PREPARATION OF LIFEPO4 · $LI_3V_2(PO_4)_3$/C CATHODE MATERIALS BY SOLID STATE METHOD

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Abstract- In this study, the lithium carbonate, ferric oxalate, ammonium hydrogen phosphate and ammonium metavanadate were used as raw materials to synthesize the carbon-coated lithium iron phosphate/lithium vanadium phosphate ($LiFePO_4 \cdot Li_3V_2(PO_4)_3$/C) composite cathode materials through the solid state reaction at different calcining temperatures of 700°C, 750°C and 800°C for 10 h under a 95% argon/5% hydrogen atmosphere and the ratio of iron: vanadium= 7:3. The carbon coating was achieved at 350°C for 4 h at 700°C for 10 h in an atmosphere of 95% argon /5% hydrogen. The results show that the calcination temperature has a significant effect on the electrochemical performance of $LiFePO_4 \cdot Li_3V_2(PO_4)_3$/C composite cathode materials. The discharge capacity at 0.1C/0.1C obtained from the cathode materials prepared at different calcination were 108 mAh/g at 800°C, 121 mAh/g at 750°C, 133 mAh/g at 700°C, 130 mAh/g for 650°C, and 129 mAh/g for 600°C, respectively.

Index Terms- lithium iron phosphate, carbon coating, solid phase method, cathode material, lithium ion battery

I. INTRODUCTION

At present, the energy crisis and environmental pollution problems are becoming more and more serious, which seriously affects the sustainable development of economy and society [1]. The search for clean energy alternative to fossil fuels has become a research trend in the world, but the solar energy and wind energy will be unstable because of weather changes, so many researchers develop the lithium ion battery technology to solve the above problems [1-3]. Among the lithium ion secondary battery, lithium iron phosphate battery is considered to be a low theoretical cost due to the low cost, environmental friendliness, cycling stability, and its high theoretical capacitance of 170mAh/g and thus is worthy to study [4-6]. However, lithium iron phosphate has a bottleneck for commercial applications because of low lithium ion diffusion rates and low electronic conductivity [7, 8].
Two methods have been used to improve the electronic conductivity of lithium iron phosphate. One is to synthesize smaller and monodisperse cathode particles for shortening the Li^+ ions diffusion path. Another way is to dope some metal ions into the crystal structure of lithium iron phosphate or to coat a carbon layer on the particle surface of lithium iron phosphate to improve the conductivity and enhance the oxidation and reduction potential [9, 10]. According to our knowledge, lithium phosphate and vanadium phosphate have the same crystal structure and space group, and lithium vanadium in 3.59, 3.67 and 4.06V appear three redox platforms, so if the use of lithium vanadium phosphate instead of lithium iron phosphate, will be expected to produce a higher oxidation-reduction potential. Therefore, in this study, we prepared the carbon-coated lithium iron phosphate/lithium vanadium phosphate composite cathode materials to enhance its electrochemical properties [11-13].

II. EXPERIMENTAL

6.30 g of iron oxalate, 2.96 g of lithium carbonate, 10.56g of dihydrogen phosphate, 3.51 g of ammonium metavanadate and acetone were placed in a ball mill and wet-milled for two hours with a planetary ball mill at 250rpm. The acetone was separated from the material by means of a vacuum concentrator. The obtained mixture was placed in a furnace for a first calcination at 150°C for 2 hours and then 400°C for 6 hours in an atmosphere of 95% argon/5% hydrogen to produce the precursor. The precursor powder was placed in a furnace for a second calcination at 150°C for 2 hours and then 700°C (or 750°C, 800°C) for 10 hours in an 95% argon/5% hydrogen atmosphere to obtain the lithium iron phosphate/lithium vanadium phosphate composites. The product powder and the sucrose were placed in a planetary ball mill and the ball milling process was conducted at 250 rpm for one hour. Then, the mixture was spray dried to form a spherical secondary aggregate and placed in a furnace for calcination at 350°C for 4 hours at 700°C for 10 hours in an 95% argon/5% hydrogen atmosphere to obtain the carbon-coated lithium iron phosphate/lithium vanadium phosphate composites. The effect of calcination temperature on the electrochemical properties of these composite cathode materials was discussed.
The crystalline phases of the synthesized materials were characterized by X-ray powder diffraction measurement using Cu Ka radiation. The diffraction angle was scanned from 10° to 70° at the scanning

speed of 0.02°/s. SEM (Hitachi/S-2600H) is used for observing the morphology of the prepared powders. The structural variations of carbonaceous material in the multiple carbon coated $LiFePO_4 \cdot Li_3V_2(PO_4)_3$/C materials are identified by Raman spectroscopy (Confocal micro-Renishaw). The electrochemical measurements are performed by using CR2032 type coin cells with lithium anode assembled in an argon filled glove box. For the preparation of the $LiFePO_4 \cdot Li_3V_2(PO_4)_3$/carbon cathode electrode, the carbon coated $LiFePO_4 \cdot Li_3V_2(PO_4)_3$/carbon composite and Super P are blended. Then, polyvinylidene fluoride (7 wt.%) dissolved in N-methyl-2-pyrrolidone is added in and stirred for 3h. Typically, the weight ratio of active material, con-ductive additive and PVDF is 85:5:10. Subsequently, the resultant slurry, pasted on Al foil, is dried at 120°C under vacuum for 2 h. The electrolyte is 1.0M $LiPF_6$ in ethylene carbonate (EC) and dimethylcarbonate (DMC) (1:1, v/v). Li-foil and polyethylene micro-porous film are used as the counter electrode and separator, respectively. The cells are charged and discharged over a voltage range of 2.5-4.3 V at 0.1 C.

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of as-prepared $LiFePO_4 \cdot Li_3V_2(PO_4)_3$/C composite cathode materials prepared at different calcining temperature. The XRD patterns of the as-prepared $LiFePO_4 \cdot Li_3V_2(PO_4)_3$/C composites agrees with that reported in the literature [1]. The diffraction peaks in the patterns of $LiFePO_4 \cdot Li_3V_2(PO_4)_3$/C are composed of both LFP and LVP peaks and no other phase was observed. The sharp peaks in the patterns show that the composite materials are well crystallized. which may be attributed to the Fe-doped LVP. In earlier literatures [14,15], the LFP doping with Fe^{2+} as well as the LVP doping with V^{3+} are beneficial to their conductivity and electrochemical performance. It is worthy to notice that the XRD pattern for calcination temperature over 700°C, a peak at 2θ=13° was observed, and disappear as the temperature increase. the content of carbon bears samples are similar. The electrochemical differences can be attributed to the different calcining temperature.

Figure 2 shows the SEM images of as-prepared $LiFePO_4 \cdot Li_3V_2(PO_4)_3$/C powders prepared from different calcining temperature. The primary particles agglomerated during elevated temperature treatment to form the irregular secondary particles with the size of 10-15 micrometer.

The porous structure of these secondary particles is advantage for the penetration of electrolyte. It is worthy to notice that the tabular grain formed obviously as the calcination temperature reached to 800°C and with the calcining temperature decreased, the tabular grain is gradually reduced.

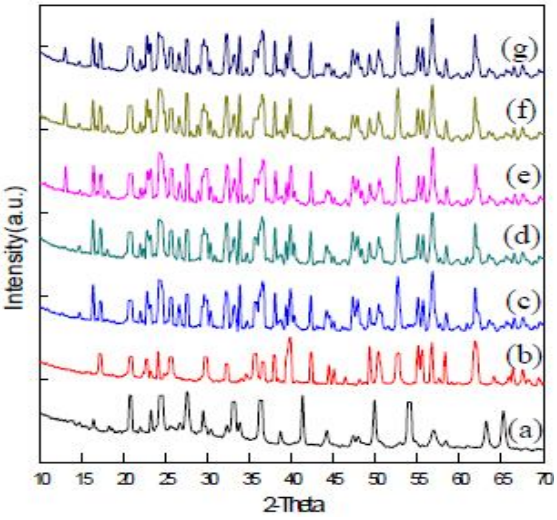


Fig. 1 XRD patterns of (a) LVP, (b)LFP, (c)LFP/LVP (800℃) (d)LFP/LVP(750℃) (e) LFP/LVP (700℃) (f)LFP/LVP (650℃) (g) LFP/LVP (600℃)

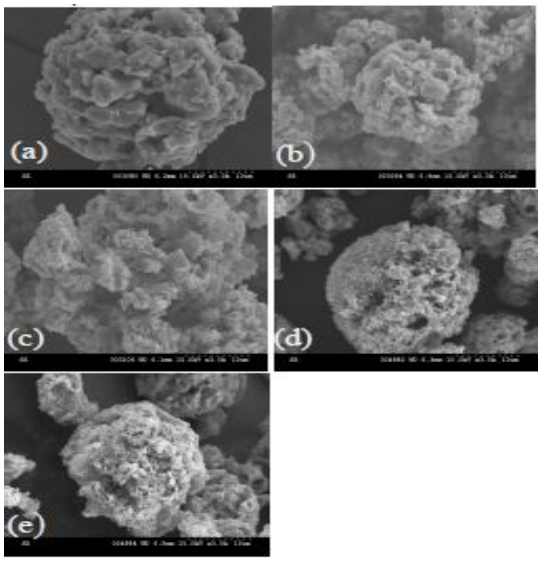


Fig. 2 SEM images of (a)LFP/LVP (800℃) (b)LFP/LVP (750℃) (c) LFP/LVP (700℃) (d)LFP/LVP (650℃) (e)LFP/LVP (600℃)

Figure 3 shows the Raman spectra of $LiFePO_4 \cdot Li_3V_2(PO_4)_3$/C calcined at 600°C, 650°C, 700°C, 750°C, 800°C, respectively. The related peak intensity of Raman spectra is also listed in Table 1. It is found that the strong Raman band at 1600 cm^{-1} is one of the G modes, which has been assigned to the vibrational mode corresponding to the movement in opposite directions of two neighboring carbon atoms in a graphene sheet. The 1358 cm^{-1} band is assigned to the D mode which originally is not a Raman-active mode of the graphene sheet. This mode is generally associated with the defects in the curved graphene sheet and staging disorder. The peak intensity ratio (I_D/I_G) between 1358 and 1600 cm^{-1} in Raman shifts was calculated to be an index of the degree of

disordering. An increase in the I_D/I_G ratio reflects more disorder [16]. In Table 1, it indicates that the cathode materials prepared from 700°C and 750°C have a higher ratio of graphitic carbon in carbon layer and have a more complete carbon coverage on particle surface.

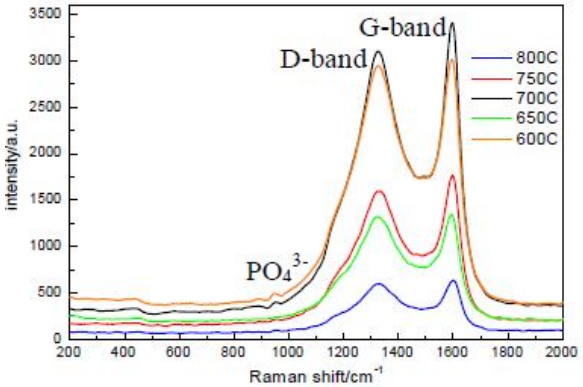


Fig. 3 Raman spectra of $LiFePO_4 \cdot Li_3V_2(PO_4)_3$/C calcined at 600°C, 650°C, 700°C, 750°C, 800°C

$LiFePO_4 \cdot Li_3V_2(PO_4)_3$/C	D-band Intensity	G-band Intensity	PO_4^{3-} Intensity	$R=I_D/I_G$	$(I_D+I_G)/PO_4^{3-}$
800°C	624.16	718.29	124.78	0.87	10.76
750°C	1693.35	1840.27	250.63	0.92	14.10
700°C	2346.81	2533.6	389.96	0.93	12.52
650°C	1414.48	1414.48	274.02	1.00	10.32
600°C	3018.25	3081.71	574.95	0.98	10.61

Table 1 The peak intensity of D band, G band, and PO_4^{3-} in Raman spectra for LFP/LVP/C obtained from different calcining temperatures.

Figure 4 shows the charge/discharge profiles of $LiFePO_4 \cdot Li_3V_2(PO_4)_3$/C cathode composites for different calcination temperatures. The cathode material delivers a first cycle with the discharge capacity of 108 mAh/g for 800°C, 121 mAh/g for 750°C, 134 mAh/g for 700°C, 130 mAh/g for 650°C, and 129 mAh/g for 600°C, respectively.

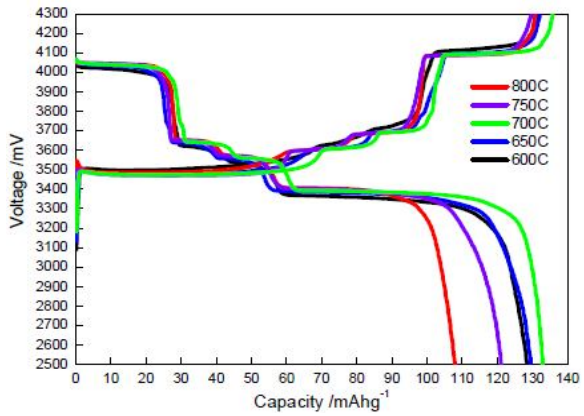


Fig. 4 Charge/discharge profiles of LFP/LVP/C composites prepared from different calcining temperature

All samples exhibited a typical flat charge and discharge potential plateau in the potential range of 3.5V 、3.4V and 4.3V, respectively. The best discharge capacity obtained in the present study is about 134mAh/g at 0.1C for the $LiFePO_4 \cdot Li_3V_2(PO_4)_3$/C cathode materials prepared from 700°C.

CONCLUSIONS

The carbon-coated lithium iron phosphate/lithium vanadium phosphate ($LiFePO_4 \cdot Li_3V_2(PO_4)_3$/C) composite cathode materials were successfully synthesized by using the solid state reaction at different calcining temperatures. Because lithium phosphate and vanadium phosphate have the same crystal structure and space group, the addition of vanadium in lithium iron phosphate can be expected does not affect its crystal structure. XRD patterns confirmed that the characteristic peaks are not offset. It was found that the material properties and thus the discharge capacity were changed due to the different calcination temperature. The best discharge capacity at 0.1C was 134 mAh/g that was obtained from the cathode materials through the calcination temperature of 700℃.

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