCVD at 650 °C) cathodes measured with different rates at 25 °C
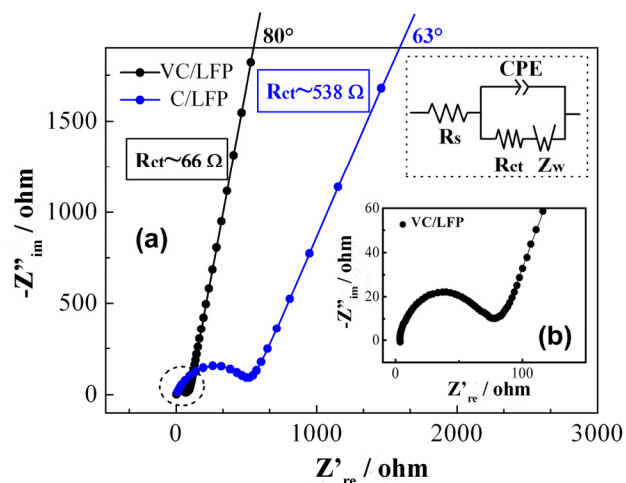

Figure 4. (a) EIS of VC/LFP and C/LFP (both obtained by MCVD at 650 °C) cathodes and (b) partial enlarged EIS of VC/LFP sketched by the elliptic dashed zone shown in (a). The symbols R_s, R_{ct}, Z_w, and CPE, denote the solution resistance, the charge-transfer resistance, the Warburg impedance, and the constant phase angle element, respectively

Fig. 3 shows the charge/discharge curves and cycling performances of the composite cathode materials. At 0.1C rate and 0.5C rate, the initial discharge capacities of VC/LFP obtained by MCVD at 650 °C are 148 mAhg⁻¹ and 144 mAhg⁻¹, respectively, which are slightly better than those of some others [14]. Furthermore, the capacity fading on cycling VC/LFP is surprisingly negligible after 20 cycles. However, the discharge capacity of C/LFP at 0.5C rate after 1 cycle is only 109 mAhg⁻¹ and then lost ~7.4% after 20 cycles. In conclusion, compared to C/LFP, the VC/LFP composite cathode material shows much better electrochemical performance in relation to rate behavior and cycling life.

The impedance spectra of C/LFP and VC/LFP composite electrodes are both combinations of a depressed semicircle in high frequencies and a straight line in low frequencies (Fig. 4). The calculated values resulted from the equivalent circuit shown in the rectangular dashed inset, fit well to the measured values. In the high-frequency region, the intercepts with the real impedance [Z'_{re}] axis of C/LFP and VC/LFP corresponding to the electron jumping vary from 538 Ω to 66 Ω. The decrease of total electric resistance

could have attributed to the in situ formation of network-like VGCFs in the prepared materials. In the low-frequency area, the slope of the impedance of VC/LFP is bigger than that of C/LFP, indicating that VGCFs improve the electrochemical activity of the LFP effectively.

4. CONCLUSIONS

In situ network-like VGCFs improved LiFePO₄ composite cathode materials were designed and synthesized by a novel MCVD method in the temperature range between 550 °C and 800 °C. Compared with C/LFP, the VC/LFP composite cathode materials show much better electrochemical performances in relation to rate behavior and cycling life because of the in situ formation of network-like

VGCFs which could provide a three-dimensional pathway for electron transfer. This study makes it possible to obtain excellent performance of VGCFs enhanced LiFePO$_4$ cathode materials by a simple process with high efficiency and low cost.

5. ACKNOWLEDGEMENTS

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