Preparation and Electrochemical Performance of V$_2$O$_3$-C Dual-Layer Coated LiFePO$_4$ by Carbothermic Reduction of V$_2$O$_5$

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The V$_2$O$_3$-C dual-layer coated LiFePO$_4$ cathode materials with excellent rate capability and cycling stability were prepared by carbothermic reduction of V$_2$O$_5$. X-ray powder diffraction, elemental analyzer, high resolution transmission electron microscopy and Raman spectra revealed that the V$_2$O$_3$ phase co-existed with carbon in the coating layer of LiFePO$_4$ particles and the carbon content reduced without graphitization degree changing after the carbothermic reduction of V$_2$O$_5$. The electrochemical measurement results indicated that small amounts of V$_2$O$_3$ improved rate capability and cycling stability at elevated temperature of LiFePO$_4$/C cathode materials. The V$_2$O$_3$-C dual-layer coated LiFePO$_4$ composite with 1wt% vanadium oxide delivered an initial specific capacity of 167 mAh/g at 0.2 C and 129 mAh/g at 5 C as well as excellent cycling stability. Even at elevated temperature of 55 °C, the specific capacity of 151 mAh/g was achieved at 1 C without capacity fading after 100 cycles.

Key words: Lithium iron phosphate, Vanadium oxide, Carbon coating, Li-ion battery

I. INTRODUCTION

LiFePO$_4$ has attracted extensive attention as cathode material for the large-sized lithium-ion batteries in application of electric vehicles (EVs) and the energy storage systems, owing to its excellent safety and long lifespan [1]. In the last work, huge advances have been made to improve intrinsically poor electronic conductivity and slow Li$^+$ extraction-insertion kinetics, including surface coating or admixing with electronically conductive materials [2-6], reducing particle size to nanoscale and controlling morphology [7-11], and doping with supervalent cations [12-16]. Nanostructure design can shorten Li$^+$ transport distance and bulk doping is an effective way to expand the lattice paths, both of which can facilitate the Li$^+$ insertion-extraction kinetics. Surface coating is an indispensable technique in commercial products, in order to enhance the electronic conductivity of LiFePO$_4$.

Coating a conducting component, such as carbon, metals or conducting polymers on the particle surface is very effective to improve the electronic conductivity of LiFePO$_4$. Among them, carbon coating is particularly attractive due to its high conductivity, low cost for sources and preparation technology, and excellent chemical stability in the battery. On one hand, a homogeneous coated carbon layer can definitely improve the electronic conductivity between the LiFePO$_4$ particles. On the other hand, the rigorous carbon layer can effectively suppress the particles agglomeration during the solid-state preparation of LiFePO$_4$ [17]. Both these two points require a thick carbon layer coating, inevitably along with a compromise to volumetric energy density [18]. A combination of carbon coating and particle refinement for LiFePO$_4$ has been commercialized in the state-of-the-art battery industry. Many researches focus on carbon coating on LiFePO$_4$ particles by firing one carbon source (organic or polymeric compounds) during or after the LiFePO$_4$ synthesis [2-5]. However, it is difficult to meet the rigorous requirement of applications in EVs and smart grids by simple carbon coating. Recently, introduction of the second phase has been proven a promising route to satisfy the development of LiFePO$_4$. Oh et al. reported a double carbon coating on microscale nanoporous LiFePO$_4$ to improve the uniformity of carbon coating combining with high tap density [4]. Carbon coated FePO$_4$ was first prepared by using sucrose as the first carbon source, and finally the LiFePO$_4$/C microspheres containing about 0.5wt% carbon with a high tap density of 1.5 g/cm$^3$ were synthesized by using pitch as the second carbon source. Other non-carbon second phase (e.g. metal oxides, polymers) coatings were widely reported to modify the LiFePO$_4$ surface [19-22]. Metal oxide has been used to improve the performance of LiFePO$_4$. It was also found that CeO$_2$, ZrO$_2$ and TiO$_2$ can not only enhance the electrochemical performance but also improve the thermal stability. The metal oxide layer functioned as a protecting layer against HF was attacked from the
electrolyte [23]. As a result, ferrous dissolution in the electrolyte can be effectively suppressed, and thus the electrochemical performance of LiFePO$_4$, especially the cycling lifetime, was enhanced at both room temperature and elevated temperature.

Most recently, vanadium oxides have become one of the most attractive candidates as surface coating material for various cathode materials [24–27]. V$_2$O$_3$ and VO$_2$ have been extensively investigated as a protective surface layer on LiCoO$_2$, LiNiO$_2$, LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$, and Li$_{1.2}$Ni$_{0.16}$Co$_{0.08}$Mn$_{0.56}$O$_2$ particles against side reactions with the electrolyte and the cations dissolution into the electrolyte. However, just similar to most metal oxides, the low electronic conductivity of V$_2$O$_3$ results in its failure as the surface layer of LiFePO$_4$ particles. It is interesting to recognize that V$_2$O$_3$ exhibits quasi-metallic conductivity of over 10$^{-3}$ $\text{S/cm}$ at room temperature, which is even higher than V$_2$O$_5$ by 6–7 orders of magnitude [28–31]. Recently, Jin et al. used ammonium metavananadate as the vanadium source to synthesize V$_2$O$_5$-modified LiFePO$_4$/C materials via a one-step solid-state process [32]. The V$_2$O$_5$-modified LiFePO$_4$/C materials exhibit improved rate and low-temperature performance. However, during the one-step process, the adjustment on the V$_2$O$_5$ coating layer on the LiFePO$_4$ particles is still a big challenge.

In this work, we attempt to develop a novel approach for V$_2$O$_5$/C dual-layer coating on LiFePO$_4$ by carbothermal reduction of V$_2$O$_5$. As illustrated in Fig.1, a thick carbon layer on the carbon-coated LiFePO$_4$ is facile to form a uniform coating and also effectively limit the growth of LiFePO$_4$ particles. But the high content of carbon will significantly reduce the tap density of the LiFePO$_4$/C composite and thus cause the energy density of the related batteries. Herein, V$_2$O$_3$ as the second phase is introduced into the LiFePO$_4$ composite by the carbothermal reduction of V$_2$O$_5$ (2C+V$_2$O$_5$→V$_2$O$_3$+2CO). During the carbothermal reduction process of V$_2$O$_5$, partial carbon is transferred into CO gas so that the resulting thin carbon layer is helpful to achieve the high tap density of LiFePO$_4$ materials. In addition, V$_2$O$_3$ is expected to give more efficient protection on LiFePO$_4$ against the electrolyte without reducing the electronic conductivity so that the cycling stability of LiFePO$_4$ at elevated temperature can be improved.

II. EXPERIMENTS

A. Synthesis of V$_2$O$_5$/C coated LiFePO$_4$

Firstly, LiFePO$_4$/C composite was prepared by a simple solid-state reaction. A mixture of ferrous oxalate hydrate (FeC$_2$O$_4$·2H$_2$O), ammonium dihydrogen phosphate (NH$_4$H$_2$PO$_4$) and lithium carbonate (Li$_2$CO$_3$) in a stoichiometric molar ratio (1:1:0.53) was grounded in cyclohexane for 8 h by wet ball-milling at the rate of 300 r/min. After being dried at 80 ℃, the mixture was heated at 350 ℃ for 6 h under N$_2$ atmosphere to obtain the intermediate powders. Then, the intermediate was mixed with polyvinyl alcohol (PVA, as carbon source) and milled for 4 h under the same conditions as above. Here, the weight of PVA was 20wt% of the final LiFePO$_4$. After the milling and dry, the collected powders were subsequently sintered at 700 ℃ for 5 h under N$_2$ atmosphere to get the LiFePO$_4$/C composite. In order to achieve V$_2$O$_5$/C dual-layer coating, the LiFePO$_4$/C composite was mixed with different amounts of V$_2$O$_5$. After 4 h milling and 5 h sintering, the V$_2$O$_5$/C dual-layer coated LiFePO$_4$ composites were obtained through the carbothermal reduction of V$_2$O$_5$. The obtained V$_2$O$_5$/C coated LiFePO$_4$ composites were named as V0, V1, and V5, corresponding to 0wt%, 1wt%, and 5wt% V$_2$O$_5$ addition, respectively.

B. Characterization and electrochemical measurements

The crystal structures of the V$_2$O$_5$/C coated LiFePO$_4$ composites were identified by X-ray diffraction (XRD) measurements (D/max2500V) using Cu Kα ($\lambda$=1.5406 Å) radiation in 2θ range of 10°–60°. The amount of carbon in the samples was estimated using an elemental analyzer (Vario EL c). Raman spectra were obtained on a Raman spectrometer employing a 10 mW helium/neon laser with a wavelength of 632.8 nm. The morphologies of the LiFePO$_4$ composites were investigated by high resolution transmission electron microscopy (HRTEM) (JEM-2100F).

In order to make the electrode laminate for the electrochemical measurements, a slurry containing 80wt% samples as active material, 10wt% super P and 10wt% polyvinylidene fluoride (PVDF) dispersed in N-methyl-2-pyrrolidinone (NMP) was cast onto an aluminum current collector. After vacuum drying at 80 ℃, the laminate was punched into discs (Φ14 mm) for assembling the CR2032-type coin cells. The mass loading in the electrode was controlled at about 6 mg/cm$^2$. Celgard 2400 microporous polypropylene membrane was used as separator. The electrolyte was 1 mol/L LiPF$_6$ in a mixture of ethylene carbonate (EC) and diethyl carbonate.

![FIG. 1 Schematic illustration for the formation of the V$_2$O$_5$/C dual-layer coated on the LiFePO$_4$ particles by carbothermal reduction of V$_2$O$_5$.](image-url)
(DEC) (1:1 mass ratio). The cells were assembled in an Ar-filled glove box (MBraun) using highly pure lithium foil as the counter and reference electrode.

All the cells were galvanostatically charged and discharged in the range of 4.2–2.0 V at 0.2 C (1 C=170 mAh/g) for the two formation cycles on a multichannel battery cycler (Neware BTS2300, Shenzhen) at room temperature. Then the cycling tests were performed at a current rate of 1 C. For the high temperature tests, the cells were cycled at 55 °C in an oven. To evaluate the rate capability, the cells were charged to 4.2 V at 0.2 C and discharged to 2.0 V at various rates. Electrochemical impedance spectroscopy (EIS) of the cells was performed on a CHI 604D electrochemistry workstation (Shanghai Chenhua Instruments Co. Ltd.) with the frequency range and potential perturbation set as 100 kHz to 10 mHz and 10 mV, respectively.

III. RESULTS AND DISCUSSION

A. Structure and morphology

Figure 2 shows the XRD patterns and the carbon contents of the V2O3-C coated LiFePO4 composites. From Fig.2(a), it is obvious that the main phase in these composites is orthorhombic olivine LiFePO4 with a space group of Pnma. Besides the peaks of LiFePO4, the main diffraction peaks corresponding to (104), (110), (113) and (116) planes of V2O5 and (310) plane of V2O5 are clearly detected in V5. The formation of V2O5 is resulted from the carbothermic reduction of V2O3. With the addition of 5wt% V2O5, the carbothermic reduction is not performed completely so that still some V2O5 residues existed in V5. In V1, no any diffraction peak was shown owing to the low contents (<1wt%) of vanadium oxides, just similar to the ZrO2, SiO2 and CuO-coated LiFePO4/C composites [20, 33, 34]. Carbon in all the composites was amorphous and no diffraction peak was detected. Figure 2(b) shows the carbon contents in the composites by elemental analysis. Because of the carbon consumption during the carbothermic reduction of V2O3, the carbon content decreases with increasing the content of vanadium. The carbon contents in V0, V1, and V5 are 6.3wt%, 3.8wt% and 2.4wt%, respectively. It is interesting that the carbothermic reduction of V2O5 in V1 and V5 (Fig.3(b) and (c)), the surface layer on the LiFePO4 particles became quite complicated, and some clear lattice fringes were observed in the surface layer. After calculating the XRD pattern set as 100 kHz to 10 mHz and 10 mV, respectively.

FIG. 2  (a) XRD pattern of the V2O3-C dual-layer coated on the LiFePO4 nanoparticles and (b) the relationship of carbon content vs. vanadium oxide content.

To further determine the surface structure of the V2O3-C LiFePO4 composites, we observe these composites by HRTEM (Fig.3). As shown in Fig.3(a), a carbon layer with the thickness of ~4 nm was coated on the surface of LiFePO4 particle in V0. This carbon was amorphous and uniform. However, after the carbothermic reduction of V2O5 in V1 and V5 (Fig.3(b) and (c)), the surface layer on the LiFePO4 particles became quite complicated, and some clear lattice fringes were observed in the surface layer. After calculating the plane spacing, we can confirm that some V2O3 grains exist in the surface coating layers of V1 and V5. Hence, the surface of LiFePO4 particles in V1 and V5 is actually modified by V2O3 grains that are embedded in an amorphous carbon layer.

Jin et al. claimed that the presence of vanadium oxide can increase the degree of graphitization in the LiFePO4/C composite [32]. Raman spectrum is an effective method to detect the graphitization degree of the carbon component. As shown in Fig.4, each spectrum consists of two broad peaks at 1350 and 1600 cm−1, corresponding to the D-band and G-band, respectively. G-band is a typical characteristic of graphitic carbon, but D-band is usually related to the defects, edge sites and pores [35, 36]. According to previous literatures [37, 38], these two peaks can be fitted with four separated dotted-line peaks at 1194, 1347, 1510, and 1585 cm−1, respectively. The peaks at 1347 and 1585 cm−1 are contributed to sp2-type carbon. While...
FIG. 3 HRTEM images of (a) V0, (b) V1, and (c) V5.

FIG. 4 Raman spectra of V0, V1, and V5. 1: 1194 cm\(^{-1}\), 2: 1347 cm\(^{-1}\), 3: 1510 cm\(^{-1}\), 4: 1585 cm\(^{-1}\).

the peaks at 1194 and 1510 cm\(^{-1}\) reflect to sp\(^3\)-type carbon. Herein, the degree of graphitization of carbon can be calculated by the integrated intensity ratio \(I_{\text{sp}^2}/I_{\text{sp}^3}\), where \(I_{\text{sp}^2}\) and \(I_{\text{sp}^3}\) are the total areas of the sp\(^2\)-type peaks (1347 and 1585 cm\(^{-1}\)) and the sp\(^3\)-type peaks (1194 and 1510 cm\(^{-1}\)). Herein, the \(I_{\text{sp}^2}/I_{\text{sp}^3}\) values of V0, V1 and V5 are 1.76, 1.78 and 1.79, respectively. Therefore, it is concluded that the graphitization degree of the carbon component did not change during the carbothermic reduction of V\(_2\)O\(_5\).

B. Electrochemical performance

Figure 5 shows typical initial charge-discharge voltage profiles of V\(_2\)O\(_5\)-C coated LiFePO\(_4\) composites. The tests were performed galvanostatically at 0.2 C in the range 2.0–4.2 V. The charge-discharge voltage profiles appeared with the typical voltage plateau (at 3.45 V vs. Li\(^+\)/Li), which is attributed to the two-phase reaction of the \((1-x)\)FePO\(_4\)+\(x\)LiFePO\(_4\) system. The initial discharge capacities of V0, V1, and V5 are 147, 167, and 162 mAh/g, respectively. The V\(_2\)O\(_5\)-C coated LiFePO\(_4\) composites (V1 and V5) exhibited a higher reversible capacity than the pristine LiFePO\(_4\)/C composite (V0). Especially for V1, its initial capacity of 167 mAh/g at 0.2 C is over 98.6% of the theoretical capacity of LiFePO\(_4\). In addition, the charge and discharge voltage plateaus of V0 and V1 are very close. But V5 has the slightly lower discharge voltage plateau than the others. The gap between charge and discharge voltage plateaus, which is one of the indicators of polarization, of V5 is bigger than that of V1. The high polarization of V5 is possibly attributed to the existence of non-conductive V\(_2\)O\(_5\).

In order to further explain the difference of the electrochemical behaviors between V0, V1 and V5, electrochemical impedance spectra were carried out after the initial cycle (Fig.6). All impedance curves include a semicircle in high-to-medium frequency region and an inclined line in low frequency region. The semicircle is due to the charge transfer impedance and the inclined line is considered as Warburg impedance, which repre-
FIG. 6 Nyquist plots of the cells using V0, V1, and V5 after the initial cycle.

sents lithium-ion diffusion process. Here it is clear that V1 has the lowest charge transfer impedance among three composites, indicating the fast transfer rate of Li ions and electrons in V1. The contributions of electron conduction and lithium transport from the V2O3-C dual-layer promote together the excellent electrochemical performance of V1.

The cycling performance of V0, V1, and V5 at room temperature and elevated temperature is shown in Fig.7. Figure 7(a) shows the cycling behaviors of these three samples at 25 °C at 1 C. At the first cycle after the two formation cycles, the discharge capacities of V0, V1, and V5 are 129, 152 and 143 mAh/g, respectively. After 100 cycles, V0 and V1 have similarly negligible capacity fading, but V5 exhibits a gradual capacity drop from the initial 143 mAh/g to 117 mAh/g. Therefore, the coating layer in V5 composed of too much vanadium oxides (5wt%), especially including V2O5, is not stable enough to long-term charge-discharge cycling. However, V0 and V1 both have the excellent cycling stability, and the V2O3-C dual-layer coated LiFePO4 composite delivers the higher capacity than V0 at 1 C at room temperature. The cycling stabilities of V0 and V1 at elevated temperature (55 °C) at 1 C are further compared in Fig.7(b). The initial discharge capacities of V0 and V1 are 151 and 158 mAh/g. During 100 cycles, V1 has no capacity fading, but V0 exhibits a gradual capacity drop after the 80th cycle. According to previous studies [39, 40], it is a common problem that the LiFePO4/C cathode material has capacity attenuation at elevated temperature. The main reason is that the decomposition of materials and side reactions would occur at electrode/electrolyte interface [41]. The reaction between LiFePO4 and the electrolyte made a part of Fe^{2+} ions dissolve into the electrolyte, which resulted in the cycling fading of LiFePO4/C (V0). Basically, it is concluded that the coating of vanadium oxide in V1 can suppress the Fe^{2+} dissolution and improve the cycling stability of LiFePO4 at elevated temperature.

The discharge profiles of LiFePO4/C and V2O3-C dual-layer coated LiFePO4 composites at different rates are shown in Fig.8. All the cells using V0, V1 and V5 as cathode material were charged at the same current of 34 mAh/g (corresponding to 0.2 C rate) to ensure identical initial conditions for each discharge and then discharged at progressively increasing rates from 0.2 C (34 mAh/g) to 5 C (850 mAh/g). The electrode polarization becomes larger with the increase of current rate due to the limitation of electrochemical kinetics (Fig.8 (a)–(c)). Among the three LiFePO4 composites, V1 displays the best rate performance, with the discharge capacities of about 167, 161, 156, 147 and 129 mAh/g at 0.2, 0.5, 1, 2, and 5 C, respectively. From Fig.8(d), it is distinct that V1 exhibits the highest discharge capacity at all rates. However, the discharge capacity decreases sharply for V5, especially at the high rate of 5 C. The high-rate discharge performance and excellent cycling stability of V1 indicated that the V2O3-C dual-layer coating improves surface electronic conductivity of LiFePO4 particles and decreases the thickness of surface carbon layer, resulting in the excellent rate performance and cycling stability at elevated temperature.

IV. CONCLUSION

In this study, the V2O3 second phase was successfully impregnated into the surface carbon layer of the LiFePO4/C cathode and the carbon content reduced without graphitization degree changing by carbothermic reduction of V2O5. The comparing study on the
FIG. 8 Rate discharge curves of the cells using (a) V0, (b) V1, and (c) V5 at 0.2, 0.5, 1, 2, 5 C rates, as arrows show. (d) Discharge capacity values.

electrochemical performance of the V$_2$O$_3$-C dual-layer coated LiFePO$_4$ and the pristine LiFePO$_4$/C composites indicates that small amounts of V$_2$O$_3$ significantly improved rate capability and cycling stability at elevated temperature of LiFePO$_4$/C cathode materials in lithium ion batteries. The V$_2$O$_3$-C dual-layer coated LiFePO$_4$ with 1 wt% vanadium oxide shows excellent electrochemical performances with initial specific capacity of 167 mAh/g at 0.2 C and the specific capacity of 151 mAh/g at 1 C maintains no fading after 100 cycles at 55 °C. The dual-layer coating of carbon and V$_2$O$_3$ by the carbothermic reduction of V$_2$O$_5$ on the LiFePO$_4$ particles can not only improve the electronic conductivity, but also suppress the dissolution of Fe$^{2+}$ and improve its cycling stability at elevated temperature. In addition, this coating approach is facile to reduce the coated carbon content without the compromise on the conductivity and particles agglomeration, which is very attractive to increase the energy density of the state-of-the-art LiFePO$_4$ batteries.

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