



Facile synthesis of porous LiNiVO_4 powder as high-voltage cathode material for lithium-ion batteries

Mu-lan QIN¹, Wan-min LIU¹, Shu-quan LIANG^{2,3}, An-qiang PAN^{2,3}

1. School of Chemistry and Chemical Engineering, Hunan Institute of Engineering, Xiangtan 411104, China;
2. School of Materials Science and Engineering, Central South University, Changsha 410083, China;
3. Key Laboratory of Nonferrous Metals Materials Science and Engineering, Ministry of Education, Central South University, Changsha 410083, China

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Abstract: Porous LiNiVO_4 powder was synthesized via solution combustion synthesis method using lithium nitrate, nickel nitrate, ammonium metavanadate and citric acid as raw materials. Thermogravimetry (TG) and differential scanning calorimetry (DSC), X-ray diffraction (XRD), Fourier-transform infrared (FT-IR) spectroscopy and transmission electron microscopy (TEM) were used to evaluate the structures and morphologies of samples. The results show that the calcination temperature has significant effect on the crystallinity and morphologies. Pure LiNiVO_4 flaky nanoparticles with a mean particle size around 20 nm can be readily prepared by calcining the precursor in air at 500 °C for 2 h. As a cathode material for lithium-ion batteries, the porous LiNiVO_4 powder exhibits a good structural reversibility.

Key words: lithium-ion battery; LiNiVO_4 ; cathode material; solution combustion synthesis; nanoparticle

1 Introduction

Inverse spinel LiNiVO_4 powder was proposed as a cathode material for lithium-ion batteries due to its high operation voltage of 4.8 V [1]. High voltage always possesses high energy density, thus the use of LiNiVO_4 is expected to enhance the energy density of lithium-ion batteries [2]. However, the electrochemical performance is strongly related to the synthesis processes [3] which result in different degrees of crystallinity, particles sizes and morphologies.

LiNiVO_4 prepared by the conventional solid-state reaction has the drawbacks of high temperature processing, long duration, large crystallite size and impurities [4–6]. These problems can be alleviated by soft chemistry reactions, such as sol–gel method [7,8], hydrothermal synthesis [9,10], solution precipitation method [11], rheological phase synthesis [12,13], polymerized complex method [14,15], Pechini method [16] and combustion synthesis [17–20]. Among these soft chemistry routes, the combustion synthesis is a versatile, simple and cost effective process for the

synthesis of multi-component oxide powders.

In this work, a modified combustion method was used by directly transferring the mixture precursor solution into an electrical oven. The resulting LiNiVO_4 powder was of highly porous and has good uniformity. Moreover, its electrochemical performance as a cathode material for lithium-ion battery was evaluated.

2 Experimental

2.1 Synthesis of LiNiVO_4

LiNiVO_4 nanoparticles were prepared by a facile solution combustion synthesis method. In a typical processing, lithium nitrate, nickel nitrate and ammonium metavanadate in a molar ratio of 1:1:1 ($n(\text{Li}):n(\text{Ni}):n(\text{V})=1:1:1$) were dissolved in de-ionized water. Then, a citric acid solution was added into the obtained solution under constant stirring and the molar ratio of total metal ions to citric acid was kept constant as 1:1. The resulting solution was heated at 50 °C under constant stirring to evaporate excess water, yielding a high concentration solution which was then placed in a preheated muffle furnace at 400 °C. The solution boiled and then

decomposed. The decomposition was accompanied by a mass of bubbles followed by the generation of gases such as NO_x and ammonia. The entire reaction was completed within 5 min, giving rise to a pale brown precursor powder. The precursor was then calcined at 400–600 °C for 2 h to get the yellow product.

2.2 Characterization

The thermal decomposition process of the precursor was investigated by thermogravimetry (TG) and differential scanning calorimetry (DSC) using a simultaneous TG–DSC thermal analyzer (NETZSCH STA 449 C) at a heating rate of 10 °C/min under air atmosphere. The phase structures of the synthesized LiNiVO_4 powders were determined by X-ray diffraction (XRD) (Rigaku D/max2500 XRD with $\text{Cu K}\alpha$ radiation, $\lambda=1.54178 \text{ \AA}$). Infrared (IR) spectra were recorded with a WQF-410 Fourier transform infrared spectrometer (FT-IR, Nicolet). A field emission transmission electron microscope (FETEM, JEOL JEM-2100 F) was used to characterize the structural morphologies of the synthesized products.

The LiNiVO_4 powders were assembled into coin-type cells (CR 2016) to evaluate their electrochemical properties. LiNiVO_4 powders, acetylene black and polyvinylidene fluoride (PVDF) binder in a mass ratio of 7:2:1 were dispersed in *N*-methyl-2-pyrrolidone (NMP) solution to prepare the slurry, which was coated on an aluminum foil and dried in a vacuum oven at 90 °C for 20 h to make the cathode. The half-cells were assembled in a glove box (Mbraun, Germany) filled with ultrahigh purity argon, using polypropylene membrane as the separator and 1 mol/L LiPF_6 dissolved in ethylene carbonate/dimethyl carbonate ($V(\text{EC})/V(\text{DMC})=1:1$) as the electrolyte. Cyclic voltammetry measurement was performed on a CHI660C electrochemical workstation (CHI660C, Shanghai, China) at a scan rate of 0.1 mV/s in the voltage range of 3.0–4.9 V (vs Li/Li^+). The galvanostatic charge–discharge characteristics of the cells were recorded with a Land battery tester (Land CT 2001A, Wuhan, China) at room temperature, and the specific capacity is based on the mass of active material only.

3 Results and discussion

3.1 Thermal analysis

The TG and DSC measurements were carried out for the precursor obtained by solution combustion synthesis method to find out the exact complete crystallization temperature of the LiNiVO_4 powder. The TG and DSC curves of the precursor are shown in Fig. 1. In the TG curve, the mass loss before 250 °C is due to

the removal of water molecule present in the precursor, and the DSC curve shows one distinguishable endothermic peak at about 100 °C. The decomposition process mainly occurs in the temperature range of 250–500 °C. The mass loss after 250 °C is attributed to the complex decomposition of lithium, vanadium and nickel citrates. The DSC curve shows three exothermic peaks with a peak maximum at 478 °C. The combustion nature of citric acid together with the presence of nitrate in the precursor gives rise to enormous heat energy for initiating the crystallization of LiNiVO_4 . At temperature higher than 500 °C, there is no mass loss. This indicates that the decomposition of precursor is completed at 500 °C.

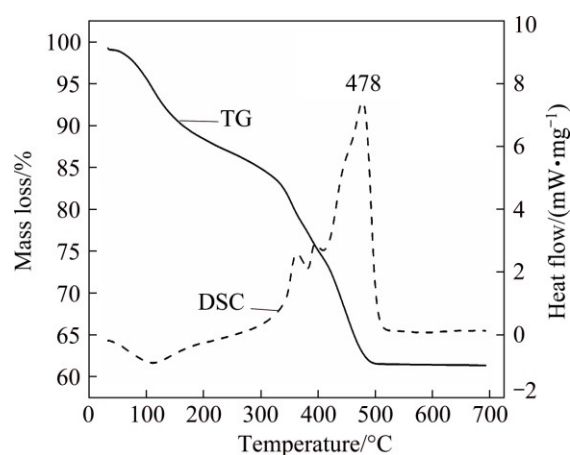


Fig. 1 TG and DSC curves of precursor

3.2 Structure and morphology

Figure 2 shows the XRD patterns of LiNiVO_4 obtained by calcining the precursor at different temperatures. From Fig. 2, it can be seen that some visible diffraction peaks of LiNiVO_4 compound appear in the pattern recorded at 400 °C. By increasing the heating temperature, the crystallinity of the samples increases and the main diffraction peaks become sharper.

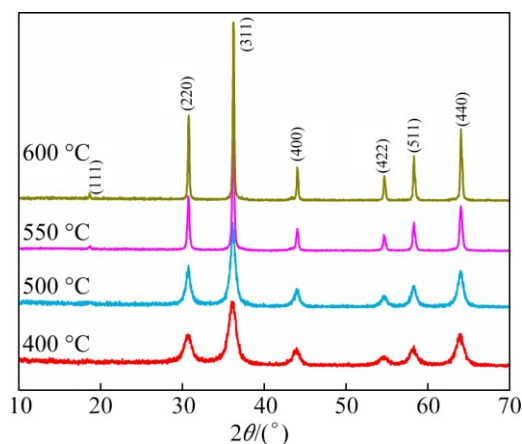


Fig. 2 XRD patterns of LiNiVO_4 powders obtained at various temperatures

From 500 °C, all the peaks of samples exhibit the characteristic diffraction lines of LiNiVO_4 without any miscellaneous phase, which is completely consistent with the pattern of JCPDS card No. 38–1395 [2] and indexed to the cubic system with space group $Fd\bar{3}m$. The main peaks for the material are labeled with (*hkl*) indexes. The XRD patterns also display a strong (220) line but (111) line is so weak that it can be hardly distinguished, which is ascribed to the inverse spinel structure of $\text{V}_{\text{tetra}}(\text{LiNi})_{\text{octa}}\text{O}_4$ [21,22]. The XRD results show that the LiNiVO_4 is synthesized successfully by calcining the precursor at 500 °C, and the temperature required for the formation of LiNiVO_4 is much lower compared with that required for the conventional solid state product [6].

The FT-IR spectra of the synthesized powders are shown in Fig. 3. In the sample obtained at 400 °C, the band at 3397 cm^{-1} is characteristic of the O—H group, and those at 1500 and 1434 cm^{-1} result from the absorption of C=O group [23]. The band in 900–600 cm^{-1} region is associated with the stretching vibrations of V—O bonds of VO_4 tetrahedron [9] in LiNiVO_4 . The presence of the organic remnants is probably originated from citric acid or citrate. With increasing the sintering temperature, the absorption intensities of C=O and O—H groups significantly decrease. The products obtained at 500, 550 and 600 °C show well-defined V—O bands. The results of FT-IR spectra also show that LiNiVO_4 can be well formed at 500 °C.

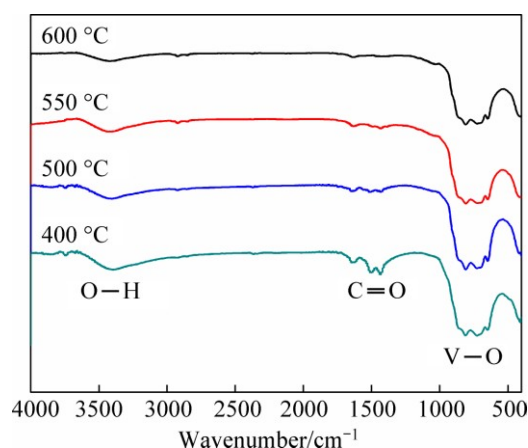


Fig. 3 FT-IR spectra of LiNiVO_4 powders obtained at various temperatures

The influence of temperature on the morphology of LiNiVO_4 was studied by TEM. As shown in Fig. 4, the synthesized LiNiVO_4 is composed of flaky nano-sized particles. The particle size becomes larger as the calcination temperature increases, which agrees with the results of XRD. The particles of product calcined at 400 °C are coated by a layer of organic remnants with the particle size about 10 nm. The product obtained at 500 °C has a large amount of porous structures between the particles with the particle size about 20 nm. The porosity between particles probably results from the decomposition of the residual organics. The particle size

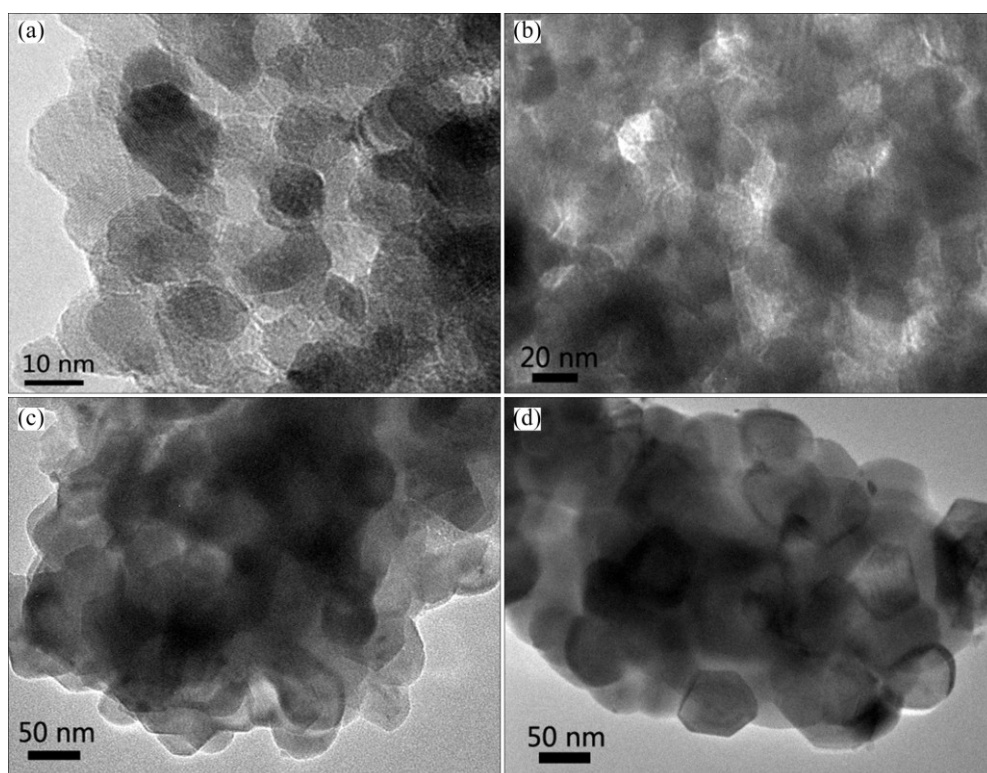


Fig. 4 TEM images of LiNiVO_4 powders obtained at 400 °C (a), 500 °C (b), 550 °C (c) and 600 °C (d)

increases to around 40 nm as the calcination temperature rises to 550 °C and there is an aggregation of small flaky particles. When the temperature further increases to 600 °C, the morphology is more regular and the particle size is about 60 nm.

3.3 Electrochemical performance

The electrochemical properties of LiNiVO_4 powders were evaluated by cyclic voltammetry (CV). Figure 5 shows the first cyclic voltammogram of the electrode prepared from the porous LiNiVO_4 powders obtained at 500 °C in the voltage range of 3–4.9 V (vs Li/Li^+) at a scan rate of 0.1 mV/s. An anodic peak at 4.81 V and a cathodic peak at 4.72 V can be observed, which correspond to the electrochemical lithium deinsertion and insertion processes, respectively. The appearance of redox peaks illustrates the considerable structure reversibility of the sample.

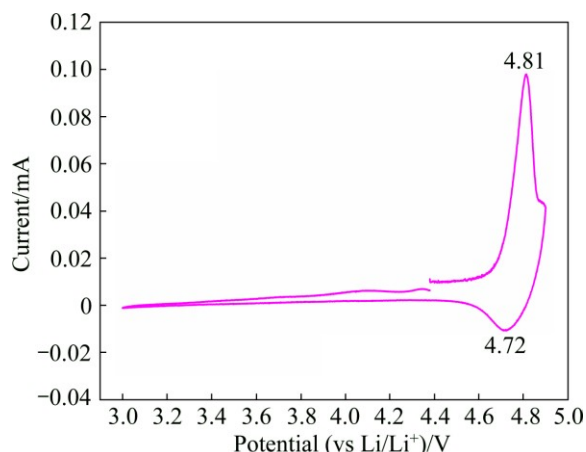


Fig. 5 Cyclic voltammogram of LiNiVO_4 powder electrode at scan rate of 0.1 mV/s

The charge–discharge technique was used to study the electrochemical performance of LiNiVO_4 as a cathode material for lithium-ion batteries. Figure 6 shows the charge–discharge curves of the 1st, 2nd and 5th cycles of the LiNiVO_4 nanoparticle obtained at 500, 550 °C and a current density of 15 mA/g in the potential window of 3–4.9 V (vs Li/Li^+). The products display a voltage plateau at 4.6–4.9 V corresponding to Li deinsertion/insertion process [24,25], which is consistent with the CV results. As shown in Fig. 6(a), the specific discharge capacities of 28, 21 and 14 mA·h/g for the 1st, 2nd and 5th cycles can be obtained for the product obtained at 500 °C, respectively. While for the product obtained at 550 °C, the specific discharge capacities are 30, 21 and 8 mA·h/g, respectively (Fig. 6(b)). The product obtained at 500 °C exhibits better electrochemical performance, which should be attributed to the fact that the product obtained at 500 °C has smaller particle sizes with more porous structure between the

particles (Fig. 4(b)). The small particle size results in a short diffusion path for lithium ions and restrains the concentration polarization effectively, which should benefit the battery with high discharge capacity. Moreover, the porous structure would facilitate the electrolyte penetration and increase the contact area between the active materials and the electrolyte. Furthermore, the porous structure may be also of advantage to accommodate the volume variations during the lithium ion intercalation and deintercalation. The products synthesized by solution combustion synthesis method display much higher discharge capacity compared with the conventional solid state product [5]. However, compared with the theoretical capacity of LiNiVO_4 , the discharge capacity of the products is still low. PRAKASH et al [7] proposed that the decomposition of electrolyte at high voltage is the main reason for low capacity of LiNiVO_4 . There is scope for further investigations to understand the mechanism of Li extraction/insertion and improve the electrochemical properties of LiNiVO_4 .

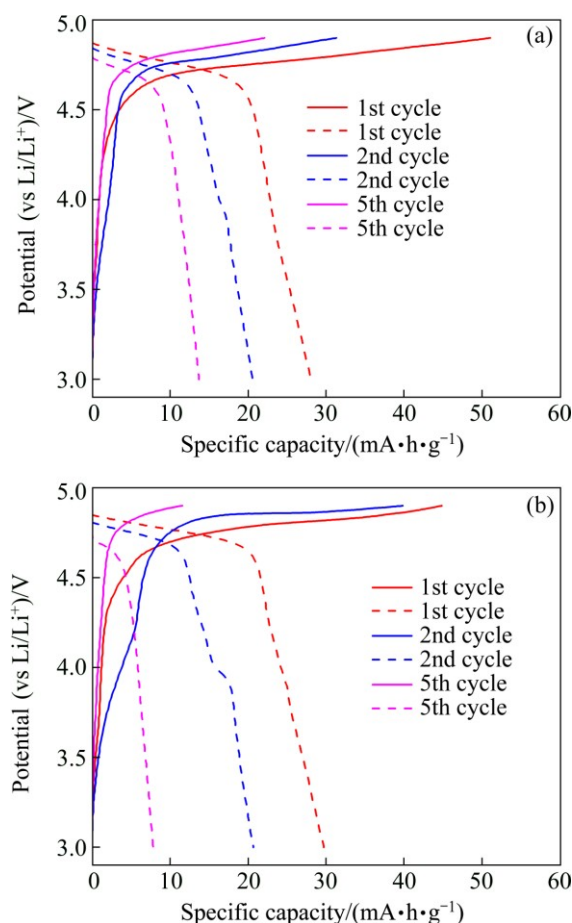


Fig. 6 Galvanostatic charge–discharge curves of samples obtained at 500 °C(a) and 550 °C(b)

4 Conclusions

1) LiNiVO_4 nanoparticles with the particle size

around 20 nm were synthesized using solution combustion synthesis method by calcining the precursor at 500 °C for 2 h.

2) As a cathode material for lithium-ion batteries, the porous LiNiVO_4 powder exhibits good structural reversibility.

3) The solution combustion synthesis not only endows this work simplicity and feasibility but also provides a superiority of processing condition over the conventional solid state method.

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锂离子电池用多孔高电压正极材料 LiNiVO_4 粉末的简便合成

秦牡兰¹, 刘万民¹, 梁叔全^{2,3}, 潘安强^{2,3}

1. 湖南工程学院 化学化工学院, 湘潭 411104;
2. 中南大学 材料科学与工程学院, 长沙 410083;
3. 中南大学 有色金属材料科学与工程教育部重点实验室, 长沙 410083

摘 要: 以硝酸锂、硝酸镍、偏钒酸铵和柠檬酸为原料, 采用溶液燃烧合成方法制备多孔 LiNiVO_4 粉末。采用热重-差示扫描量热法(TG-DSC)、X 射线衍射技术(XRD)、傅里叶变换红外光谱(FT-IR)和透射电镜(TEM)对样品的结构和形貌进行表征。结果表明, 煅烧温度对样品的结晶度和形貌有显著影响。将前驱体在空气中于 500 °C 煅烧 2 h 可制备薄片型 LiNiVO_4 纳米颗粒, 其颗粒尺寸约为 20 nm。作为锂离子电池正极材料, 多孔 LiNiVO_4 粉末具有较好的结构可逆性。

关键词: 锂离子电池; LiNiVO_4 ; 正极材料; 溶液燃烧合成; 纳米颗粒

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