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Malic acid complex method for preparation of $LiNiVO_4$ nano-crystallites

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Abstract $LiNiVO_4$ nano-crystallites were prepared by the polymerized complex method using Li_2CO_3, $Ni(CH_3COO)_2{\cdot}4H_2O$ and NH_4VO_3 as starting reagents and malic acid as a complexing agent. With the subsequent calcination at 450 °C, the powder analyzed by XRD, FTIR, Raman, electron diffraction, SEM and TEM techniques was found to be inverse spinel $LiNiVO_4$ with ~20 nm in diameter. TGA shows continuous weight loss at 40–450 °C due to the evaporation and decomposition processes. Above 450 °C, weight percent tended to be constant. In addition, formation mechanism of the purified $LiNiVO_4$ was proposed to relate with the experimental results.

Introduction

The demand for portable energy storage with high specific energy has received careful consideration for use in electronic and medical devices and electric vehicles [1]. Among them, lithium-ion batteries are widely accepted to be the most attractive. At present, intensively investigated materials are mainly based on $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$ [1–4]. $LiNiVO_4$ has been found to be an alternative for cathode materials used in rechargeable lithium-ion batteries [5, 6]. Due to the inverse spinel structure of the oxide, it can display very well even at a voltage as high as 4.8 V [7, 8]. It is believed that single phase, homogeneity, uniform morphology and large surface area are the characteristics required to achieve the best electrochemical properties [9]. There are several methods that can be used for preparing the oxides. They are coprecipitation [10], sol–gel [11], hydrothermal [12] and others. Currently, nano-structure materials have been found to exhibit anomalous properties which are totally different from the bulk materials [1]. The electrochemically inactive materials are able to be active by decreasing the electron path length, tunneling of electrons and increasing the specific surface area [1]. For the present research, $LiNiVO_4$ nano-crystallites were prepared by using the polymerized complex method at a low temperature and for a short time. Malic acid was used as a complexing agent and a fuel supplier to accelerate the combustion process.

Experiment

A 0.5:1:1 mole ratio of Li_2CO_3:$Ni(CH_3COO)_2{\cdot}4H_2O$:$NH_4VO_3$ was separately dissolved in deionized water and mixed to form a starting solution. Malic acid was dissolved in deionized water, added into the starting solution and stirred at 80 °C for 3 h. Mole ratios of total metal ions (M) to malic acid (MA) used for the research are 1:1, 1:2, 1:3 and 1:4. The mixture was stirred until carboxylate precursors (blue-green xerogel) were obtained. The gel was dried at 80 °C for 24 h and calcined at 450 °C for 6 h to form powder. The samples were intensively analyzed using XRD operated at 20 kV, 15 mA and using the K_α line from a Cu target, TGA with the heating rate of 20 °C min^{-1} over

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the temperature range 40–600 °C, FTIR with KBr as a diluting agent and operated in the range 400–4000 cm^{-1}, Raman spectrometer using 30 mW He–Ne Laser with $\lambda = 632.8$ nm, SEM operated at 15 kV and TEM operated at 200 kV.

Results and discussion

XRD

The powder with M:MA = 1:1–1:4 was analyzed using XRD and JCPDS standard [13]. The spectra are shown in Fig. 1. At a 1:1 mole ratio, there was the detection of $LiNiVO_4$ with NiO impurity. The purity of $LiNiVO_4$ is increased with an increase in the amount of acid. At 1:2, 1:3 and 1:4 mole ratios, a single phase of $LiNiVO_4$ was detected. The excess acid is likely to play a role in the precursor formation. It may assist in forming the complex that is complete. The strongest peak is at $2\theta = 36.2°$ and diffracts from (311) plane. The weak ($2\theta = 18.6°$) and strong ($2\theta = 30.7°$) peaks diffracting from (111) and (220) planes, respectively, are the specification of the inverse spinel structure [3, 7, 14]. When the diffraction intensity of (111) peak is higher than that of (220) peak, it is the normal spinel structure such as $LiMn_2O_4$ [7]. The $I_{(220)}/I_{(311)}$ intensity ratios are very close to 0.5 showing that the degree of crystallinity of $LiNiVO_4$ is very high [3].

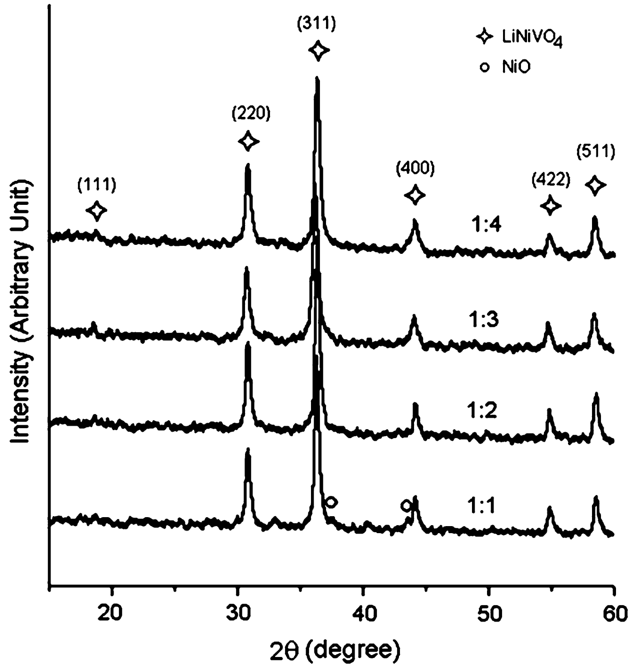

Fig. 1 XRD spectra of $LiNiVO_4$ with M:MA = 1:1, 1:2, 1:3 and 1:4

TGA

TGA of the carboxylate precursors is shown in Fig. 2. The curves show continuous weight loss over the temperature range 40–450°C. They are the evaporation of residual water at 40–200°C, and the decomposition and combustion of malate ions, acetate ions and other residual organic compounds at 200–450°C. During the decomposition and combustion processes, the evolution of gases was going on with the formation of $LiNiVO_4$. At a temperature higher than 450°C, weight percent tended to be constant showing that purified $LiNiVO_4$ was about to be obtained. Comparing the four curves, the percentage of weight loss tended to increase with an increase in the amount of malic acid. This shows that the acid functioned as a fuel supplier for the combustion process.

FTIR

FTIR spectra of the powder are shown in Fig. 3. At M:MA = 1:1 mole ratio, very small bands of carboxylate groups were detected. For all of M:MA mole ratios, three splitting bands were detected at 635, 710 and 806 cm^{-1} specified as the stretching bands of VO_4 tetrahedrons [6]. These are the characteristics of the inverse spinel structure [6]. The splitting is likely to be from bonding of Li and Ni with O in VO_4 tetrahedrons [6, 15]. Asymmetric stretching band of Li–O in LiO_6 environment was detected at 420 cm^{-1} [6, 8]. With the exception of M:MA = 1:4, asymmetric stretching band of NiO_6 octahedrons was detected at 1119 cm^{-1} [6, 15]. The excess acid seems to play a role in the disappearance of NiO_6 octahedral band. In some cases, asymmetric stretching band of NiO_6 octahedrons was not detected [5, 16].

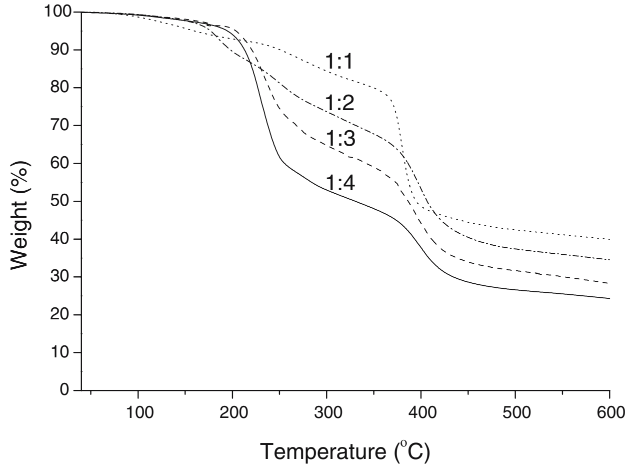

Fig. 2 TGA curves of the carboxylate precursors with M:MA = 1:1, 1:2, 1:3 and 1:4

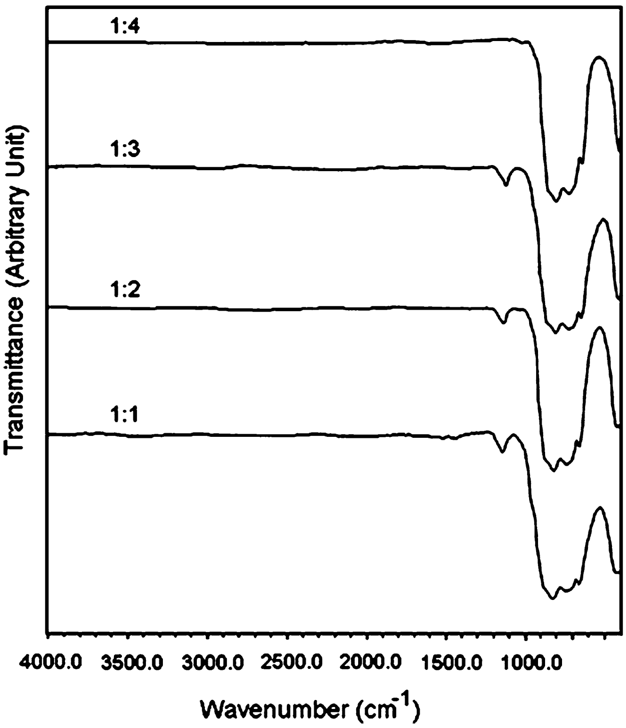

Fig. 3 FTIR spectra of $LiNiVO_4$ with M:MA = 1:1, 1:2, 1:3 and 1:4

Raman Spectrum

Raman spectrum of $LiNiVO_4$ (M:MA = 1:4) was analyzed and is shown in Fig. 4. For cubic spinel structure, it is in possession of $Fd\bar{3}m$ (O_h^7) symmetry [6–8]. Five modes being symmetrical with the inversion center ($A_{1g} + E_g + 3F_{2g}$) are Raman active [6–8]. A strong band was detected at 700–850 cm^{-1} which are the VO_4 tetrahedral stretching frequencies [6, 7]. They are the vibrational modes of bonding between O^{2-} and V^{5+} [6, 7]. The 824.4 cm^{-1} is the stretching mode of VO_4 tetrahedrons with A_{1g} symmetry [6–8]. It is broadened due to the asymmetric bonding of VO_4 tetrahedrons [6–8]. The 794.8 cm^{-1} seems to be the stretching frequency of ideal VO_4 tetrahedrons [6]. The 337.0 cm^{-1} is the bending mode of VO_4 tetrahedrons with E_g symmetry [6–8]. In addition, two stretching bands of Li–O and Li–O–Ni were detected at 416.5 and 479.7 cm^{-1}, respectively [6–8].

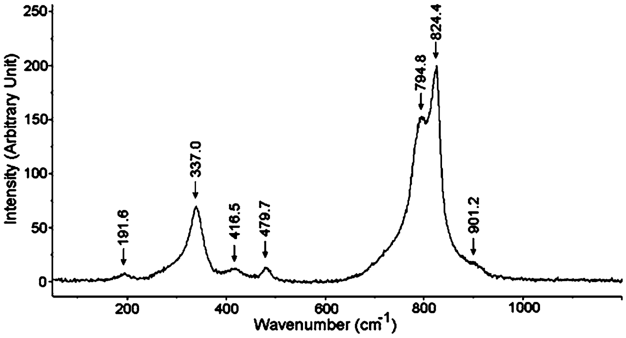

Fig. 4 Raman spectrum of $LiNiVO_4$ with M:MA = 1:4

SEM

SEM of $LiNiVO_4$ for a variety of mole ratios are shown in Fig. 5. The powder shows fluffy morphology due to the aggregation of small round particles. Particle size diameter decreased with an increase in the amount of acid. At M:MA = 1:4 mole ratio, the average diameter is ~20 nm.

TEM and electron diffraction

TEM and electron diffraction (ED) of the powder with M:MA = 1:4 were studied and the results are shown in Fig. 6. TEM shows that the powder is nano-crystallite with a mean diameter of ~20 nm. When electrons diffract through nano-crystallites, the diffraction pattern shows a variety of intensities of concentric rings. They correspond to the crystallographic planes of the powder. The diameters of the rings were measured and the values of d-spacing of the diffraction planes were calculated [17]. Comparing the calculated d-spacing values with those of the JCPDS standard [13], the diffraction pattern corresponds to $LiNiVO_4$ with inverse spinel structure. The diffraction planes are (111), (220), (311), (400), (422), (511) and (440). Intensity diffracting from (311) plane is the highest.

Proposed Mechanism

Reactions for the formation of carboxylate precursors and purified $LiNiVO_4$ are proposed on according to the following: [5]

$$\begin{aligned}&2Li_2CO_3 + 4Ni(CH_3COO)_2 \cdot 4H_2O + 2C_4H_6O_5\\&\quad + 10O_2 \rightarrow 4LiNiC_4H_3O_5 + 10CO_2 + 28H_2O\end{aligned} \tag{1}$$

$$\begin{aligned}&4NH_4VO_3 + 4C_4H_6O_5\\&\rightarrow 4(NH_4)(VO)(C_4H_3O_5) + 6H_2O + O_2\end{aligned} \tag{2}$$

Equations 1 and 2 are combined,

$$\begin{aligned}&2Li_2CO_3 + 4Ni(CH_3COO)_2.4H_2O\\&+ 4NH_4VO_3 + 6C_4H_6O_5 + 9O_2\\&\rightarrow 4LiNiC_4H_3O_5 + 4(NH_4)(VO)(C_4H_3O_5) + 10CO_2\\&+ 34H_2O\end{aligned} \tag{3}$$

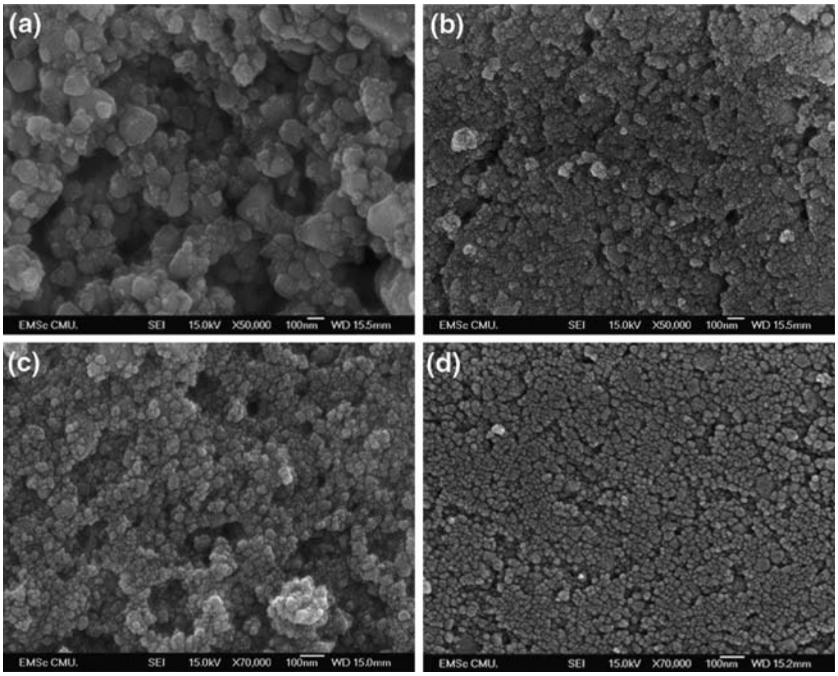

Fig. 5 SEM images of $LiNiVO_4$. (**a**)–(**d**) are for M:MA = 1:1, 1:2, 1:3 and 1:4, respectively

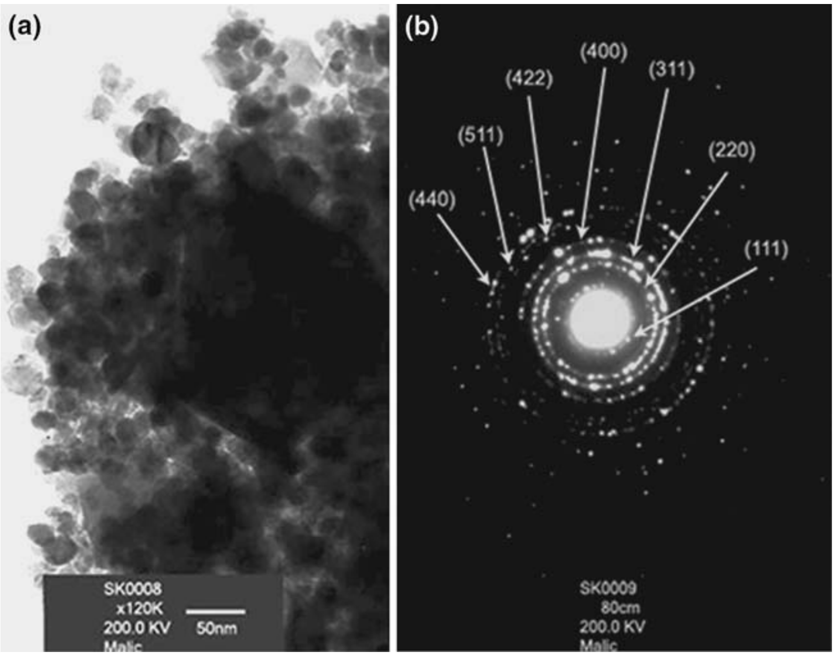

Fig. 6 (**a**) TEM image and (**b**) ED pattern of $LiNiVO_4$ with M:MA = 1:4

Two solids in Eq. 3 are expected to be the carboxylate precursors which are calcined in air to form purified $LiNiVO_4$ by the reaction

$$4LiNiC_4H_3O_5 + 4(NH_4)(VO)(C_4H_3O_5) + 25O_2 \rightarrow 4LiNiVO_4 + 32CO_2 + 14H_2O + 4NH_3 \quad (4)$$

Conclusions

Purified $LiNiVO_4$ nano-crystallites were successfully prepared by the polymerized complex method using 1:2, 1:3 and 1:4 of M:MA mole ratios with subsequent calcination at 450 °C for 6 h. By using XRD, FTIR, Raman and electron diffraction analyses, $LiNiVO_4$ with inverse spinel structure was detected. Particle size determined by SEM and TEM is ~20 nm in diameter. During calcination, TGA shows that the combustion process is increased with an increase the amount of acid. In addition, a formation mechanism for the purified $LiNiVO_4$ is proposed.

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