HYDROTHERMAL SYNTHESIS OF SILVER EMBEDDED LiFePO_4/C

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ABSTRACT

Silver embedded LiFePO_4/C were prepared by direct hydrothermal synthesis of Li_2CO_3 , FeSO_4 and H_3PO_4 in mixed solution of Glucose and $\text{Ag}(\text{NH}_3)_2\text{OH}$. Samples were characterized by XRD, SEM and galvanostatic charge-discharge test. Results show that silver particles are located in the inner part of synthesized diamond-like and rectangular particles. The reversible capacities of prepared samples are 141.3 mAh g^{-1} and no capacity loss are detected after 800 cycles at 1C .

Key words: Li-ion batteries; LiFePO_4 ; Hydrothermal; Silver

INTRODUCTION

Lithium iron phosphate (LiFePO_4) has received considerable attention as a cathode material for lithium ion batteries because of its low toxicity and good capacity retention [1-2]. The performance of LiFePO_4 , however, is limited by its poor electronic conductivity and by the inability of lithium ions to diffuse easily through the $\text{LiFePO}_4/\text{FePO}_4$ interface [3], which can result in a significant loss of capacity at high discharge currents. Most of the research groups take measures of preparing fine particles [4-7], coating the particles with electrically conductive materials [7-9] and doping other atoms [10-11] to overcome these limitations and good electrochemical performance are achieved. L. N. Wang et al [7] developed a simple, one step rheological phase reaction to synthesize LiFePO_4/C powders using PEG as the carbon source, and its electrochemical performance is satisfactory. In the paper, two approaches have developed to overcome this problem. One is to prepare evenly distributed diamond-like and rectangular LiFePO_4/C particles by hydrothermal method, the other is to embed silver particles in the inner part of the particles in addition to coat LiFePO_4 particles with carbon. Li_2CO_3 is developed as the lithium resources in the hydrothermal method which is seldom and most of the previous papers take LiOH or CH_3COOLi which are unstable to air, and so it limited the industrialized application. C.H. Mi et al [8] try to prepare $\text{LiFePO}_4/\text{C}+\text{Ag}$ composite particles by Sol-gel and Co-precipitation method but hydrothermal method can prepare particles with special morphology easier by controlling different experimental parameters. On the other aspect, wrapped silver particles and surface coated carbon improve the conductivity of LiFePO_4 effectively.

EXPERIMENTAL

Silver embedded LiFePO_4/C were prepared by direct hydrothermal synthesis of Li_2CO_3 , FeSO_4 and H_3PO_4 in the stoichiometric ratio of 1.5 : 1.0 : 1.0 and 1.5 : 1.0 : 3.0. First, Glucose was added into $\text{Ag}(\text{NH}_3)_2\text{OH}$ solution to obtain silver particle along with stirring and $\text{Ag} : \text{LiFePO}_4 = 1 : 99(\text{wt}\%)$. Second, FeSO_4 was mixed with Ascorbic acid in order to avoid Fe^{2+} was oxidized to Fe^{3+} . Third, Li_2CO_3 and H_3PO_4 were mixed with different molar ratios. At last, all solutions were quickly transferred to Parr reactor for up to 10h at 180°C , and all the reactions are under the protection of N_2 (99.9% purity). After the samples were cooled, the precipitates were filtered and dried at 65°C for 8h in vacuum oven. Dried samples were fired at 750°C for 5h to decompose residual glucose and ascorbic acid.

In order to testify the existence of conducting silver particles, prepared samples were dissolved in 11.6 mol/L HCl solution, stirred and filtered, residue of samples were obtained separately.

Samples and residue were characterized by X-ray diffraction using a PANalytical X Pert PRO diffractometer with Cu K α radiation. SEM observation of samples were performed on a JEOL scanning electrode microscope(JSM-5610LV),

Electrodes were made by dispersing 85wt.% active materials, 8wt.% carbon black and 7wt.% polyvinylidene fluoride(PVDF) binder in 1-Methyl-2-pyrrolidone solvent to form a slurry. The slurry was then spread uniformly on to a electrode slice and dried in the vacuum oven at 65°C for at least 12h. the cells were assembled in an argon filled glove-box(MBraun, Unilab, USA). The electrolyte was 1M LiPF_6 in a mixture of ethylene carbonate(EC) and dimethyl

carbonate(DMC)(1:1 by volume). The cells were galvanostatically charged and discharged in the voltage range of 2.7-4.2V versus Li/Li^+ counter electrode.

RESULTS AND DISCUSSION

Most of the reported papers about hydrothermal method took LiOH as Lithium resource and using Li_2CO_3 as starting materials was seldom. Reactions using Li_2CO_3 as starting materials in this paper could be described as follows:

Reaction (1) was difficult and not complete because partial products were LiH_2PO_4 and Li_2HPO_4 . $\text{NH}_3 \times \text{H}_2\text{O}$ was added in to mixed solution until pH value was 7 in reaction (2) in order to get LiFePO_4 grain easier. Obtained sample from reaction (1) was called sample 1 and the other one was sample 2.

XRD patterns of samples and residue of samples were shown in Fig.1 and 2. We performed a cell refinement to samples using MDI Jade 5.0 software. Samples were indexed in the orthorhombic system with space group Pmnb and cell parameters of sample 1 was, $a = 6.017(1) \text{ \AA}$, $b = 10.34(57) \text{ \AA}$, $c = 4.709(8) \text{ \AA}$ and $V = 293.1(9) \text{ \AA}^3$. sample 2 was, $a = 6.010(2) \text{ \AA}$, $b = 10.350(5) \text{ \AA}$, $c = 4.70(45) \text{ \AA}$ and $V = 292.6(7) \text{ \AA}^3$. Fig.2 showed XRD patterns of residue of samples. Ag and AgCl were detected and AgCl should be come from the reaction of HCl and minor silver salt contained in samples.

Fig.1 XRD patterns of sample 1 (a) and sample 2 (b).

Fig.2 XRD patterns of residue of sample 1 (a) and sample 2 (b).

Morphology for prepared samples were observed on SEM, as shown in Fig.3, samples were uniformly distributed. Sample 1 was composed of diamond and slightly agglomerated particles, particle size was 1-5 μm . Particles of sample 2 was rectangular and agglomerated, grain size was 1-8 μm .

Fig.3 Particle morphology of $\text{LiFePO}_4/\text{C}+\text{Ag}$ prepared by reaction (1) and (2).

Electrochemical performance of prepared samples were shown in Fig.4. Cycle performance of sample 1 are better than that of sample 2. After 1, 400, 500 and 800 cycles, the specific capacity of sample 1 are 111.1, 122.5, 133.2 and 141.3 mAh g^{-1} separately at 1C ($1\text{C}=150\text{mA g}^{-1}$); after 1, 400 and 800 cycles, the specific capacity are 87.4, 89.6 and 80.7 mAh g^{-1} separately at 15C. The specific capacity of sample 2 are 129.5, 130.6 and 126.3 mAh g^{-1} separately at 1C after 1, 200 and 300 cycles. Good cycle performance were achieved and it might because that LiFePO_4 grain grow up on the surface of reduced silver particles since $\text{Ag}(\text{NH}_3)_2^+$ ions were firstly reduced to Ag under stirring and Wrapped silver particles enhance the conductivity of LiFePO_4 .

Fig.4 Cycle performance of prepared samples at the current density of 750mA g⁻¹.

CONCLUSIONS

Diamond-like and rectangular particles of silver embedded LiFePO₄/C were successfully synthesized through hydrothermal reactions. At ambient temperature, the discharge capacities of sample 1 are 141.3 mAh g⁻¹, and no capacity loss were detected after 800 cycles at 1C. Good electrochemical performance could be correlated with wrapped silver particles which might lead to the enhancement of conductivity of individual particle.

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