Preparation and characterization of nano-crystalline LiCoVO$_4$ and LiNiVO$_4$ used as cathodes for lithium ion batteries

Anukorn Phuruangrat$^{a,b,*}$, Titipun Thongtem$^b$ and Somchai Thongtem$^a$
$^a$Department of Physics, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
$^b$Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

Nano-crystalline LiCoVO$_4$ and LiNiVO$_4$ were prepared using Li$_2$CO$_3$, Co(NO$_3$)$_2$·6H$_2$O or Ni(NO$_3$)$_2$·6H$_2$O and NH$_4$VO$_3$ 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 LiCoVO$_4$ and LiNiVO$_4$ with an inverse spinel structure. FTIR and Raman analyses showed the V-O stretching vibration of VO$_4$ tetrahedrons and Li-O bending vibration of LiO$_6$ octahedrons. TEM showed nano-powders of LiCoVO$_4$ and LiNiVO$_4$ which have high specific areas for improving lithium ion migration in lithium ion batteries.

Key words: Lithium ion batteries, LiNiVO$_4$, LiCoVO$_4$.

The precursors were prepared using stoichiometric Li$_2$CO$_3$, Co(NO$_3$)$_2$·6H$_2$O or Ni(NO$_3$)$_2$·6H$_2$O and NH$_4$VO$_3$. Each of them was dissolved in deionized water, mixed, stirred and adjusted at a pH 5 using HNO$_3$. 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 X-ray diffraction (XRD, Siemens D500) was carried out using Cu K$_α$ radiation with a graphitic monochromatized and a Ni filter. Fourier transform infrared spectroscopy (FTIR, Bruker TERNOR 27) was recorded. 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, Oxford 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
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 that of LiNiVO₄ because a Co atom in octahedrally coordinated 16a is 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 shown 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 VO₄ tetrahedron can from bonds with Li and Co or Ni atoms which can lead to some asymmetry. Therefore, the broad band around 810-850 cm⁻¹ is tentatively assigned to the asymmetrical stretching mode in the distorted VO₄ unit [1]. It can be considered that all Li atoms are accommodated in octahedron LiO₆ environments. Therefore, Raman- and IR-active modes are normally split 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 O₆ symmetry of which five modes are Raman-active (A₁g+Eg+3F₂g) and four modes are infrared-active (4F₁u) [3, 7]. The strong band in the range 700-850 cm⁻¹ is specified as the stretching of the VO₄ tetrahedrons. The peaks at 820 cm⁻¹ and 335 cm⁻¹ are due to the stretching and bending modes of the VO₄ tetrahedrons corresponding to A₁ and E symmetries, respectively. In the lower region, two weak modes of 253 and 416 cm⁻¹ are the vibrations of the LiO₆ 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
Anukorn Phuruangrat, Titipun Thongtem and Somchai Thongtem

(SADP) of LiCoVO$_4$ and LiNiVO$_4$ are shown in Fig. 4. For 450°C calcination, LiCoVO$_4$ and LiNiVO$_4$ 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 calcination temperature was increased to 600°C, the particle size of both fine products increased. At 600°C, those of LiCoVO$_4$ and LiNiVO$_4$ are 185 and 98 nm, respectively. 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 presence 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.

Acknowledgements

We are grateful to the National Research Council of Thailand, and the Thailand Research Fund for funding the research, and Graduate School of Chiang Mai University, Thailand, for general funding.

References


[Fig. 4. TEM images of (a, b) LiCoVO$_4$ and (c, d) LiNiVO$_4$ calcined at 450 and 600°C for 12 h, respectively.]