Enhancement of Electrochemical Performance of LiFePO$_4$@C by Ga Coating

Dawei Yi, Xumei Cui,* Nali Li, Liu Zhang, and Dingyu Yang

ABSTRACT: LiFePO$_4$ (LFP) is one of the cathode materials widely used in lithium ion batteries at present, but its electronic conductivity is still unsatisfactory, which will affect its electrochemical performance. Ga-coated LiFePO$_4$@C (LFP@C) samples were prepared by a hydrothermal method and ultrasonic dispersion technology. Ga has good electrical conductivity and can rapidly conduct electrons within the LFP cathode material under the synergistic effect with C coating, thus improving the dynamic performance of the LFP cathode material. The experimental results show that LFP@C/Ga samples exhibit good electrochemical performance. Compared with the pristine LFP@C, the 1.0 wt % Ga-coated LFP@C cathode exhibits excellent discharge capacity and cycle stability. The former shows a discharge capacity of 152.6 mA h g$^{-1}$ at 1 C after 100 cycles and a discharge capacity retention rate of 98.77%, while pristine LFP@C shows only a discharge capacity of 114.5 mA h g$^{-1}$ and a capacity retention rate of 95.84% after 100 cycles at 1 C current density.

1. INTRODUCTION

Energy is the driving force for social development; with the environmental pollution caused by fossil energy consumption, people urgently need green new energy to improve this situation. With this opportunity, lithium-ion batteries are developing rapidly,\(^1\sim\)\(^3\) and commercial lithium-ion batteries have already occupied most of the market, including electronic devices and pure electric and hybrid electric vehicles because of the long-term cycle life and high energy density.\(^4\sim\)\(^6\) The current commercial cathode materials are LiCoO$_2$, LiMn$_2$O$_4$, LiNi$_x$Co$_y$Mn$_z$O$_2$, LiFePO$_4$ (LFP), and so forth. The LiCoO$_2$ cathode material has low safety and high synthesis cost; in addition, the shortage of Co resources and environmental toxic effects are not good for sustainable development; LiMn$_2$O$_4$ has poor cycle performance.\(^7\sim\)\(^10\) Among all cathode materials, the olivine-structured LFP has attracted much research interest because of its high specific capacity, high thermal stability, and low price.\(^11\sim\)\(^13\) In 1997, Padhi et al. first reported LFP.\(^14\) However, because of its low lithium ion diffusion rate and low electronic conductivity, the development and application of LFP are subject to certain restrictions, and so at present, a lot of research has been done to optimize LFP cathode materials.\(^15\)\(^,\)\(^16\) LFP doped with Zr$^{4+}$ showed excellent rate performance; the discharge capacity reaches 125 mA h g$^{-1}$ at 20 C with a discharge capacity retention rate of 98.5%.\(^17\) LiFePO$_4$@C (LFP@C) doped with Cu$^{2+}$ shows a capacity of 148 mA h g$^{-1}$ at 0.1 C and still maintains a capacity of 111 mA h g$^{-1}$ at 10 C, and after 100 cycles, the capacity retention is 99.9% at 1 C.\(^18\) Goonetilleke et al. found that doping LFP with Mg$^{2+}$ can improve the reaction kinetics and increase its capacity.\(^19\) Additionally, reducing the size of LFP particles is helpful to shorten the lithium-ion diffusion route and accelerate the transfer rate of lithium ions.\(^20\) In addition, the surface of the LFP particles could be coated with a conductive material to increase its electron transfer rate. For example, carbon coating is widely used in LFP.\(^21\)\(^,\)\(^22\) Kim et al. used biomass-derived carbon to uniformly coat on the LFP, and its
charge and discharge capacity at 1 C reached 147.3 and 139.8 mA h g⁻¹, respectively. However, the increase in carbon content during carbon coating will reduce the tap density of LFP particles, while metal coating can ensure the electronic density of LFP particles without reducing its tap density and can form electron channels in the outer layer of the cathode material to improve the electron transport speed. Metal Ga has the physical properties of a low melting point but a high boiling point. It will melt at 29.75 °C and boil at 1983–2070 °C. In addition, studies have shown that superconductivity occurs in ultrathin Ga films, which also indicates that Ga has excellent electrical conductivity. Up to now, there is no report on Ga coating on LFP. In this work, we use metal Ga to modify the electrochemical performance of LFP@C cathode materials. Specifically, through a moderate amount of Ga coating, the electron conductivity of the LFP@C cathode material is improved without damaging the original LFP olivine structure. In addition, compared with pristine LFP@C, the cycling performance and charge–discharge capacity of LFP cathode materials are better under the synergistic effect of Ga coating and C coating.

2. RESULTS AND DISCUSSION

The X-ray diffraction (XRD) patterns of the Ga-coated LFP@C (with a Ga content of 0, 1.0, 2.0, and 4.0 wt %) samples are shown in Figure 1. All diffraction peaks can be identified well to the standard LFP olivine structure (JCPDS 81-1173) with the Pnma space group. The sharper diffraction peaks of all samples indicate that all the samples have good crystallinity. In addition, it can be seen that there are no obvious impurity peaks in the diffraction patterns of the four samples, which indicates that the purity of the samples is relatively high. At the same time, the diffraction peak of metal Ga and C could not be found in the spectra, which may be because of the very low content of metal Ga and C dispersed in the samples.

Scanning electron microscopy (SEM) was used to observe the morphology and grain size of each sample. The morphology images are shown in Figure 2. As can be seen from the figures, the grain size of all samples is approximately between 100 and 500 nm and the shape of the particles is oval, which is beneficial for improving compact density and shortening the transmission path of Li⁺. In addition, compared with the pristine LFP@C, Ga coating has no effect on the structure and morphology of the LFP@C cathode material, which is consistent with the XRD spectrum test results.

In order to confirm the existence of Ga, energy-dispersive system (EDS) elemental mapping scanning was performed on the LFP@C/Ga-1 sample, and the mapping image is shown in Figure 3. Figure 3a–e shows the SEM image, and Ga, P, Fe, and O elemental mapping. It can be seen that all elements are well distributed in the LFP@C/Ga-1 sample, which indicates that Ga is present in the material as other elements. At the same time, because of the small coating amount of Ga, the Ga mapping is less dense than that of other elements. In order to further understand the surface coating of the samples, we carried out transmission electron microscopy (TEM) tests on LFP@C and LFP@C/Ga-1 samples. TEM images are shown in Figure 4; from the figure, we can see that the carbon coating thickness of the sample LFP@C is about 2.3 nm, and Ga grows on the carbon layer in the form of nanoparticles with about 3 nm. In addition, Figure 4b shows an enlarged view of the crystal plane of Ga; the crystal plane spacing is about 0.209 nm, corresponding to the (510) plane of metal gallium (PDF card no. 25-0344). The growth of Ga makes the conductive layer more compact and complete, which could increase the conductivity and also protect the electrode from corrosion while transmitting electrons. In addition, because of the existence of the Ga coating on the particle surface, it can greatly enhance the electron conduction between the sample particles and reduce the contact resistance between the sample particles, thereby improving the electrochemical performance of the samples.

In order to further understand the surface composition and chemical bonding of the LFP@C/Ga samples, the samples were tested by X-ray photoelectron spectroscopy (XPS) (Figure 5a). The test results show that the binding energies of Li 1s, P 2p, C 1s, O 1s, Fe 2p, and Ga 2p are determined and the corresponding binding energies are 56.13, 133.91, 284.85, 532.15, and 710.4 eV with Ga 2p, and 1145.5 eV with Ga 2p. Figure 5b shows that the C 1s peak is deconvoluted into three peaks: C=C (284.77 eV), C=O (286.02 eV), and C=O (287.03 eV). Figure 5c,d show the high-resolution spectra of the Ga 2p1/2 and Ga 2p3/2 peaks, respectively. The binding energy of the corresponding peaks is...
1145.5 and 1118.1 eV, and these peaks are fitted. The difference between the two peaks is 27.4 eV, which is consistent with the binding energy of Ga 2p.31 It also confirms the presence of gallium oxide (Ga$_2$O or Ga$_2$O$_3$) in the composite and the appearance of secondary peaks in the spectrum, mainly the presence of metal Ga; this matches the value published by the NIST XPS standard reference database.32–34 In addition, it is also observed in Figure 5a that the peak intensity of gallium oxide (Ga$_2$O or Ga$_2$O$_3$) is higher than that of metal Ga. This may be caused by the oxidation of some metal Ga to form an oxide (Ga$_2$O or Ga$_2$O$_3$) during the process of heating and dispersing the metal Ga. Therefore, metal Ga and gallium oxide (Ga$_2$O or Ga$_2$O$_3$) coexist in the composite material. It is reported that gallium oxide (Ga$_2$O$_3$) is a semiconductor oxide, which has good thermal and chemical stability and also has the characteristics

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**Figure 3.** EDS element mapping images of LFP@C/Ga-1: (a) SEM image, (b) Ga element, (c) P element, (d) Fe element, and (e) O element.

**Figure 4.** TEM images of LFP@C (a) and LFP@C/Ga-1 (b).

**Figure 5.** XPS spectra of LFP@C/Ga: (a) wide XPS spectrum, (b) C 1s, (c) Ga 2p$_{1/2}$, and (d) Ga 2p$_{3/2}$. 
Subsequently, the effect of Ga coating on the electrochemical performance of LFP@C was studied. Cyclic voltammetry (CV) scans were performed on all samples at a scan rate of 0.1 mV s⁻¹ with 2.0–4.2 V voltage range. Figure 6a shows the CV curves of the second cycle. It can be seen from the figure that all of the four samples have only one pair of redox peaks, in which the oxidation peaks are all around 3.61 V and the reduction peaks are around 3.25 V. As can be seen, Ga coating can improve the electrochemical performance of LFP@C with higher redox peak intensity and larger enclosed area. Comparing the four sets of curves, it can be clearly seen that the redox peak of LFP@C/Ga-1 is the sharpest and the polarization is the smallest, indicating that the electrochemical kinetics of intercalation/de-intercalation of Li⁺ into/from the LFP@C/Ga could be improved by Ga coating. The reason may be that the incorporation of Ga improves the reversibility of lithium-ion insertion/extraction during charge and discharge.

Figure 6b shows the plots of the LFP@C and LFP@C/Ga electrochemical impedance spectroscopy (EIS) tests with 10 mHz–100 kHz frequency range and 5 mV amplitude. The EIS diagram consists of two parts, including a semicircular area and a linear area. The intercept of the semicircular arc on the Z’ axis corresponds to the Ohmic resistance (Rₛ), which is mainly caused by the electrolyte and the electrode material; the semicircular arc represents the charge transfer resistance (Rₜ). The charge transfer resistance is expressed as an electrochemical reaction occurring at the electrode/electrolyte interface. The linear portion indicates the diffusion resistance of the lithium ion, Warburg impedance (Zₜ), which is related to the diffusion of Li ions in the electrode active material. The larger the slope of the straight line, the faster the lithium ion diffusion during transmission and the smaller the diffusion resistance. The equivalent circuit diagram of the LFP@C and LFP@C/Ga electrodes is obtained using a Biologic SP-150 electrochemical workstation, as inserted in Figure 6b, where CPE is the related constant phase elements, which is expressed as the dispersion effect caused by the heterostructure. As can be seen from the figure, the Ga-coated samples have smaller charge transfer resistance and faster lithium-ion diffusion; this may be due to the existence of the Ga coating on the surface of the sample particles, which reduces the contact resistance between the particles and enhances the electronic conductivity of the sample. The Rᵢ of Ga-coated LFP@C with a Ga content of conductivity and light emission and has a wide range of uses.

Figure 6. Electrochemical properties of LFP@C and LFP@C/Ga: (a) CV curve, (b) EIS curve, (c) relationship plot between Z’ and ω⁻⁰.⁵ in a low-frequency region, (d) first charge−discharge curves at 1 C, (e) rate capability, and (f) cycling performances at 1 C of LFP@C/Ga-x.
of 0, 1.0, 2.0, and 4.0 wt % is 323, 132, 169, and 220 Ω, respectively. In addition, we calculated the electronic conductivity of the samples from the charge transfer resistance value. The electronic conductivity is calculated with the following formula:

$$R = \frac{I}{A\sigma}$$

(1)

where $R$ is the resistance, $A$ is the area of the electrode ($1.5386 \times 10^{-4} \text{ m}^2$), $I$ is the thickness of the active material ($5 \times 10^{-3} \text{ m}$), and $\sigma$ is the electronic conductivity of the material. The $\sigma'$ of Ga-coated LFP@C with a Ga content of 0, 1.0, 2.0, and 4.0 wt % was calculated to be $1.0061 \times 10^{-3}$, $2.4619 \times 10^{-3}$, $1.9229 \times 10^{-3}$, and $1.4771 \times 10^{-3} \text{ S m}^{-1}$, respectively.

Obviously, LFP@C/Ga-1 has the smallest charge transfer resistance and higher conductivity, indicating that the Ga coating can reduce the charge transfer resistance and increase the conductivity of the sample, and 1 wt % is the optimal content of Ga. At the same time, the lithium-ion diffusion coefficient can be accurately calculated by EIS, which is calculated with the following equation:

$$D = \frac{R_{fl}^2L^2}{2A^2n^2F^2C^2\sigma^2}$$

(2)

where $R$ is the gas constant, $T$ represents room temperature (298.15 K), $A$ is the electrode surface area, $n$ is the number of electrons during the redox reaction, $F$ is the Faraday constant, $C$ is the concentration of Li$^+$ ($7.69 \times 10^{-3} \text{ mol cm}^{-3}$), and $\sigma$ is the Warburg factor correlated with $Z'$. Therefore, $Z' = R_x + R_{fl} + \sigma o^{-1/2}$

(3)

As shown in Figure 6c, from the relationship diagram of $Z'$ and $o^{-1/2}$, the lithium ion diffusion coefficients of the sample Ga-coated LFP@C with 0, 1.0, 2.0, and 4.0 wt % Ga are calculated to be $4.01 \times 10^{-15}$, $3.73 \times 10^{-14}$, $3.26 \times 10^{-14}$, and $3.09 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$, respectively. It is clear that the samples with Ga coating have a higher diffusion coefficient than the pristine one, and among them, the LFP@C/Ga-1 sample has the highest diffusion coefficient, showing the fastest lithium ion migration.

The first charge and discharge curves of Ga-coated LFP@C/Ga (with a Ga content of 0, 1.0, 2.0, and 4.0 wt %) at 1 C rate are shown in Figure 6d, which show that the first initial discharge specific capacity is 115.1, 152.7, 136.7, and 125 mA h g$^{-1}$ at 1 C for LFP@C, LFP@C/Ga-1, LFP@C/Ga-2, and LFP@C/Ga-4, respectively. It shows that Ga coating can improve the first charge and discharge specific capacity of the samples, and among them, LFP@C/Ga-1 shows the highest discharge specific capacity. It can also be seen from the curves that the charging and discharging platforms of the samples are relatively flat, indicating that the samples have good reversibility. In this charging and discharging process, the redox reaction of Fe$^{2+}$ and Fe$^{3+}$ and the insertion and extraction of lithium ions are accompanied. Figure 6e shows Ga-coated samples have better rate performance than the pristine LFP sample, and among the samples, the LFP@C/Ga-1 sample shows the best discharge rate performance and stability with average discharge capacities of 165.4, 156.4, 152.6, 145.9, 122.1, and 164.8 mA h g$^{-1}$ at 0.2, 0.5, 1.0, 2, S, and 0.2 C, respectively. When the rate was returned to 0.2 C, the discharge capacity returned to 164.8 mA h g$^{-1}$. However, the average discharge capacities of the pristine LFP@C are 143.1, 136.5, 114.5, 103.6, 85.2, and 141.5 mA h g$^{-1}$ at 0.2, 0.5, 1.0, 2, S, and 0.2 C, respectively. The 100 times cycling performance of LFP@C/Ga (with a Ga content of 0, 1.0, 2.0, and 4.0 wt %) is shown in Figure 6f. It can be seen that all Ga-coated samples have better cyclic capability than the pristine LFP@C sample, and LFP@C/Ga-1 retains 152.6 mA h g$^{-1}$ discharge capacity after 100 cycles at 1 C with 98.77% discharge capacity retention rate, while the pristine LFP@C demonstrates a capacity of 114.5 mA h g$^{-1}$ after 100 cycles, with only 95.84% capacity maintained. Compared with LFP@C, the incorporation of Ga greatly improved the performance of the samples. The reason is that the electrochemical kinetics of intercalation/de-intercalation of Li$^+$ into/from the LFP@C/Ga could be improved by Ga coating; the charge transfer resistance and lithium ion diffusion coefficients are all optimized with Ga coating, especially 1.0 wt % Ga coating. However, as the amount of Ga added increases, the cycling performance of the sample gradually decreases. This may be due to the increase in the coating amount of Ga; the thicker coating on the surface of the sample led to a larger particle size distribution and the dispersion began to deteriorate, increasing the migration distance of Li$^+$ in the sample LFP@C, which gradually deteriorated the electrochemical performance of the sample. In addition, compared with similar work, Gao et al. synthesized a Zr and Co codoped composite material, Li$_{10.99}$Zr$_{0.0025}$Fe$_{1-x}$Co$_x$PO$_4$ ($x = 0.005, 0.01, 0.015$, and 0.02), by a high-temperature solid-state method. The coding method enhances the performance of the cathode material without destroying the olivine structure, showing a discharge capacity of 139.9 mA h g$^{-1}$ at a rate of 0.1 C and a capacity retention rate of 85% after 50 cycles. However, we have adopted a dual-coating method to enhance the performance of the cathode material without damaging the olivine structure and obtain better results, showing a discharge capacity of 152.6 mA h g$^{-1}$ at a rate of 1 C, and after 100 cycles, the capacity retention rate was 98.77%.

3. CONCLUSIONS

In summary, LFP@C/Ga cathode materials were prepared by a hydrothermal method and ultrasonic dispersion technology. The structure, morphology, and electrochemical properties of the samples were analyzed by a series of characterization methods. The results show that the samples coated with Ga have better electrochemical performance than the pristine samples. Among them, the sample with 1 wt % Ga exhibits the best electrochemical performance with discharge capacities of 165.4 and 122.1 mA h g$^{-1}$ at 0.2 and 5 C, respectively. At the same time, it also shows good cycle stability; the discharge capacity retention rate reaches 98.77% after 100 cycles at 1 C current density. The reason may be the super conductivity of metal Ga, which can provide a good conductive net with the carbon layer in LFP. Under the synergistic effect of metal Ga coating and the carbon layer, the electron transfer ability of LFP is effectively enhanced during charging and discharging and the sample has good reversibility. This study shows that coating metal Ga is an effective method to improve the electrochemical performance of LFP materials in some special cases, although the cost of Ga is high and it is not suitable for large-scale industrial applications.
4. EXPERIMENTAL SECTION

4.1. Synthesis of LFP@C/Ga. LFP cathode materials were prepared via a hydrothermal method. Analytical-grade LiOH·H2O, H3PO4, and FeSO4·7H2O (with a molar ratio of 3:1:1) were used as the raw materials. First, the raw materials were separately dissolved in deionized water, and the concentration of the reactant is 0.3 mol L⁻¹ in terms of lithium ion concentration. The H3PO4 solution was added dropwise to the FeSO4 solution to prevent Fe²⁺ oxidation, and then, the suspension was added to the FeSO₄ solution and stirred for 30 min to form a light blue suspension, which was finally transferred to a 100 mL polytetrafluoroethylene lined and kept at 180 °C for 10 h in a high-temperature stainless-steel reactor. After cooling down to room temperature, the obtained precursor was washed with deionized water and absolute ethanol, filtered, dried at 110 °C for 2 h under vacuum, and ground to obtain the LFP precursor. Then, 20 wt % glucose was dissolved in deionized water, followed by the addition of the LFP precursor and stirring for 2 h, it was dried at 110 °C for 5 h under vacuum. After grinding, the precursor was incubated at 750 °C for 6 h under an argon atmosphere. After cooling to room temperature, carbon-coated LFP powders (i.e., LFP@C) were obtained.

To synthesize LFP@C/Ga, different amounts of the solid metal Ga (0.01, 0.02, and 0.04 g) were added into 40 mL of absolute ethanol solution separately and then, the solutions were heated in a 50 °C water bath until Ga melted. Subsequently, the solutions were ultrasonically dispersed for 1 h, and then, the LFP@C precursors (0.99, 0.98, and 0.96 g) were added to the solutions and stirred for 2 h at room temperature. Finally, the obtained solutions were vacuum-dried at 80 °C for 6 h and after grinding, an LFP@C/Ga material was obtained. The coating amounts of Ga are 1.0, 2.0, and 4.0 wt % with a Ga to the LFP@C powder ratio, and the finally obtained powders are denoted as LFP@C/Ga-1, LFP@C/Ga-2, and LFP@C/Ga-4, respectively.

4.2. Material Characterizations. The phase of LFP@C and LFP@C/Ga materials was characterized using a Dutch Panaco Xpert3 Powder (Cu Kα radiation) with a measurement step of 0.05° in the 2θ range of 10–90°. The microscopic morphology of the samples was measured using a SU8020 field emission scanning electron microscope. TEM and high-resolution TEM images were obtained using a Tecnai G2 F20 S-TWIN (200 kV) electron microscope, and XPS was performed on a Thermo escalab 250Xi photoelectron spectrometer.

4.3. Electrochemical Measurements. CR2016 half cells were assembled for electrochemical performance tests. The cathodes were prepared with LFP@C (or LFP@C/Ga, 80 wt %) as the active material, polyvinylidene fluoride (10 wt %) as the binder, super-P (10 wt %) as the conductive agent, and sufficient N-methyl-2-pyrrolidone as the solvent. The prepared slurry was uniformly coated on aluminum foil and then dried under vacuum at 110 °C for 10 h. After cooling to room temperature, it was rolled five times on a roll press at a certain pressure and then pressed into 14 mm diameter round electrode sheets. After weighing on a high-precision electronic balance, the mass of the active material of the electrode is calculated, and the specific capacity could be calculated according to the mass of the active material. CR2016 half cells were assembled in a high-purity argon glove box with metal Li as the anode and LP30 as the electrolyte [1 M LiPF₆ in a mixture of ethylene carbonate, ethylmethyl carbonate, and dimethyl carbonate (1:1:1 by volume)]. The fabricated coin batteries were placed for 24 h and then tested in a LANHE battery test system with a voltage range of 2.0–4.2 V (1 C = 170 mA g⁻¹). EIS testing and CV were performed on a Biologic SP-150 electrochemical workstation with 5 mV ac signal over the impedance test frequency range of 10 mHz–100 kHz and 0.1 mV s⁻¹ CV test rate.

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Notes

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