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Characterization of nanocrystalline $LiNi_{1-x}Co_xVO_4$ prepared by the polymerized complex method

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Nanocrystalline $LiNi_{1-x}Co_xVO_4$ (x = 0.00, 0.25, 0.50, 0.75 and 1.00) was prepared from Li_2CO_3, $Ni(NO_3)_2.6H_2O$, $Co(NO_3)_2.6H_2O$ and NH_4VO_3, using tartaric acid as a complexing agent, followed by 450 °C calcination for 12 h. TGA results show that nanocrystallites started to form at 450–550 °C. Inverse spinel $LiNi_{1-x}Co_xVO_4$ was detected using the XRD and SAED methods. The calculated lattice parameter increased upon increasing Co concentration. It was in accordance with the increase in the particle size determined using TEM images. A stretching band of VO_4 tetrahedra was detected at 651–820 cm^{-1} using FTIR. V–O vibrational bands analyzed with a Raman spectrometer were shifted to the lower wavenumbers, due to the increase of Co concentration. The selected elements were also analyzed using EDX and AAS to determine the stoichiometric values (x) of the oxides.

Key words: *nanocrystalline $LiNi_{1-x}Co_xVO_4$; polymerized complex method; tartaric acid*

1. Introduction

Lithium transition metal oxides are appropriate for use as cathode materials in Li ion batteries. To improve their electrochemical properties, cathode materials containing a variety of transition metal oxides have been developed and investigated. Among transition metal oxides with inverse spinel structures, $LiNiVO_4$, $LiNi_{0.5}Co_{0.5}VO_4$ and $LiCoVO_4$ can perform very well even at voltages as high as 4.3–4.8 V [1–4]. Currently, nanocrystals are found to exhibit novel properties by decreasing the electron path length, promoting the tunneling property of electrons, and increasing the specific surface area [5]. For the present research, nanocrystalline $LiNi_{1-x}Co_xVO_4$ was prepared by the polymerized complex method, using tartaric acid as a complexing agent, and analyzed to specify phase, morphology and other features.

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2. Experimental

Li_2CO_3, $Ni(NO_3)_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$ and NH_4VO_3 were separately dissolved in water and then mixed together. pH of 5 was adjusted using HNO_3. Then tartaric acid was added. The solution was stirred at 80 °C until it became a gel consisting of tartaric complexes of the metal ions (precursors). The gel was dried at 80 °C for 12 h and calcined at 450 °C for 12 h to form powder. The final products were analyzed by the TGA at the heating rate of 20 °C/min in ambient atmosphere, XRD operated at 20 kV, 15 mA and using the K_α radiation from a Cu target, TEM as well as SAED operated at 200 kV, EDX operated at 15 kV, AAS to determine Li, Ni and Co atomic percents, FTIR with KBr as a diluting agent and operated in the range 400–4000 cm^{-1}, and a Raman spectrometer using 50 mW Ar laser with $\lambda = 514.5$ nm.

3. Results and discussion

3.1. TGA curves

Pure tartaric acid and non-calcined precursors were analyzed using TGA (Fig. 1). The curves for the different stoichiometric values (x) are very similar, showing that

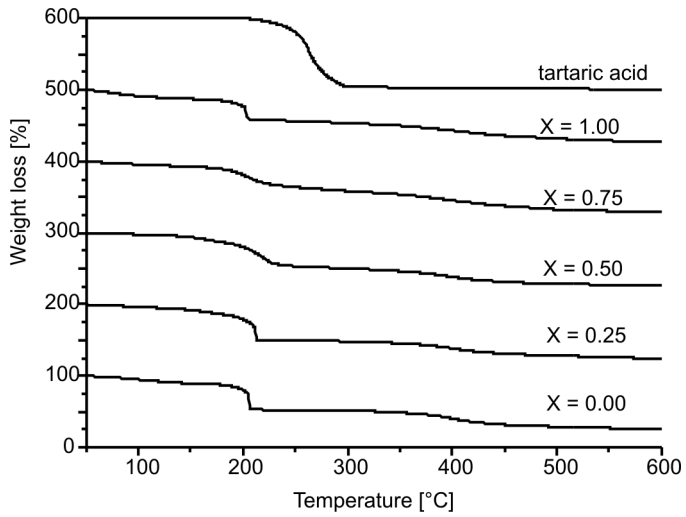

Fig. 1. TGA curves of pure tartaric acid and non-calcined precursors for $LiNi_{1-x}Co_xVO_4$

weight losses were controlled by the same processes. Their weight losses were divided into four stages over the temperature range 50–550 °C. They are the evaporation of adsorbed and lattice water at 50–200 °C, the decomposition of residual tartaric acid at 200–290 °C (compared with pure tartaric acid), and the decomposition and combustion of residual starting agents and other organic compounds at 290–450 °C. At

450–550 °C, the weights are almost constant and different atoms are arranged in a particular order or positions to form crystalline oxides.

3.2. XRD spectra

XRD spectra of the oxides are shown in Fig 2. At x = 0.00 and 1.00, they correspond to those of the JCPDS standard for $LiNiVO_4$ (38–1395) and $LiCoVO_4$ (38–1396), respectively [6]. At x = 0.25, 0.50 and 0.75, the spectra are similar to those of their pure oxides (x = 0.00 and 1.00) specified as the solid solution (mixture) of $LiNiVO_4$ and $LiCoVO_4$ [1, 3, 4].

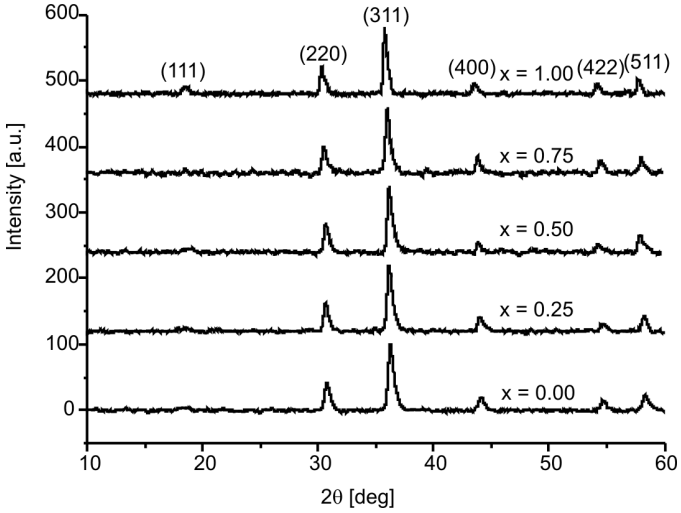

Fig. 2. XRD spectra of $LiNi_{1-x}Co_xVO_4$

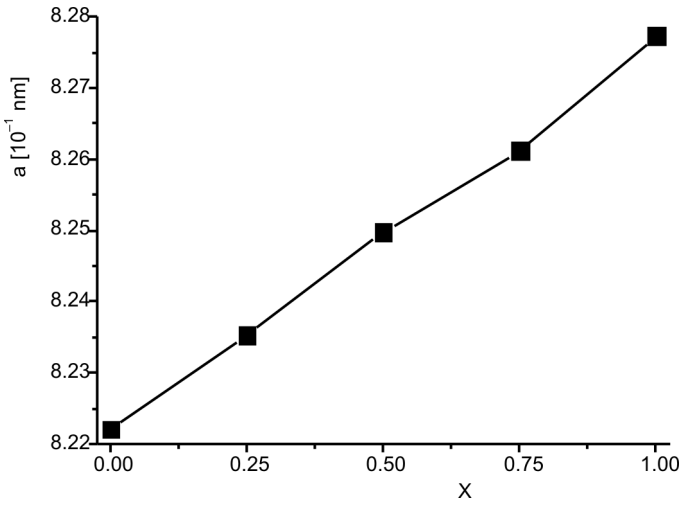

Fig. 3. Cubic lattice parameter (a) vs. stoichiometric values (x)

$LiNi_{1-x}Co_xVO_4$ (x = 0.00, 0.25, 0.50, 0.75 and 1.00) forms a single phase with inverse spinel structure identified by (111) and (220) peaks of weak and strong intensities, respectively [2, 7]. For inverse spinel structure, Li and M (M = Ni and Co) atoms equally occupy octahedral sites at random, and V atoms are in tetrahedrally coordinated 8a sites [2, 4, 7]. The cubic lattice parameter (a) of $LiNi_{1-x}Co_xVO_4$ was calculated (Fig. 3) [8]. It was monotonically increased with the increase in stoichiometric value x. At x = 0.00 and 1.00, the lattice parameters are respectively 0.8222 nm and 0.8278 nm which are very close to the values shown in the JCPDS standard (0.8220 nm for $LiNiVO_4$ and 0.8279 nm for $LiCoVO_4$) [6].

3.3. FTIR and Raman analyses

FTIR spectra of $LiNi_{1-x}Co_xVO_4$ (Fig 4) show a stretching band of VO_4 tetrahedra at 651–820 cm^{-1}. It splits into three bands (651, 722 and 820 cm^{-1}) characterized as the inverse spinel structure [4, 9–11]. The splitting extent becomes lesser when the stoichiometric values are larger, and no longer exists at x = 1.00. An asymmetric stretching band of MO_6 (M = Ni and Co) octahedrons was detected at 1136 cm^{-1} [10]. At x = 0.00 and 1.00, they are the stretching bands of Ni–O and Co–O, respectively.

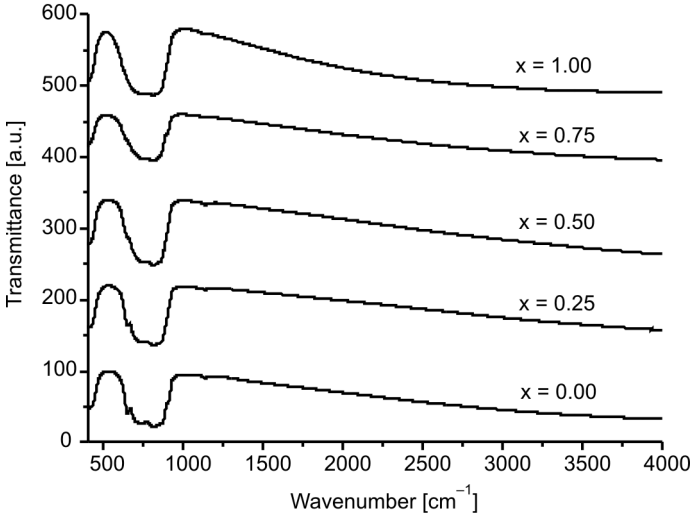

Fig. 4. FTIR spectra of $LiNi_{1-x}Co_xVO_4$

Raman spectra of $LiNi_{1-x}Co_xVO_4$ (Fig. 5) show bands of the stretching (A_{1g} symmetry) and bending (E_g symmetry) V–O modes in VO_4 tetrahedra [3, 4]. The stretching and bending modes were respectively detected at 811 and 327 cm^{-1} for $LiNiVO_4$, and at 803 and 304 cm^{-1} for $LiCoVO_4$ [3, 4]. The bands of $LiNiVO_4$ appear at higher wavenumbers than those of $LiCoVO_4$. The stretching and bending bands of $LiNi_{0.75}Co_{0.25}VO_4$, $LiNi_{0.50}Co_{0.50}VO_4$ and $LiNi_{0.25}Co_{0.75}VO_4$ are between those of

$LiNiVO_4$ and $LiCoVO_4$. The substitution of Ni in $LiNiVO_4$ by Co makes the vibration bands of all metal–oxygen in the solid solution weaker by shifting the bands from high to low wavenumbers [3].

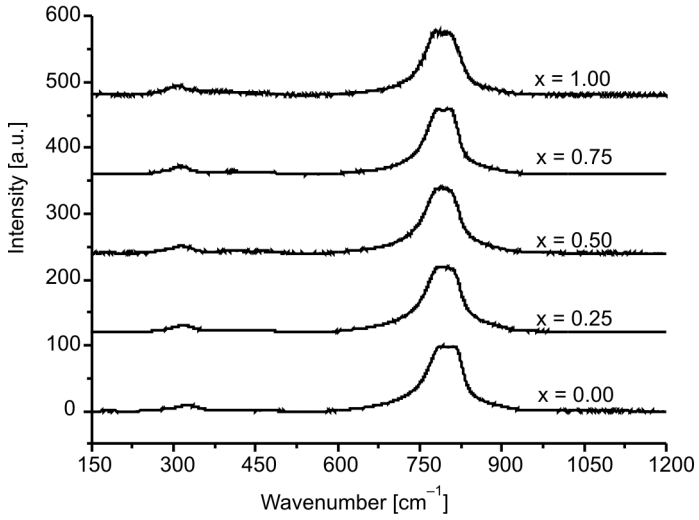

Fig. 5. Raman spectra of $LiNi_{1-x}Co_xVO_4$

3.4. TEM and SAED

TEM images and SAED patterns of $LiNiVO_4$, $LiNi_{0.50}Co_{0.50}VO_4$ and $LiCoVO_4$ are shown in Fig 6. The oxides are composed of rather round particles with dimensions of 19, 60 and 98 nm, respectively. The average particle sizes are increased with the

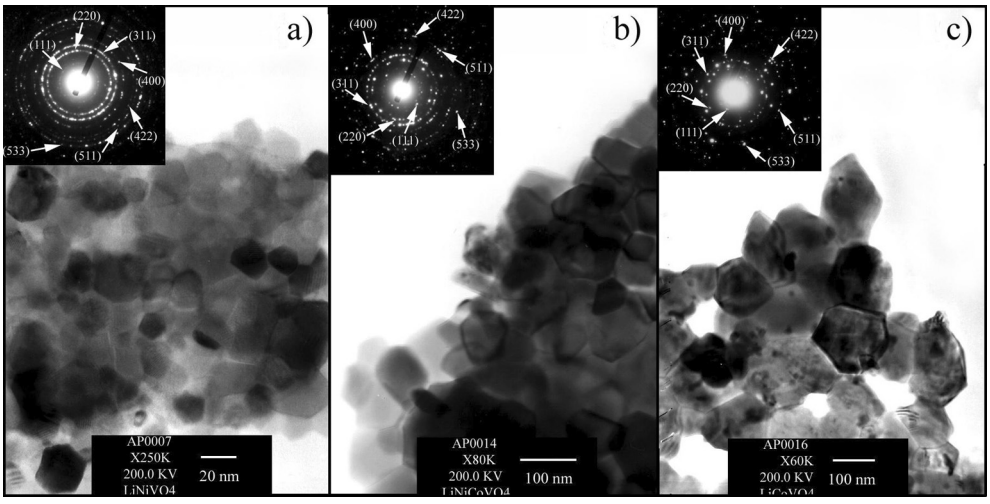

Fig. 6. TEM images and SAED patterns of: a) $LiNiVO_4$, b) $LiNi_{0.50}Co_{0.50}VO_4$, and c) $LiCoVO_4$

increase of Co concentration corresponding to the increase of the lattice parameter. SAED patterns show a number of bright spots arranged in concentric rings. They diffract from the crystallographic planes of the unit cells of the oxides. The calculated interplanar spaces (*d*) [12] of the SAED patterns in Fig. 6a and 6c are in accordance with those of the JCPDS standard of $LiNiVO_4$ and $LiCoVO_4$, respectively [6]. The diffraction planes are (111), (220), (311), (400), (422), (511) and (533). The *d* values of the SAED pattern in Fig 6b correspond to those of pure oxides (x = 0.00 and 1.00) showing that $LiNi_{0.50}Co_{0.50}VO_4$ is the solid solution of $LiNiVO_4$ and $LiCoVO_4$ [1, 3, 4].

3.5. EDX and AAS

Li is too light to be detected using the EDX. At x = 0.00, only Ni, V and O were detected. Additional Co was detected at x = 0.25, 0.50 and 0.75. The results are in accordance with those of using both Ni and Co salts as the starting agents. At x = 1.00, only Co, V and O were detected. To determine the atomic percentages of Li, Ni and Co, the oxides were analyzed using AAS. The stoichiometric values are very close to those of the expected oxides (Table 1).

Table 1. Formulas from expectation and AAS

Expected formula	Formula from AAS
$LiNiVO_4$	$Li_{1.045}Ni_{1.087}VO_4$
$LiNi_{0.75}Co_{0.25}VO_4$	$Li_{1.012}Ni_{0.779}Co_{0.263}VO_4$
$LiNi_{0.50}Co_{0.50}VO_4$	$Li_{1.025}Ni_{0.523}Co_{0.533}VO_4$
$LiNi_{0.25}Co_{0.75}VO_4$	$Li_{1.023}Ni_{0.266}Co_{0.777}VO_4$
$LiCoVO_4$	$Li_{1.034}Co_{1.065}VO_4$

4. Conclusions

Nanocrystalline $LiNi_{1-x}Co_xVO_4$ was successfully prepared by the polymerized complex method using tartaric acid as a complexing agent, with the subsequent calcination at 450 °C for 12 h. TGA shows that the oxides started to form at 450–550 °C. By using XRD, TEM, SAED, FTIR and Raman analyses, nanocrystalline $LiNi_{1-x}Co_xVO_4$ with inverse spinel structure was detected. The calculated lattice parameter and particle size were increased with the increase of the Co concentration. The vibration bands analyzed by a Raman spectrometer were also shifted to the lower wavenumbers. With the exception of Li, the elements contained in the oxides were detected using EDX. The atomic percentages of Li, Ni and Co analyzed using AAS are very close to the expected values.

Acknowledgements

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References

[1] VIVEKANANDHAN S., VENKATESWARLU M., SATYANARAYANA N., Mater. Chem. Phys., 91 (2005), 54.
[2] CHEN W., MAI L.Q., XU Q., ZHU Q.Y., YANG H.P., Mater. Sci. Eng., B 100 (2003), 221.
[3] FEY G.T.K., HUANG D.L., Electrochim. Acta, 45 (1999), 295.
[4] JULIEN C., MASSOT M., PÉREZ-VICENTE C., Mater. Sci. Eng., B 75 (2000), 6.
[5] PRABAHARAN S.R.S., MICHAEL M.S., IKUTA H., UCHIMOTO Y., WAKIHARA M., Solid State Ion., 172 (2004), 39.
[6] Powder Diffract. File, JCPDS Int. Centre Diffract. Data, PA 19073–3273, U.S.A., 2001.
[7] KALYANI P., KALAISELVI N., MUNIYANDI N., Mater. Chem. Phys., 77 (2002), 662.
[8] SURYANARAYANA C., NORTON M.G., *X-Ray Diffraction*, Plenum Press, New York, 1998.
[9] BHUVANESWARI M.S., SELVASEKARAPANDIAN S., KAMISHIMA O., KAWAMURA J., HATTORI T., J. Power Source, 139 (2005), 279.
[10] LAI Q.Y., LU J.Z., LIANG X.L., YAN F.Y., JI X.Y., Inter. J. Inorg. Mater., 3 (2001), 381.
[11] LIU J.R., WANG M., LIN X., YIN D.C., HUANG W.D., J. Power Source, 108 (2002), 113.
[12] ANDREWS K.W., DYSON D.J., KEOWN S.R., *Interpretation of Electron Diffraction Patterns*, Plenum Press, New York, 1971.

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