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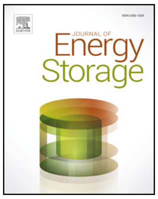

Influence of sintering temperature on the morphology and cycle performance of nanoscale porous materials $LiFe_{0.75}Mn_{0.25}PO_4/C$

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ABSTRACT

Nano porous materials $LiFe_{0.75}Mn_{0.25}PO_4/C$ were prepared by sol-gel method. The influences of sintering temperature on particle size, pore size distribution and cycling performance were studied. The results show that ratio of the mesopore in diameter 9.5 nm increases gradually with the increase of sintering temperature. The material sintered at 750 °C has high crystallinity, the particle size under 100 nm, the specific surface area of $80.3 m^2 g^{-1}$, about 3 nm carbon coating, and higher ratio of the mesopore in diameter 9.5 nm. These are beneficial to the diffusion of lithium ion and the transfer of electrons, and high electrochemical performance material has been obtained. The initial discharge specific capacity is $120.28 mAhg^{-1}$, it remains $80.71 mAhg^{-1}$ at 10C after 600 cycles.

1. Introduction

As a result of the existence of strong covalent bond P—O, olivine type $LiFePO_4/C$ has high security. Compared with Fe^{3+}/Fe^{2+} 3.4 V voltage platform, the Mn^{3+}/Mn^{2+} of 4.1 V voltage platform has high energy density, the preparation of olivine type $LiFe_{1-x}Mn_xPO_4/C$ has attracted wide attention.

Yamada etc. [1] prepared $Li(Mn_{0.6}Fe_{0.4})PO_4$ by solid phase method, and its discharge specific capacity is $160 mAhg^{-1}$ at $0.12 mA cm^{-2}$. Li etc. [2] prepared $LiMn_{0.75}Fe_{0.25}PO_4/C$ composite, its discharge specific capacity was $164 mA hg^{-1}$ at $0.28 mAcm^{-2}$. It is considered that the carbon coating of high conductivity and small particle size are the cause of high electrochemical performance. Martha etc. [3] synthesized nano particles $LiMn_{0.8}Fe_{0.2}PO_4/C$ by solid phase method, its discharge specific capacity is close to $100 mAhg^{-1}$ at 10C, its carbon content is 10%. The carbon coating of the high conductivity, nano scale particle (20–100 nm), high the specific surface area ($65 m^2 g^{-1}$) are the cause of the high rate performance. Wang etc. [4] prepared $LiMn_{0.8}Fe_{0.2}PO_4/C$ composite by solid state method, its discharge specific capacity is $122 mA hg^{-1}$ at 10C, and its carbon content is 4.1%. The high degree of crystallinity, nano size (40–100 nm) particle, high the specific surface area ($40.1 m^2 g^{-1}$) are the cause of the high rate performance. Liu etc. [5] prepared $LiMn_{0.8}Fe_{0.19}Mg_{0.01}PO_4/C$ by solid phase method, and the effect of carbon content on the electrochemical performance was studied, its discharge specific capacity is $125.7 mAhg^{-1}$ at 10C while its carbon content is 10.5%, and the discharge specific capacity is 109.6 $mAhg^{-1}$ while the carbon content is 4.1%. Yang etc. [6] synthesized $LiFe_{0.5}Mn_{0.5}PO_4/C$ by carbothermal reduction, coated with the 1 wt% $Li_4Ti_5O_{12}$, the average discharge specific capacity of 100 cycles is $138.3 mAhg^{-1}$ at 10C under 55 °C. The coating of high ionic conductive phase $Li_4Ti_5O_{12}$ improves the conductivity of the material and prevents the dissolution of the active material, thus having good cycle performance. Solid phase method has no special requirements for raw materials, such as solubility and so on, and has wide applicability.

The liquid phase method is advantageous for the preparation of homogeneous nanoscale materials. Oh etc. [7] prepared $LiMn_{0.85}Fe_{0.15}PO_4/C$ composite by spray drying combined with solid-phase sintering, and its discharge specific capacity is $121 mAhg^{-1}$ at 2C. Li etc. [8] prepared $LiMn_{0.8}Fe_{0.2}PO_4/C$ by sol-gel method, its discharge capacity is $86 mAhg^{-1}$ at 5C, and its carbon content is 33%. It is considered that the porous nanosized conductive phase acetylene black improves the electrochemical performance of the material. Li etc. [9] prepared graphene–$LiMn_{0.8}Fe_{0.2}PO_4/C$ composite by solvothermal method, the discharge specific capacity is $106 mAhg^{-1}$ at 10C. The conductive phase graphene improves the electrochemical performance. Yang etc. [10] prepared spherical $LiMn_{0.7}Fe_{0.3}PO_4/C$ by co-precipitation combined spray drying and solid-phase sintering. Its discharge specific capacity was $133 mAhg^{-1}$ at 10C. The porous morphology and

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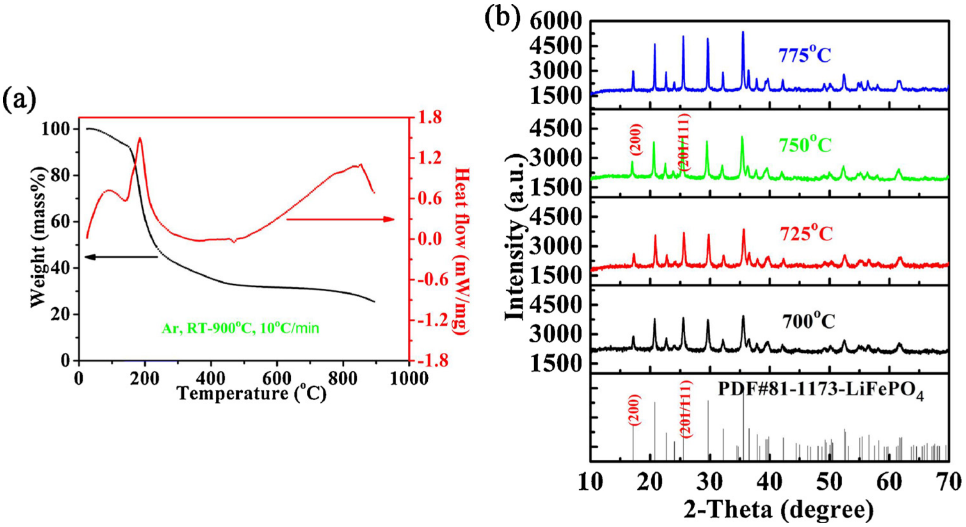

Fig. 1. (a) TG and DSC curves for the $LiFe_{0.75}Mn_{0.25}PO_4/C$ precursor, (b) XRD patterns of $LiFe_{0.75}Mn_{0.25}PO_4/C$ sintered at different temperatures.

homogeneous carbon layer improved the electrochemical performance of the material.

Preparation and process of materials determine the morphology, structure and electrochemical performances of materials. Therefore, it is very important to study the relationship between the preparation process parameters and the performances of materials. Cycle performance is a major standard of material performance. For the purpose, in this paper, nanoscale porous material $LiFe_{0.75}Mn_{0.25}PO_4/C$ was prepared by sol-gel method. The influences of sintering temperature on the crystallinity, particle size, morphology and cycle performance of the materials were investigated.

2. Experimental

2.1. Synthesis of $LiFe_{0.75}Mn_{0.25}PO_4/C$

The $LiFe_{0.75}Mn_{0.25}PO_4/C$ composite was prepared by a sol-gel method referred to the literature [11] and some changes were made. Firstly, a stoichiometric ratio of iron citrate and manganese acetate were dissolve in deionized water at 70 °C, following by adding citric acid as a carbon source (the mole amount of citric acid is 2 times as much as that of $LiFe_{0.75}Mn_{0.25}PO_4$). Besides, lithium hydroxide and ammonium dihydrogen phosphate were also separately dissolved in deionized water, then mixed and added into the front solution and kept stirring at 70 °C until the gel was generated. After that, the gel was dried at 90 °C under air and subsequently grinded by mortar and pestle. Finally, to obtain $LiFe_{0.75}Mn_{0.25}PO_4/C$ composite, the precursor powder was sintered in a tube furnace for 7 h under argon atmosphere. The effects of different sintering temperature (700 °C, 725 °C, 750 °C and 775 °C) on material performance were investigated.

2.2. Materials characterization

The thermal behavior of the precursor was determined by thermogravimetric (TG) and differential scanning calorimeter (DSC, NETZSCH STA 449F3, Germany) in Al_2O_3 crucibles under Ar atmosphere, the maximum temperature was set at 900 °C, and the heating rate was $10\,°C\,min^{-1}$. The structure of synthesized materials was identified by X-ray diffraction (XRD, MiniFlex 600, Rigaku), using Cu kα radiation over the 2θ range of 10° to 70°. The morphology of samples was observed by scanning electron microscopy (SEM, NOVA NANOSEM250, FEI company) and the microstructure of the material was observed on copper foil by transmission electron microscopy (TEM) with energy dispersive spectrometer (EDS) and high-resolution transmission electron microscopy (HRTEM, Tecnai G^2 TF30 S-Twin, FEI company). The carbon content of materials was characterized with infrared carbon-sulfur analyzer (Corey-230B, Kerui). N_2 adsorption and desorption test was carried out by Quantachrome Nova2400, BET was fitted with data under 0.25 P/P_o, and BJH was calculated according to the desorption branch.

2.3. Electrochemical measurements

Electrochemical performance of the materials was assessed using CR2025 coin-type cells. The cathode was made by mixing active material, super P and polyvinylidene fluoride (PVDF) in a weight ratio of 80:15:5 and stirred to slurry in *N*-methyl-2-pyrrolidone (NMP). Then the slurries were coated on aluminum foil by a doctor blade coater. The electrolyte was 1 M $LiPF_6$ in EC/DMC (1/1volume) solution. All cells were assembled in an argon-filled glove box with lithium metal as the anode. The rate performance and cycle performance were evaluated by battery test system (Neware) within the potential range of 2.0–4.5 V at 30 °C, charging mode is CC-CV, the cut-off current of constant voltage charging is 0.021 mA, the rate performance is carried out at different rates ($1C = 170\,mAg^{-1}$), the cycle performance is tested at 10C after 3 cycles at 0.1C, charge discharge current and specific capacity were calculated by the mass of active substances excluding carbon. After the rate performance finished, cyclic voltammetry (CV) measurement was carried out on a CHI660C electrochemical work station at $0.1mVs^{-1}$ ranging from 2.0 to 4.5 V.

3. Results and discussion

3.1. Materials characterization

As shown in Fig.1(a) TG and DSC curves of the $LiFe_{0.75}Mn_{0.25}PO_4/C$ precursor, the curves reflect the different reactions in the Ar atmosphere with the increase of temperature. From room temperature (RT) to 147.5 °C, the precursor has 7.3% of mass loss. It is mainly from the loss of adsorbed water, which corresponds to the 89.5 °C endothermic peak of DSC. From 147.5 °C to 375.7 °C, it has 55.4% of mass loss. It is from mainly the decomposition reaction of the precursor, which corresponds to the 184.3 °C endothermic peak of DSC. From 375.7 °C to 762.5 °C, it has 6.9% of mass loss. It is mainly from the decomposition reaction of the precursor furtherly and the generation reaction of $LiFe_{0.75}Mn_{0.25}PO_4$ crystal phase. The latter reaction corresponds to the 468.5 °C exothermic peak of DSC. It indicates that the crystal phase begins to form, and the reaction is completed at 762.5 °C. The