

Research Article

Electrode Composite LiFePO_4 @Carbon: Structure and Electrochemical Performances

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This work aimed at preparing the electrode composite LiFePO_4 @carbon by hydrothermal and the calcination process was conducted at 600, 700, and 800°C. The structure and morphology were determined by X-ray diffraction (XRD), SEM, Raman spectroscopy, X-ray photon spectroscopy (XPS), and thermal analysis. The XRD refinement's results point out the orthorhombic structure without impurity phase and the high crystalline of synthesized olivines. The results of Raman spectroscopy and XPS confirmed the pure olivine phase as well as the successful carbon coating on the surface of olivines' powders. Moreover, the calcinated temperature affected the morphology as well as the electrochemical performance of synthesized olivines. The electrochemical measurements were conducted by cyclic voltammetry and galvanostatic cycling test. The diffusion coefficients were calculated from cyclic voltammetry curves and reached $1.09 \times 10^{-12} \text{ cm}^2/\text{s}$ for LFP600, $2.28 \times 10^{-11} \text{ cm}^2/\text{s}$ for LFP700, and $3.27 \times 10^{-12} \text{ cm}^2/\text{s}$ for LFP800. The cycling test at rate C/10 exhibited an excellent cyclability with discharge capacity of 145 mAh/g for LFP600, 170 mAh/g for LFP700, and 160 mAh/g for LFP800.

1. Introduction

The pioneer work of Padhi et al. [1] launched the reversible Li insertion into the olivine phase LiFePO_4 with a delivered capacity of 120 mAh/g. Thenceforth, the olivine has been paid attention in the context of cathode materials for lithium-ion batteries (LIBs) because of their advantages in regard to economy (low toxicity, low cost, and high safety) as well as electrochemical performance (excellent cyclability and high-rate capability) [2]. The olivine structure consists of a distorted hexagonal-close-packed oxygen framework; the Fe^{2+} ions form the octahedrons $[\text{FeO}_6]$ with six

surrounded oxygens and the P^{5+} ions form the tetrahedrons with four surrounded oxygens. The octahedrons $[\text{FeO}_6]$ connect by the corner-sharing along b-axis and link with the tetrahedrons by the edge-sharing forming the 1-D channels where Li diffusion pathway is along plan (010). The strong covalency P–O in polyanion PO_4^{3-} unit steadies the olivine structure during Li-migration and lowers the Fermi level of the redox couple $\text{Fe}^{3+}/\text{Fe}^{2+}$ through the Fe–O–P inductive effect that results the discharge voltage 3.45 V (vs. Li^+/Li) for LiFePO_4 [3–7].

However, many researches have pointed out that the drawbacks are hindered by low electronic conductivity and

TABLE 1: Summary of composite electrode LiFePO_4 @carbon prepared by hydrothermal method.

Authors	Hydrothermal condition	Grain's size	Temperature pyrolysis	Capacity
Brochu et al. [13]	185°C for 2 hours	240 nm thick and 1 μm length	650°C for 2 hours in argon	160 mAh/g at rate C/10
Chen et al. [14]	200°C for 6 hours	2–3 μm	600°C for 2 hours in argon	150 mAh/g at rate C/10
Lim et al. [15]	240°C from 2 to 36 hours	300–600 nm		180 mAh/g (50 cycles) at rate C/10
Jiang et al. [16]	180°C for 2 hours		700°C for 6 hours in argon	160 mAh/g (100 cycles) at rate C/10
Zhan et al. [17]	180°C for 12 hours	2–3 μm	550°C for 4 hours in argon	150 mAh/g (50 cycles) at rate C/5

sluggish Li transportation; therefore, the bulk LiFePO_4 electrode usually shows poor capacity retention during cycling test at both of monorate capability and high-rate capability [8–12]. To overcome these drawbacks, the strategies have been considered commonly as designing the nanostructure and coating carbon. We summarized in Table 1 the highlighted results of composite electrode LiFePO_4 @carbon prepared by hydrothermal method.

In this work, we prepared the electrode composite LiFePO_4 @carbon based on hydrothermal route and pyrolysis process at different temperature at 600, 700, and 800°C. The glucose as carbon coating source was added at the beginning of hydrothermal reaction. The electrochemical performances of LiFePO_4 @carbon were related to crystalline, carbon content as well as quality, and electronic-ionic conductivity which were characterized by powder X-ray diffraction, Raman spectroscopy, and cyclic voltammetry.

2. Experimental

2.1. Material Preparation. The composite electrode LiFePO_4 @carbon were synthesized by hydrothermal route. The 2.600 g $\text{LiOH}\cdot\text{H}_2\text{O}$ (99.9%, Sigma-Aldrich) was dissolved in 20.0 mL distilled water. The 5.0 mL H_3PO_4 8.5% was dropped gradually and stirred for 10 minutes to form a white suspension. Meanwhile, the 5.600 g $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ (99.9%, Sigma-Aldrich) and 1.500 g glucose (99.9%, Sigma-Aldrich) were dissolved in 30 mL distilled water in nitrogen atmosphere, and then it was added to the white suspension under vigorous stirring. The final mixture was transferred into a stainless-steel autoclave and sealed. The hydrothermal process was conducted at 190°C for 6 hours. The precipitation was collected by filtering, washing, and drying. After that, the collected powder was calcined under argon atmosphere at 600, 700, 800°C for 6 hours.

2.2. Physical Characterization. Powder X-ray diffraction (XRD) data were collected on a Bruker D8 Advance Diffractometer (Bruker), using a Cu $\text{K}\alpha 1$ radiation source ($\lambda = 1.5406 \text{ \AA}$). The crystal structure of synthesized materials were analyzed by Rietveld method [18] using the Topas computer software [19]. X-ray photoelectron spectroscopy (XPS) measurements were performed on an AXIS-NOVA (Kratos) under a base pressure of 2.6×10^{-9} Torr. The size and morphological feature of materials were analyzed with a scanning electron microscope (FE-SEM, S-4700N of HITACHI) with a Hitachi S-4700. Raman spectroscopy measurements were carried out on a LabRAM HR 800 Raman Spectrometer

(HORIBA Jobin Yvon) with the green line of an argon-ion laser (514 nm) as the excitation source and the Raman bands were collected in the wavelength range of 500–2000 cm^{-1} at room temperature. Thermal analysis (TGA) was conducted with a LABSYS evo TG-DSC 1600 (Setaram, France).

2.3. Electrochemical Measurements. The electrochemical measurements were performed in lithium half cell into two-electrode Swagelok cell with a Li foil as negative electrode and synthesized olivine samples LiFePO_4 @C as positive electrode, an electrolyte of 1.0 M LiPF_6 in ethylene carbonate and dimethyl carbonate (EC:DMC = 1:1) (Sigma-Aldrich) and three Whatman glass-fiber separators. The positive electrodes were prepared using the following procedure. An 80:15:5 mixture of synthesized olivine samples LiFePO_4 @C, carbon black, and copolymer poly(vinylidene fluoride-co-hexafluoropropylene) PVDF-HFP (Sigma-Aldrich) binder was mixed with 1-methyl-2-pyrrolidinone (NMP) solvent to form a viscous paste. The paste was coated uniformly on aluminum foil (Al-foil) via coating machine MSK-AFA-III (MTI, USA) with a thickness of 100 μm . The coated Al-foil was dried in a vacuum oven overnight at 120°C and then cut into pellets with a diameter of 10 mm. The cells were assembled in argon-filled glovebox.

All electrochemical measurements were operated on MPG-2 apparatus (Bio-Logic, France) at room temperature. The cyclic voltammetry (CV) were carried out with scan rate from 5 to 60 $\mu\text{V/s}$, and the galvanostatic cycling tests were performed in a voltage range of 3.0–4.0 V (vs. Li^+/Li).

3. Results and Discussion

3.1. Structure and Morphology. We conducted Rietveld refinements to identify the structure of three synthesized samples LFP600, LFP700, and LFP800 (Figure 1). The refinements were performed using the olivine orthorhombic structure and the space group $Pnma$ [20] with Li atoms at 4a sites, Fe atoms at 4c sites, P atoms at 4c sites, and O atoms at 4c and 8a sites. The pure phases were confirmed and the fitted structural parameters and the refined results (Wyckoff positions, fractional atomic coordinate parameters) are gathered in Tables 2 and 3. The refinement's results point out the orthorhombic structure without impurity phase and the high crystalline of three synthesized olivines with the “chi-square” (χ^2) below 5.

According to the Debye-Scherrer formula, the average c was calculated from the full width of half maximum (FWHM) of the highest intensity diffraction peak (311).

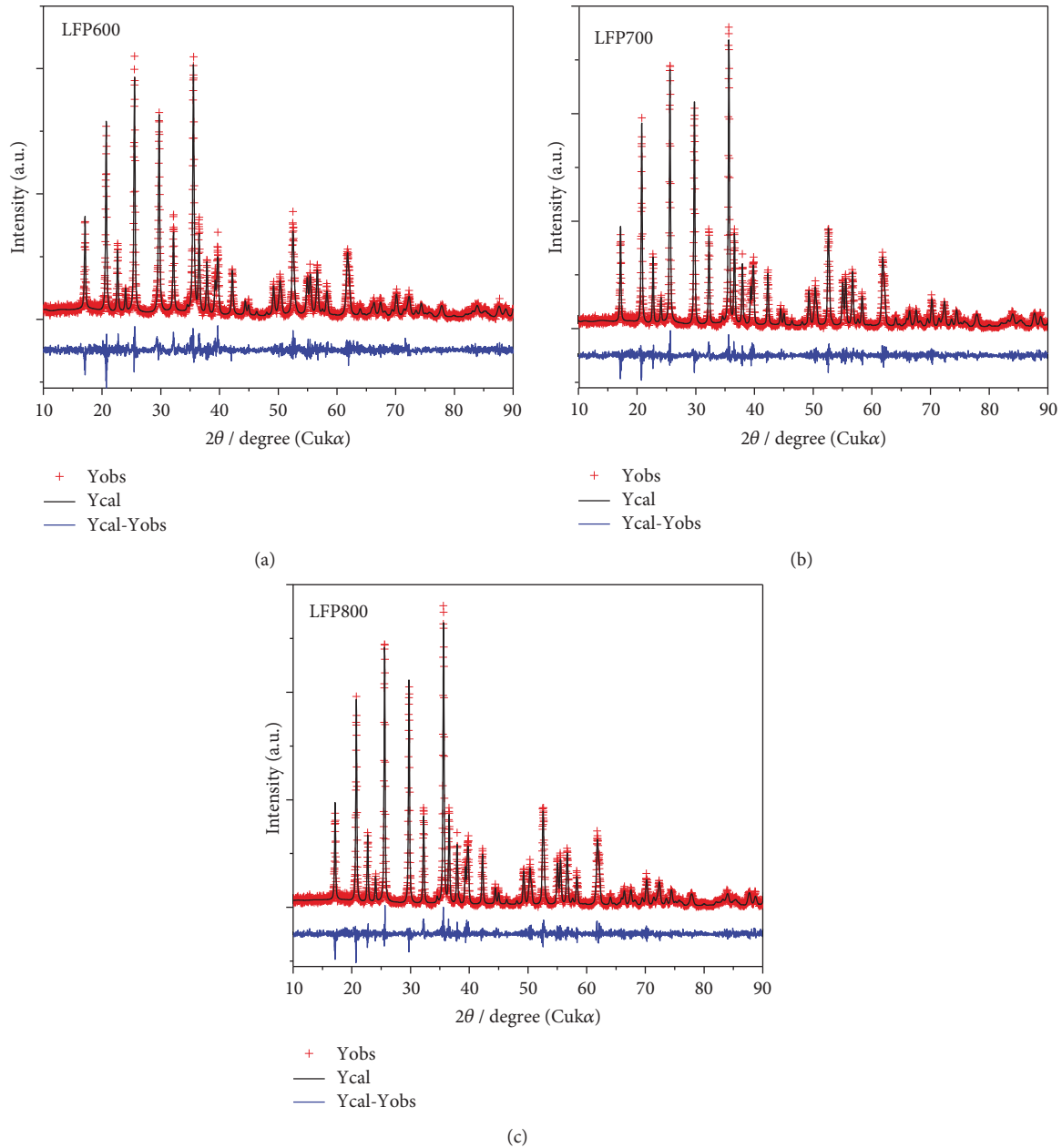


FIGURE 1: XRD patterns of olivines LFP600, LFP700, and LFP800.

TABLE 2: Lattice parameter and refinement's R-factors of LFP600, LFP700, and LFP 800.

	a/Å	b/Å	c/Å	V/Å ³	R _{exp}	R _{wp}	χ ²
LFP600	10.3272	5.9971	4.6975	290.94	37.1	24.85	2.22
LFP700	10.3203	6.0009	4.6935	290.68	27.3	18.28	2.21
LFP800	10.3205	6.0003	4.6933	290.63	30.3	19.92	2.32

The crystalline sizes of the synthesized olivines were found out of 34 nm for LFP600, 49.5 nm for LFP700, and 42.6 nm for LFP800.

Figure 2 shows the morphologies of olivines' powders. The hydrothermal synthesis promotes the significant particle-size distribution, but the temperature pyrolysis

TABLE 3: Wyckoff positions, fractional atomic coordinates for the synthesized olivines.

	Wyckoff	x	y	z	Occupy
Li	4a	0	0	0	1
Fe	4c	0.2822	0.25	0.9747	1
P	4c	0.0948	0.25	0.4192	1
O1	4c	0.0968	0.25	0.7430	1
O2	4c	0.4567	0.25	0.2060	1
O3	8d	0.1656	0.0466	0.2847	1

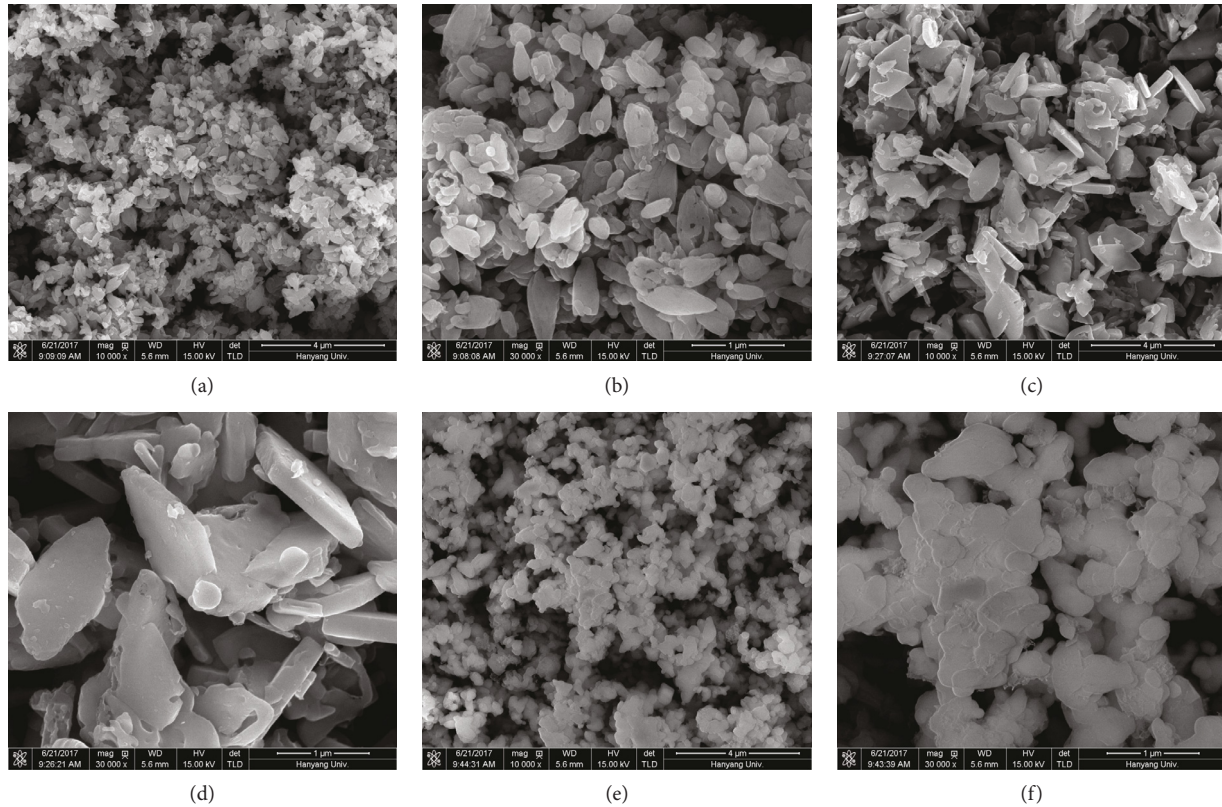


FIGURE 2: SEM images of LFP600 (a, b), LFP700 (c, d), and LFP800 (e, f).

indicates the variation of particle shape. The olivines' powders distribute in the submicrometric; the particle size of LFP600 significantly varied in a large range from 200 to 500 nm with the undefined shapes, LFP700 exhibited the thin-plate particles with a thickness of 200 nm and other dimensions around 800 nm, and LFP800 particles came up with a more spherical shape with about 250 nm dimension.

Three Raman spectra of olivines' powders in Figure 3 exhibit two broad lines in high-frequency region at 1345 and 1583 cm^{-1} which are the fingerprint of carbon. The band at 1583 cm^{-1} is assigned to the G-band of E_{2g} mode of crystalline graphite, while the band at 1345 cm^{-1} is assigned to the D-band of edge modes of disordered graphite. Note that the D-band/G-band intensity ratio characterizes to the yield of graphitic bonding in amorphous carbon and the low D-line/G-line ratio encourages the electronic and ionic conductivity [21, 22]. We observed the D-line/G-line ratio of olivine samples following 1.04 for LFP600, 0.87 for LFP700, and 0.96 for LFP800 that indicates the calcination process at 700°C could increase the graphitization of carbon coating.

X-ray photoelectron spectroscopy (XPS) analysis was performed to examine the valence state of chemical elements of synthesized olivines. Figure 4(a) shows the analog XPS profiles of three olivines' powders in the full scan. For more detail in the narrow scan, the Fe 2p spectra (Figure 4(b)) confirm the Fe^{2+} valence state with the spin-orbit coupling by two peaks at a binding energy (BE) of 710.5 (Fe 2p_{1/2}) and 723 eV (Fe 2p_{3/2}) [23–27].

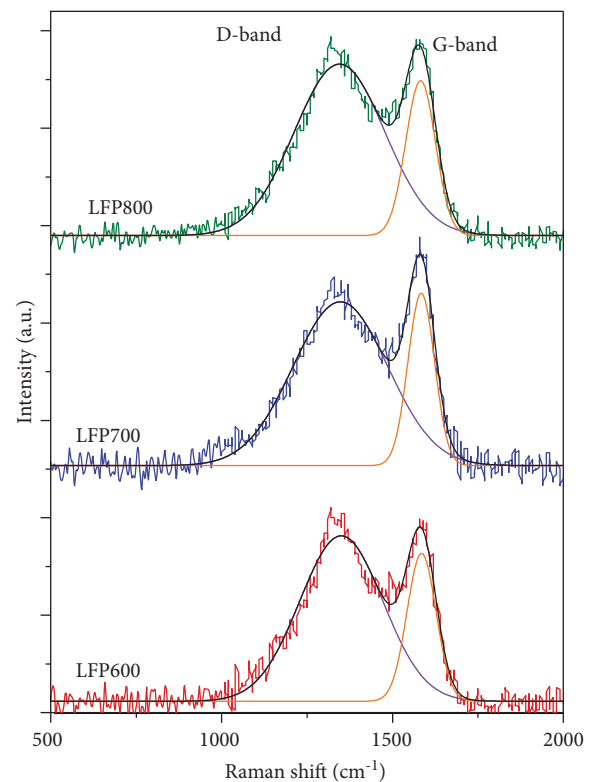


FIGURE 3: Raman spectroscopy of LFP600, LFP700, and LFP800.

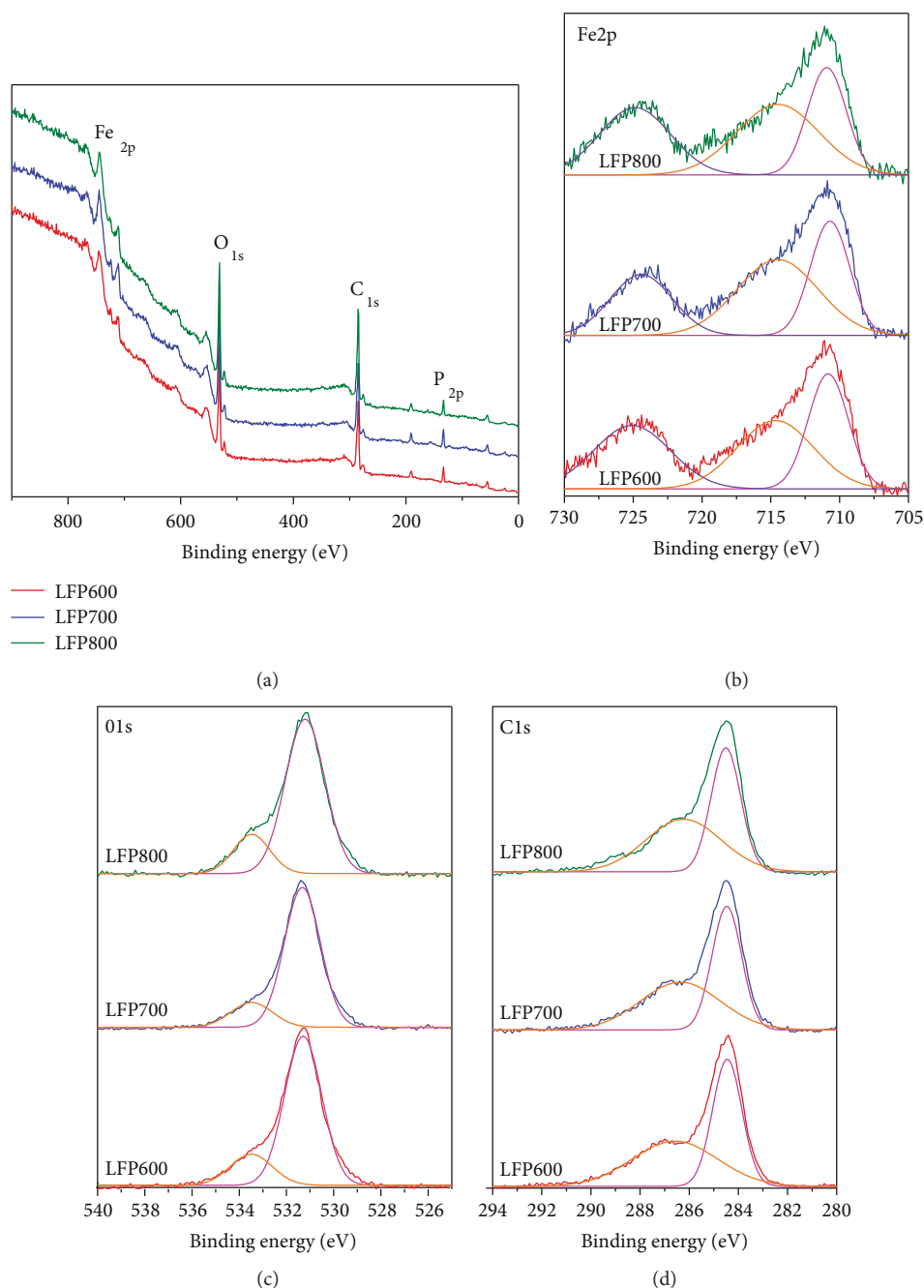


FIGURE 4: (a) Full-scan profiles of olivine samples; narrow-scan profile of Fe2p (b), O1s (c), and C1s (d).

The two peaks at BE of 531.7 eV and 533.5 eV (Figure 4(c)) can be assigned to the oxygen divalent (O1s), attributing the lattice oxygen O^{2-} in P–O bond at the normal sites of the orthorhombic structure. The C1s peak (Figure 4(d)) at BE of 284 eV corresponds to the carbon coating on the surface of olivine powders. The peak at BE of 133 eV is related to the P^{5+} valent (P1s) in PO_4^{3-} group [23, 28–30]. Both results of Raman spectroscopy and XPS confirm the pure olivine phase as well as the successful carbon coating on the surface of olivines' powders.

TGA were operated on the olivine powders to determine the amount of carbon coating under flow of air

and with heating rate of $10^\circ\text{C}/\text{min}$. The TGA curves demonstrate a similar trend as shown on Figure 5. Below 200°C , a slight weight loss was observed due to evaporation of adsorbed water on particle surface; above 200°C , a weight gain was observed which was supposed to be the result of oxidation of $LiFePO_4$ in air and a theoretical weight gain of 5.07% [31]. Meanwhile, in the same temperature range, the carbon coated on nanoparticles is also oxidized into carbon dioxide and leads to a decrease in weight. Hence, taking the initial weight loss due to evaporated water, the amount of coated carbon can be presumed in Table 4.

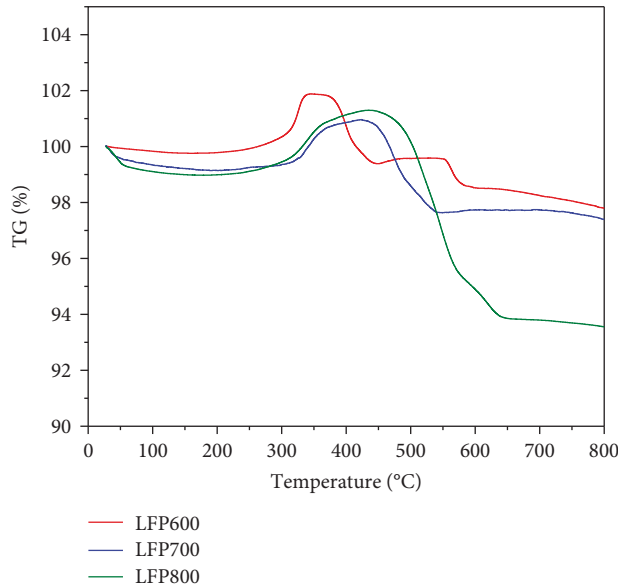


FIGURE 5: TGA curves of LFP600, LFP700, and LFP800.

TABLE 4: Amount of carbon coating on LiFePO₄.

Sample	LFP600	LFP700	LFP800
Carbon coating (%)	3	4	3.5

3.2. Electrochemical Performance. Electrochemical properties of the olivine samples were performed by cyclic voltammetry (CV) and galvanostatic cycling test between 3 and 4 V (vs. Li⁺/Li). Figures 6(a)–6(c) illustrate the CV profiles of olivines LFP600, LFP700, and LFP800 in scan rate from 5 μ V/s to 60 μ V/s. In each scan rate, the CV curve possessed one unique anodic peak as well as cathodic peak. The CV curves abided by the motif of two-phase mechanism that means the Li migration occurs through regions LiFePO₄ and FePO₄, indicated by a reversible redox couple Fe³⁺/Fe²⁺. Following the increase of scan rate, the anode peaks shifted gradually towards positive direction while the cathode peaks also step backwards in a negative direction. The reverse shift between anodic peaks and cathodic peaks gave a signal of polarization in galvanostatic charge-discharge test at high rates.

The diffusion coefficient of lithium ion (D_{Li}) can be calculated by Randles-Sevcik equation due to the reversible reaction of redox couple Fe³⁺/Fe²⁺, which is showed by the relationship between the cathodic peak current and the square root of scan rates.

$$i_p = 0.4463nFAC \left(\frac{nFvD}{RT} \right)^{1/2}, \quad (1)$$

whereas i_p (A) is cathodic peak current, n is the number of electron transfer in redox reaction ($n=1$ for LiFePO₄), F (C/mol) is the Faraday constant, A is electrode area (0.785 cm²), C (mol/cm³) is concentration of mobility ion in structure, v (V/s) is scan rate, D (cm²/s) is diffusion

coefficient, R (J/K.mol) is the gas constant, and T (K) is temperature.

Figure 6(d) shows the significant linear relationship between the cathodic peak current and the square root of scan rates of olivine samples. The slope of LFP700 was higher than those of LFP600 and LFP800, suggesting the fast Li transportation of LFP700. The D_{Li} were found out 1.09×10^{-12} cm²/s for LFP600, 2.28×10^{-11} cm²/s for LFP700, and 3.27×10^{-12} cm²/s LFP800; these results were higher than the results determined by CV, GITT, and EIS methods [6, 8]. Moreover, the Li diffusion of LFP700 was one order of magnitude larger than those of LFP600 and LFP800 due to the high amount as well as the high quality of carbon coating.

The Li insertion into olivine phase of LiFePO₄ can be described by a domino-cascade mechanism with a reciprocal phase transition between LiFePO₄ and FePO₄; the Li insertion pathway is routed through channels of (010) plane. The galvanostatic curve of LiFePO₄ is characterized by two long plateaux at 3.40 V for reduction process and 3.45 V for oxidation process, corresponding to the reversible redox peaks in CV curve. The cycling tests of olivines were conducted at rate C/10 (17 mA/g). The typical charge-discharge curves of LFP700 in Figure 7(a) illustrate a low polarization of 70 mV between the mid-discharge potential and the midcharge potential; moreover, the middischarge potential is not influenced upon cycling test. That confirms the structural stability during the Li migration.

Figure 7(b) shows the cycling performance of synthesized olivines upon 120 cycles. We observed the increase of capacities during the first twenty cycles due to the initial surface activation on the electrode LiFePO₄ [32]. The olivines pointed out the quite stable performance in cycling test at rate C/10. The capacities reached 145 mAh/g for LFP600, 170 mAh/g for LFP700, and 160 mAh/g for LFP800. The better performance of LFP700 than LFP600 and LFP800 can be explained by the high amount of carbon coating, the well-crystalline grains, and the fast kinetic of Li transportation. Our cycling results are comparable to the previous report in context of electrode composite LiFePO₄@carbon for Li-ion batteries [7, 15, 33, 34].

Figure 8(a) demonstrates the typical charge-discharge profiles of LFP700 at rate capability performance. We observed a low middischarge potential difference (70 mV) until rate 2C while a drastic difference of 200 mV is obtained at 5C. The middischarge potential difference is depended on the electrode polarization that leads the fading capacity in high rate test. A significant capacity declined when the current density increased: from 170 mAh/g at C/10 to 160 mAh/g at C/5, 151 mAh/g at C/2, 142 mAh/g at 1C, 125 mAh/g at 2C, and 105 mAh/g at 5C. The performance at high rate would be further improved by forming the composite electrodes between active material and high-conductive carbonaceous-like CNTs or graphene. Our recent report showed that the additional CNTs in LFP's electrodes could benefit the long-term performance upon 200 cycles with 200 mAh/g at rate C/10 and a remarkable capacity of 120 mAh/g at rate 10C [35].

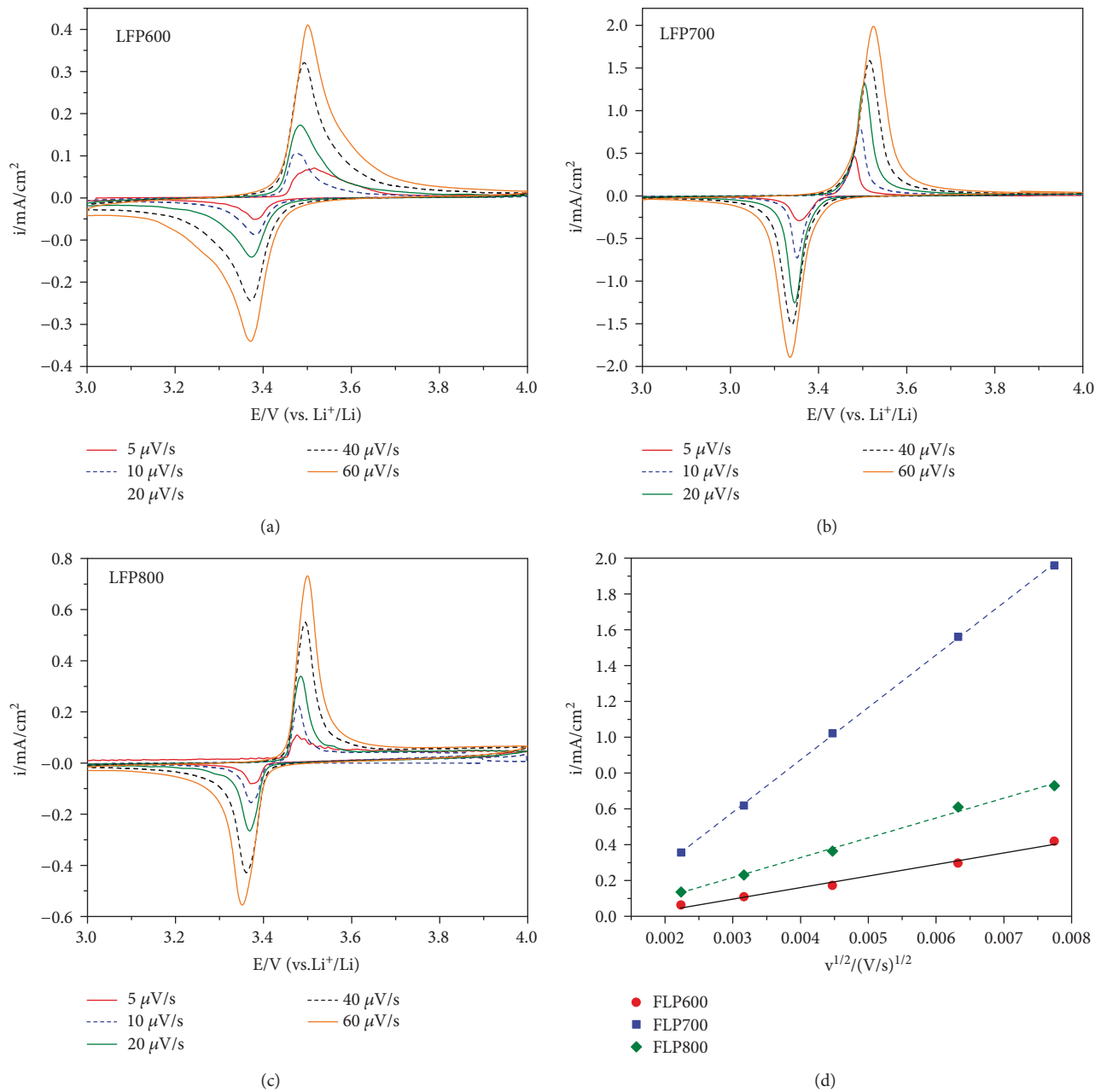


FIGURE 6: CV curves of (a) LFP600, (b) LFP700, and (c) LFP800 in scan rate 5–60 $\mu\text{V}/\text{s}$ and (d) i_{pc} as a function of the square root of the scan rate ($v^{1/2}$) of electrodes LFP600, LFP700, and LFP800.

Figure 8(b) compares the rate capability performance of olivine samples; the current densities were applied from C/10 (17 mA/g) to 5C (850 mA/g) after performing 20 cycles at C/10 to activate the electrode's surface. The cycling stability was obtained at all rates; after switching back to lowest rate C/10, the capacities can be almost fully recovered. As mentioned in cycling test at monorate C/10, the cycling test of LFP700 at rate capability also pointed out the better performance than LFP600 and LFP800. Until rate 2C, LFP800 presented a low difference of capacities around 8 mAh/g but LFP600 presented a large difference of capacities more than 30 mAh/g. For example, at rate 1C (170 mAh/g), the

capacities found out 104 mAh/g for LFP600, 141 mAh/g for LFP700, and 133 mAh/g for LFP800. At the highest rate 5C (85 mAh/g), the capacities reached 72 mAh/g for LFP600, 105 mAh/g for LFP700, and 92 mAh/g for LFP800.

4. Conclusion

In summary, our work prepared electrode composite $\text{LiFePO}_4/\text{carbon}$ by hydrothermal. The temperature of calcination process affected the morphologies, the quality of carbon coating, and the electrochemical properties. The olivine LFP700 possessed a high graphitization of carbon

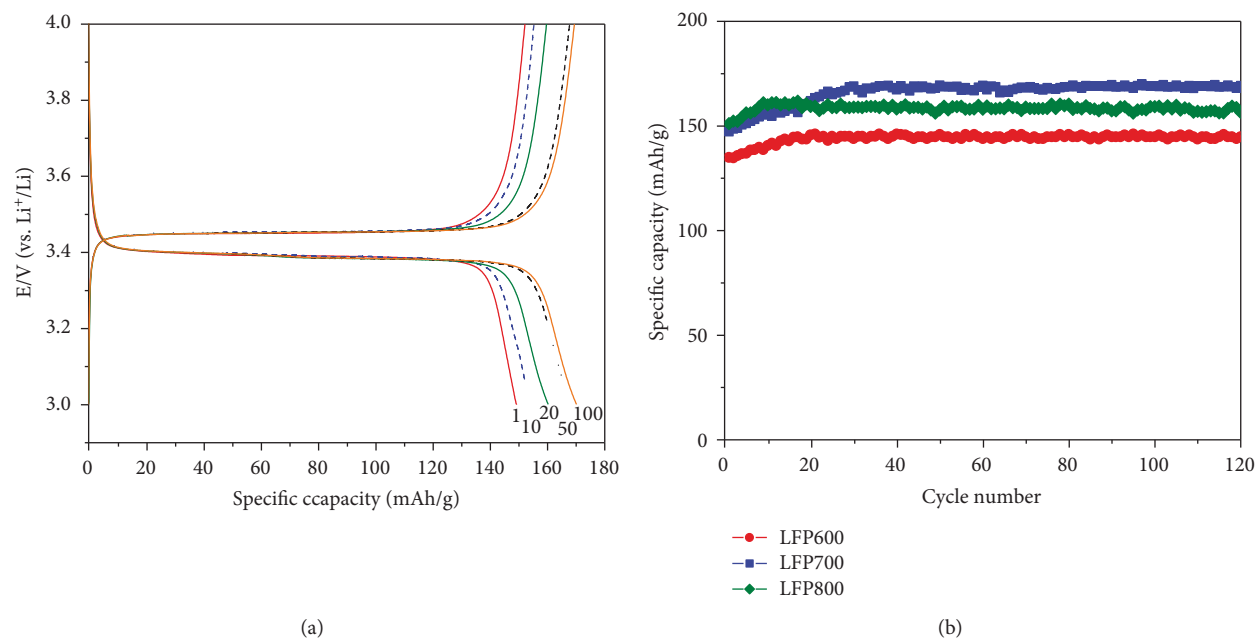


FIGURE 7: (a) Charge-discharge profile of LFP700 and (b) cycling stability of olivine samples at rate C/10.

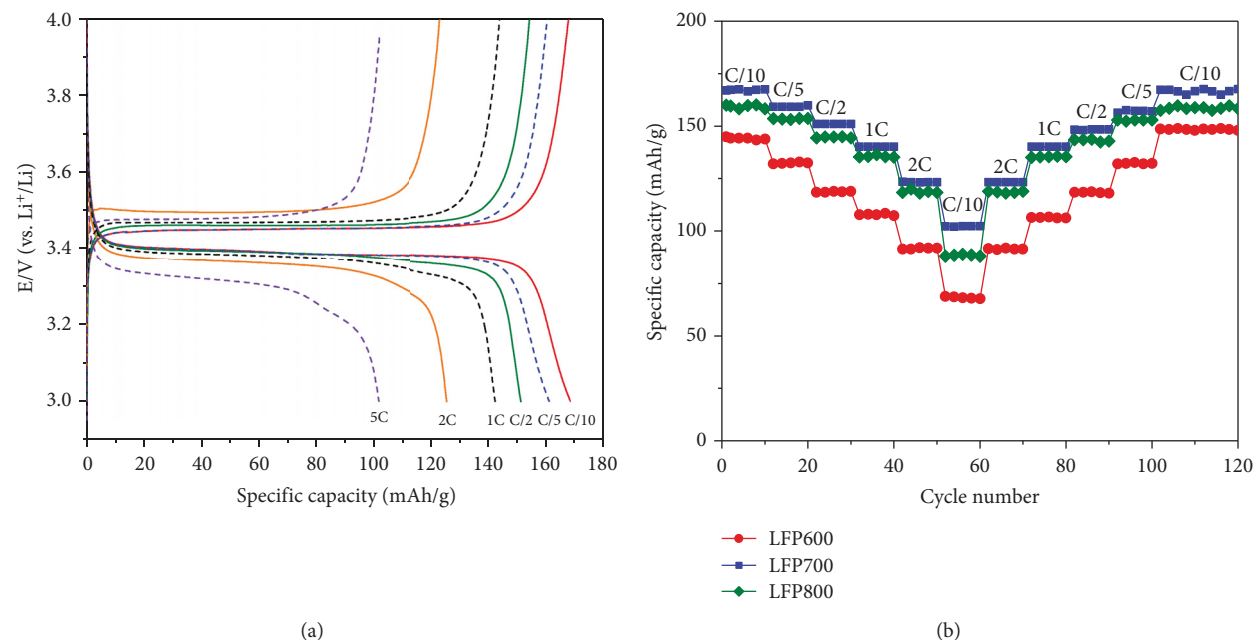


FIGURE 8: (a) Typical charge-discharge curves of LFP700 and (b) capacity stability at rate capability.

coating that lead a fast Li transportation; the Li diffusion of LFP700 was one order of magnitude larger than those of LFP600 and LFP800. The galvanostatic performances of three synthesized olivines showed an excellent cycling stability upon 120 cycles at monorate C/10 as well as rate capability from C/10 to 5C.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

Acknowledgments

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