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Novel soft solution synthesis and characterization of submicromic LiCoVO₄

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Abstract

A novel soft solution process has been used to prepare LiCoVO₄ by reacting Co(CH₃CH₂COO)₂, Li₂CO₃, NH₄VO₃ and citric acid. LiCoVO₄ powders were successfully prepared at as low as 450 °C in 4 h. Compared to the solid-state reaction processes, the soft solution process greatly reduced the temperature and the time for preparing LiCoVO₄. The inverse spinel structure and high crystallinity of the synthesized product has been confirmed by X-ray diffraction. Thermal analysis proves that the phase formation of the compound occurs at about 450 °C. The results of the IR investigations show that the band located at 820 cm⁻¹ corresponds to the stretching vibration mode of VO₄ tetrahedron with the A₁ symmetry. SEM examination reveals a spherical grain distribution, the average particle size being typically lower than 1 μm. The quantitative result from ICP-AES analysis is Li_{0.967}Co_{0.994}VO₄.

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1. Introduction

In recent years, the demand for portable power sources with high energy density has greatly increased due to the development and popularity of portable electronic devices such as camcorders, cellular phones, and notebook computers [1–4]. New lithiated transition-metal oxides, such as LiNiVO₄ and LiCoVO₄ have been recently proposed as cathode materials for modern rechargeable batteries [5,6]. These materials are very attractive for their use in the so-called Li ion or rocking-chair batteries due to their theoretical capacity of about 148 mA hg⁻¹ and their high potential of 4.8 V vs. Li⁺/Li [7].

Solid-state reactions are often used to prepare LiCoVO₄ [6,8], which is not economical owing to the amount of energy and long reaction time required, and not advantageous because of the long reaction time and high temperature used. In order to overcome those drawbacks, in the present work, we describe a simple

procedure for the preparation of bulk quantities of submicron-sized particles of high crystalline LiCoVO₄ at low temperature of 450 °C.

2. Experimental

LiCoVO₄ sample was prepared first by dissolving stoichiometric quantities of Li₂CO₃, Co(Ac)₂ and NH₄VO₃ in de-ionized water. During vigorous stirring, saturated citric acid solution was added, which gave off a great deal of gas, and a brown xerogel was obtained after being heated at 80–100 °C. The as-obtained xerogel was heated at 450 °C for 4 h, accompanied by obvious combustion, which ultimately gave rise to a pale brown powder.

Thermal analyses of the precursor complex were performed using the NETZSCH STA 449C DSC-TG apparatus. Experiment was carried out under ambient atmosphere with a heating rate of 10 °C min⁻¹. X-ray diffraction (XRD) experiments were done on a D/MAX-III X-ray diffractometer with Cu K_α radiation and graphite monochromator. Fourier transform infrared (FTIR) absorption spectra were recorded using the 60-SXB IR spectrometer with a resolution of 4 cm⁻¹. The

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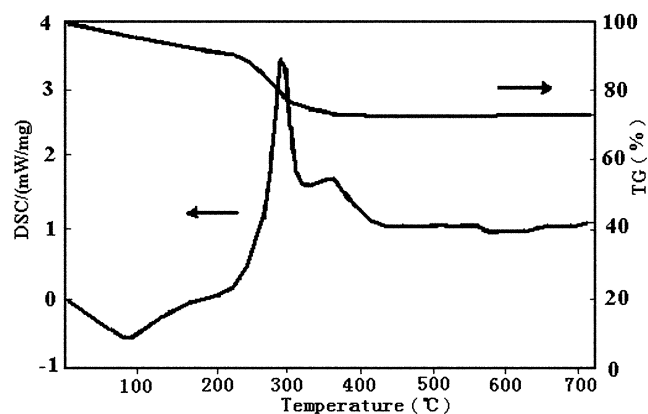


Fig. 1. TG and DSC curves of the xerogel precursor.

measuring wavenumber range is $300\text{--}3900\text{ cm}^{-1}$. SEM image was collected by employing the JSM-5610LV scanning electron microscope and the EDAX signals were recorded using an analyzer attached to the scanning electron microscope. The metal contents were determined by inductively coupled plasma-atomic emission spectroscopy (PLASMA 300) and its accuracy is $\pm 0.1\%$.

3. Results and discussion

3.1. Thermal analysis

In order to measure the exact phase formation and/or crystallization temperature of the LiCoVO_4 samples, DSC and TG measurements were carried out on the as-obtained xerogel. The DSC and TG curves are shown in

Fig. 1. The endothermic peak appearing at $40\text{--}110^\circ\text{C}$ can obviously be attributed to the removal of water molecules present in the precursor sample. After this step, two exothermic transformations are observed from the DSC graph, accompanied by a huge mass loss of 18.52%. The first exothermic process is centered at 294°C , which is attributed to the combustion of the xerogel precursor and release of CO_2 and H_2O gas. As the process of heating continuing, the mass loss increases, the combustion and complexation of citric acid together with the cobalt acetate and vanadate precursor result in a second exotherm located at 361°C . This indicates that the complex starts to decompose at 320°C and the combustion of citric acid supplies adequate heat energy for initiating the crystallization of LiCoVO_4 . The minimum heat-treatment temperature of the brown black residues for preparing LiCoVO_4 was chosen to be 450°C because its DSC and TG curve, as shown in Fig. 1, clearly indicated that the weight loss of the specimen remained almost constant above 450°C , and the high crystalline phase of the product had formed at 450°C .

3.2. XRD analysis

Fig. 2 shows the XRD pattern of synthesized LiCoVO_4 , which is consistent with that reported in JCPDS file [6]. The XRD patterns are dominated by the Bragg peak located at $2\theta = 36^\circ$, which is attributed to the (3 1 1) line. The X-ray diagram also displays a weak (1 1 1) Bragg peak and a strong (2 2 0) line, which both indicate the predominant inverse spinel structure of LiCoVO_4 without noticeable impurities. It is the presence of vanadium ions on the tetrahedrally coordinated

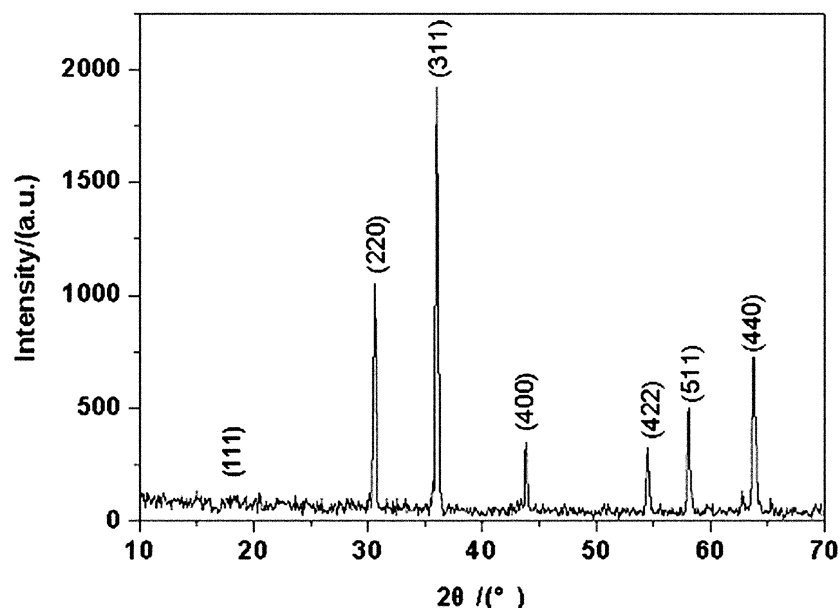


Fig. 2. XRD pattern of the synthesized LiCoVO_4 .

Table 1
Wavenumber and assignment of the IR bands of LiCoVO₄

Wavenumber (cm ⁻¹)	Assignment
428	ν (Li–O)
459	ν (Li–O–Co)
548	ν (Li–O–Co)
820	ν (VO ₄)
1447	δ (CH ₂)
1632	δ_s (H–O–H)
3432	ν_s (H–O–H)

8a site, which leads to the increase of the (2 2 0) intensity at the expense of the (1 1 1) peak. The structural features of the product could be viewed by the ratio between the intensities of the (2 2 0) and (3 1 1) line [9]. The intensity ratio $I_{(2\ 2\ 0)}/I_{(3\ 1\ 1)}$ of 0.5 indicates the high crystalline nature of the product. In comparison with the previous solid-state processes [6], the soft solution process reduces the synthesis temperature of LiCoVO₄ from 800 to 450 °C and the time from 12 to 4 h. It is evident that the soft solution environment remarkably accelerates the reaction kinetics of the formation of LiCoVO₄ although some impurities cannot be removed at low temperature of calcination.

3.3. FTIR analysis

The FTIR spectrum of synthesized LiCoVO₄ is shown in Fig. 3. The band at 3432 cm⁻¹ indicates the presence of a hydroxyl group, while the absorption bands at 1447 and 1632 cm⁻¹ suggest the presence of a carbonyl group [7], which can be removed by controlling synthesis

temperature and time and this work is underway. The characteristic absorption band of LiCoVO₄ at 820 cm⁻¹ is associated with the stretching vibrations of VO₄ tetrahedra in LiCoVO₄. These IR results are thus consistent with the XRD results.

A detailed interpretation of the medium-frequency region of FTIR spectra is difficult because different types of vibrations exist in this spectral domain, involving significant displacement of octahedral and tetrahedral cations simultaneously. Therefore, one may observe either the bending vibrations of the VO₄ tetrahedron or the vibrations involving the octahedral CoO₆, LiO₆ environments. If one considers that all the Li ions are accommodated in octahedral LiO₆ environments, the IR-active modes are normally split into (A + 2B) Raman-active and IR-active components. Therefore, IR modes having (A + 2B) symmetry are intense, whose modes are observed at 459, 548 cm⁻¹ [10,11]. The wavenumbers and the corresponding assignments of the bands of inverse spinel LiCoVO₄ are summarized in Table 1.

3.4. SEM and elemental analyses

SEM analysis was carried out on the final product annealed at 450 °C, as shown in Fig. 4. The micrograph reveals the formation of spherical grains of submicromic nature (average size of grains < 1 μm). Almost all of the grains are well connected with linear grain boundaries and exhibit a nearly pore-free state of the annealed product as seen from the micrograph (Fig. 4). As far as the SEM results are concerned, no such information is available in the literature to compare with our results.

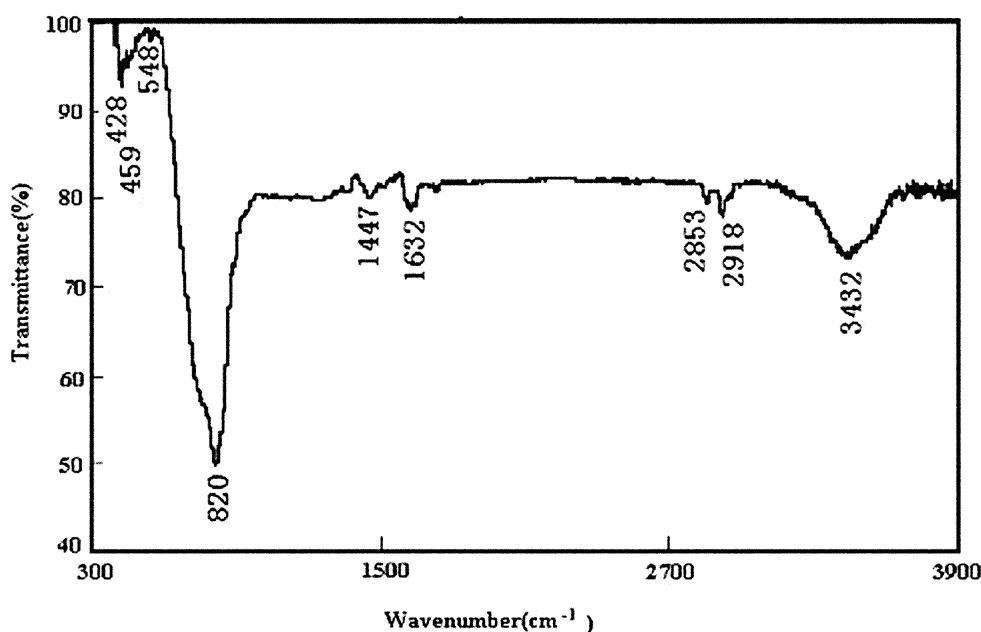


Fig. 3. FTIR spectra of the synthesized LiCoVO₄.



Fig. 4. Scanning electron micrograph of the synthesized LiCoVO_4 .

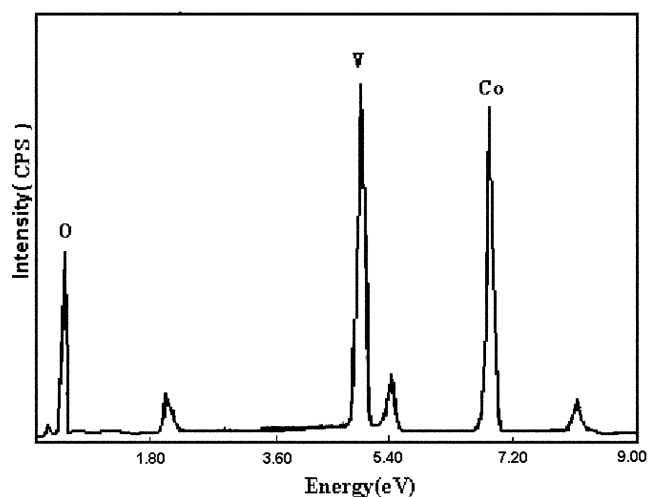


Fig. 5. EDAX pattern of the synthesized LiCoVO_4 .

However, one cannot expect the above features, such as submicrometric grains and pore-free state, in a similar compound prepared via solid-state reaction at high temperature. The aforementioned features are very desirable for a material to be employed as an active electrode material in a modern rechargeable Li ion battery. The elemental analysis of the synthesized product was performed using the EDAX technique (see Fig. 5). EDAX results were interpreted in terms of the atomic percentage and prove the presence of Co and V in their stoichiometric proportions, viz the molar ratio of Co:V is near to 1:1. The EDAX technique does not provide any information on lithium. Therefore, inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis was conducted. The quantitative result from ICP-AES analysis is $\text{Li}_{0.967}\text{Co}_{0.994}\text{VO}_4$. The results indicate that the sample is lithium deficient, and

deviate from its theoretical value, revealing that some lithium mass loss occur during the heating process, which is coincide with the finding reported by Fey et al. [6].

4. Conclusion

This work evolves a low-temperature synthesis of LiCoVO_4 at 450°C . The present method yields a high crystalline phase of the inverse spinel LiCoVO_4 as confirmed by XRD measurements. Thermal analysis proves that the phase formation of the compound occurs at about 450°C . SEM examination reveals a spherical grain distribution, the average particle size being typically lower than $1\ \mu\text{m}$. The quantitative result from ICP-AES analysis is $\text{Li}_{0.967}\text{Co}_{0.994}\text{VO}_4$. In comparison with the previous solid-state processes, the soft solution process reduces the synthesis temperature and time of LiCoVO_4 .

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