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Preparation and characterization of nano-crystalline LiCoVO₄ and LiNiVO₄ used as cathodes for lithium ion batteries

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Nano-crystalline LiCoVO₄ and LiNiVO₄ were prepared using Li₂CO₃, Co(NO₃)₂·6H₂O or Ni(NO₃)₂·6H₂O and NH₄VO₃ as raw materials in deionized water and tartaric acid as a complexing reagent, and followed by 450-600°C calcination for 12 h. TGA showed weight loss due to the combustion of the precursor at 190-500°C. The products were characterized by XRD and found to be LiCoVO₄ and LiNiVO₄ with an inverse spinel structure. FTIR and Raman analyses showed the V-O stretching vibration of VO₄ tetrahedrons and Li-O bending vibration of LiO₆ octahedrons. TEM showed nano-powders of LiCoVO₄ and LiNiVO₄ which have high specific areas for improving lithium ion migration in lithium ion batteries.

Key words: Lithium ion batteries, LiNiVO₄, LiCoVO₄.

Introduction

In recent years, research on lithium ion secondary batteries has been done to increase the energy density, life cycle and safety purpose. A challenge is to improve their energy densities for use as high voltage cathode materials [1]. The inverse spinel structure LiCoVO₄ and LiNiVO₄ make them very promising cathode materials for lithium ion batteries due to the high voltages of 4.2 V and 4.8 V versus metallic Li for LiCoVO₄ and LiNiVO₄, respectively [2]. For the lithium transition metal orthovanadate inverse spinel structure, Li and transition metal atoms are equally and randomly in the octahedrally coordinated interstices. The V atoms are in the tetrahedrally coordinated interstices [1, 2].

Conventional solid-state reactions are widely used to synthesize such metal oxides. $LiCoVO_4$ and $LiNiVO_4$ were prepared using Li_2CO_3 , NiO or Co_3O_4 and V_2O_5 as raw materials which were calcined in air at 800°C for 20 h [3]. This method is quite expensive because of the high energy usage and long reaction time [1-2, 4]. Soft chemical routes are an economically viable course which is possible for an atomic level of mixing of the ingredients for the synthesis of multi-component oxide powders [2].

For the present study, a tartaric acid complex method was used for synthesizing nano-powders of $LiCoVO_4$ and $LiNiVO_4$ at low temperature.

Experimental Procedure

LiCoVO₄ and LiNiVO₄ were prepared using stoichiometric Li₂CO₃, Co(NO₃)₂·6H₂O or Ni(NO₃)₂·6H₂O and NH₄VO₃. Each of them was dissolved in deionized water, mixed, stirred and adjusted at a pH 5 using HNO₃. A saturated tartaric acid solution was added and heated at 80°C, then the precursors were calcined at 450-600°C for 12 h.

The products were analyzed by a thermogravimetric analyzer (TGA, Perkin Elmer TGA-7) with the heating rate of 10 K·minute⁻¹ in a nitrogen atmosphere. The Xray diffraction (XRD, Siemens D500) was carried out using Cu K_{α} radiation with the scanning angle range 20 from 10 to 60°, a graphitic monochromatized and a Ni filter. Fourier transform inferred spectroscopy (FTIR, Bruker TERNOR 27) with KBr dilution was recoded. Raman spectroscopy (HORIBA JOBIN YVON T64000) was operated using a 50 mW Ar Laser with $\lambda = 514.5$ nm. Transmission Electron Microscopy (TEM, JEOL JEM-2010) and Energy Dispersive X-ray Spectroscopy (EDX, Oxfrod instruments INCA) were operated at 200 kV and 15 kV, respectively.

Results and Discussion

Thermal analysis of the precursors was studied by TGA in the temperature range 50 to 600°C in N_2 atmosphere (Fig. 1). There are two distinguishable steps of the weight loss. The first is at 50 to 190°C which is obviously attributed to the evaporation of residual water in the precursor. The second step is due to the combustion of tartates of lithium, vanadium and nickel or cobalt in the temperature range 190 to 500°C. The

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Fig. 1. TGA of the precursors prepared by the polymerization process.



Fig. 2. XRD patterns of $LiCoVO_4$ and $LiNiVO_4$ calcined at different temperatures for 12 h.

weight loss tends to be constant at 500°C and about. The total weight loss during the thermal analysis is 70% by weight.

XRD patterns of LiCoVO₄ and LiNiVO₄ are shown in Fig. 2. Comparing with the JCPDS standard (LiCoVO₄ PDF number 38:1396 and LiNiVO₄ PDF number 38:1395) [5], they correspond to LiCoVO₄ and LiNiVO₄. No impurities, such as NiO, CoO, and Co₃O₄, were detected. The XRD patterns displayed a weak (111) peak and strong (220) peak indicating the predominant inverse spinel structure. For the present analysis, vanadium cations are in the tetrahedrally coordinated 8a site leading to the higher (220) and lower (111) peaks [2, 4, 6]. The degree of crystallinity for LiCoVO₄ and LiNiVO₄ was determined from the intensity ratio $I_{(220)}/I_{(311)}$ of 0.5 which showed highly crystalline products. At 600°C for 12 h, the intensity ratios $I_{(220)}/I_{(311)}$ of LiCoVO₄ and LiNiVO₄ are very close to 0.5 indicating good crystallinity [4, 6]. The lattice parameters of LiCoVO₄ and LiNiVO₄ with 600°C calcination for 12 h are 0.8273 and 0.8223 nm, respectively. They are very close to the JCPDS standard (a=0.8279 nm for LiCoVO₄ and a=0.8220 nm for LiNiVO₄). The lattice parameter of LiCoVO₄ is larger than LiNiVO₄ because a Co atom in octahedrally coordinated 16a is



Fig. 3. (a) FTIR and (b) Raman spectra of $LiCoVO_4$ and $LiNiVO_4$ calcined at 600°C for 12 h.

larger than that of a Ni atom. The calcination temperature can play a role in improving the crystallite and grain size of the products. These correspond to an increase in XRD intensities with an increase in the calcination temperature [1].

FTIR spectra of LiCoVO₄ and LiNiVO₄ are showed in Fig. 3. The stretching vibration of VO₄ tetrahedrons and bending vibration of LiO₆ octahedrons were detected at 900-400 cm⁻¹. The asymmetric stretching vibration of VO₄ tetrahedrons showed a broad band at 810-850 cm⁻¹ and a weak band around 900 cm⁻¹ assigned to be the symmetric stretching mode in the VO₄ tetrahedrons [1-4]. In addition, the oxygen atoms in the VO_4 tetrahedron can from bonds with Li and Co or Ni atoms which can lead to some asymmetry. Hence the broad band around 810-850 cm⁻¹ is tentatively assigned to the asymmetrical stretching mode in the distorted VO₄ unit [2, 6]. It can be considered that all Li atoms are accommodated in octahedron LiO₆ environments. Therefore, Raman- and IR-active modes are normally spit into (A+2B). LiO₆ octahedrons have vibrations in IR modes observed at 430 cm⁻¹ corresponding to v(Li-O) [1, 4].

LiCoVO₄ and LiNiVO₄ have O⁷_h symmetry of which five modes are Raman-active $(A_{1g}+E_g+3F_{2g})$ and four modes are inferred-active $(4F_{1u})$ [3, 7]. The strong band in the range 700-850 cm⁻¹ is specified as the stretching of the VO_4 tetrahedrons. The peaks at 820 cm⁻¹ and 335 cm⁻¹ are due to the stretching and bending modes of the VO_4 tetrahedrons corresponding to A_1 and E symmetries, respectively. In the lower region, two weak modes of 253 and 416 cm⁻¹ are the vibrations of the LiO_6 octahedrons. The 480 cm⁻¹ corresponds to the stretching vibration of Li-O-M (M=Co or Ni) [3, 4, 7]. The frequency in the Raman spectra are decreased from LiNiVO₄ to LiCoVO₄ which indicate both the weak V-O bonding in the VO₄ tetrahedrons and M-O (M = Li, Co or Ni) bonding in the MO₆ octahedrons. A reduction in the strength between lithium and oxygen promotes the lithium migration in lithium ion batteries, resulting in a lower voltage of LiCoVO₄ cathode materials [7].

TEM images and selected area diffraction patterns

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Fig. 4. TEM images of (a, b) $LiCoVO_4$ and (c, d) $LiNiVO_4$ calcined at 450 and 600°C for 12 h, respectively.

(SADP) of LiCoVO₄ and LiNiVO₄ are shown in Fig. 4. For 450°C calcination, LiCoVO₄ and LiNiVO₄ are composed of nano-particles. Their calculated sizes are 97 and 18 nm, respectively. The SADP indicated the (111), (220), (311), (400), (422), (511) and (533) planes corresponding to the JCPDS standard. When the calci- nation temperature was increased to 600°C, the particle size of both fine products increased. At 600°C, those of LiCoVO₄ and LiNiVO₄ are 185 and 98 nm, respective- ly. A previous report shows the nano-particles cathode material which has a high specific area to improve lithium ion migration in lithium ion batteries [1].

EDX spectra of $LiCoVO_4$ and $LiNiVO_4$ about the pressence of Co or Ni, V and O (results not shown). The atomic ratio between Co or Ni:V:O are 1:1:4 which are very close to the chemical formula of a lithium transition metal orthovanadate. Metallic Li was not detected because it is the lightest metallic element [8].

Conclusions

 $LiCoVO_4$ and $LiNiVO_4$ were successfully prepared by the polymerization method. The crystallite and particle size were improved by an increase of the calcination temperature. TEM images show particle sizes of the products at 450°C for 12 h in the nano-scale which have relatively larger specific surface areas and are more favorable for lithium-ion migration as the cathode materials.

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