

# New inverse spinel cathode materials for rechargeable lithium batteries

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## Abstract

The synthesis, characterization, and electrochemical properties of  $\text{LiNi}_y\text{Co}_{1-y}\text{VO}_4$  ( $0 \leq y \leq 1$ ) as the new cathode materials for rechargeable lithium batteries were investigated. A series of  $\text{LiNi}_y\text{Co}_{1-y}\text{VO}_4$  ( $y=0.1-0.9$ ) compounds were synthesized by either a solid-state reaction of  $\text{LiNi}_y\text{Co}_{1-y}\text{O}_2$  and  $\text{V}_2\text{O}_5$  at  $800^\circ\text{C}$  for 12 h or a solution coprecipitation of  $\text{LiOH}\cdot\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  and  $\text{NH}_4\text{VO}_3$ , followed by heating the precipitate at  $500^\circ\text{C}$  for 48 h. The products from both preparation methods were analyzed by scanning electron microscopy and inductively-coupled plasma-atomic emission spectroscopy. These compounds are inverse spinels based on the results from Rietveld analysis and the fact that the cubic lattice constant  $a$  is a linear function of stoichiometry  $y$  in  $\text{LiNi}_y\text{Co}_{1-y}\text{VO}_4$ . Either a 1 M  $\text{LiClO}_4\text{-EC} + \text{PC}$  (1:1) or 1 M  $\text{LiBF}_4\text{-EC} + \text{PC} + \text{DMC}$  (1:1:4) electrolyte can be used as the electrolyte for  $\text{Li}/\text{LiNi}_y\text{Co}_{1-y}\text{VO}_4$  cells up to  $y=0.7$ . The charge and discharge capacity of a  $\text{Li}/1\text{M LiBF}_4\text{-EC} + \text{PC} + \text{DMC}$  (1:1:4)/ $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$  cell were 43.8 and 34.8 mAh/g, respectively, when the cathode material was prepared by the low temperature coprecipitation method. © 1997 Elsevier Science S.A.

**Keywords:** Inverse spinels; Cathode materials; Lithium batteries; Nickel; Vanadium; Cobalt

## 1. Introduction

Since the discovery of both  $\text{LiNiVO}_4$  and  $\text{LiCoVO}_4$  as new systems of cathode materials for rechargeable lithium batteries [1], interest in inverse spinel materials has arisen due to their high voltage behavior. Currently, three major systems of high voltage cathode materials are available for commercial lithium-ion cells: (i)  $\text{LiCoO}_2$  by Sony Energytec [2]; (ii)  $\text{LiNiO}_2$  by Moli Energy [3] in 1990, and (iii)  $\text{LiMn}_2\text{O}_4$  by Bellcore [4]. Both  $\text{LiCoO}_2$  and  $\text{LiNiO}_2$  possess a layered structure while  $\text{LiMn}_2\text{O}_4$  has a spinel structure. The upper voltage limits of these three systems are in the 4.1–4.5 V range, whereas the upper limit of inverse spinels are in the 4.2–4.8 V range.

Limited research has been conducted to elucidate the structure and properties of  $\text{LiMVO}_4$  ( $M = \text{Ni}$  or  $\text{Co}$ ) inverse spinels. Until now, little attention has been directed toward battery applications and only a few studies have focused on crystal structure [5,6], magnetic properties [5], infrared spectroscopy [7], phase diagrams [8], and electric conductivity [9].

Given their similar structure, the voltage difference between  $\text{LiNiVO}_4$  (4.8 V) and  $\text{LiCoVO}_4$  (4.2 V) is significant and implies that the presence and sites of nickel atoms

in an inverse spinel or spinel structure may play an important role in the voltage behavior of these materials. Both orthovanadates have been known to be spinels [5–10] where the cation arrangement was  $(\text{M}_x\text{V}_{1-x})^{\text{IV}}(\text{LiM}_{1-x}\text{V}_x)^{\text{VI}}\text{O}_4$  [8]. However, based on our X-ray diffraction data and Rietveld profile refinement analysis, both orthovanadates were confirmed to be inverse spinels where the cation arrangement was  $(\text{V})^{\text{IV}}(\text{LiM})^{\text{VI}}\text{O}_4$  [1].

The very high cell voltage of 4.8 V obtained using  $\text{LiNiVO}_4$  as a cathode has not been advantageous from an application point of view, because most electrolytes do not fit within its electrochemical window. However, the  $\text{LiCoVO}_4$  system exhibits 4.2 V which is more suitable for some oxidation-resistant electrolytes. Accordingly, a solid solution of  $\text{LiNiVO}_4$  and  $\text{LiCoVO}_4$  could be used to optimize cell voltage and performance and also to better understand the effects of nickel atoms on the crystal structure and lithium intercalation/de-intercalation of  $\text{LiMVO}_4$  inverse spinels.

Therefore, a series of  $\text{LiNi}_y\text{Co}_{1-y}\text{VO}_4$  compounds ( $0 \leq y \leq 1$ ) were synthesized and characterized in this work. The electrochemical behavior and preliminary cell performance of these new cathode materials are reported.

## 2. Experimental

$\text{LiNi}_y\text{Co}_{1-y}\text{VO}_4$  ( $0 \leq y \leq 1$ ) samples were synthesized by both a high temperature (HT) solid-state method and a low

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temperature (LT) coprecipitation method for comparison purposes. A standard HT- $\text{LiNi}_y\text{Co}_{1-y}\text{VO}_4$  sample was prepared by reacting stoichiometric quantities of  $\text{Li}_2\text{CO}_3$ ,  $\text{NiO}$ ,  $\text{Co}_3\text{O}_4$ , and  $\text{V}_2\text{O}_5$  in air at  $800^\circ\text{C}$  for 12 h. A standard LT- $\text{LiNi}_y\text{Co}_{1-y}\text{VO}_4$  sample was prepared first by dissolving stoichiometric quantities of  $\text{LiOH}\cdot\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ , and  $\text{NH}_4\text{VO}_3$  in de-ionized water. After vigorous stirring, a brown gel was formed (the color became darker when the Co content was higher) and dried at  $150^\circ\text{C}$  for 12 h resulting in a brown precursor. The final product was obtained by heating the precursor at  $500^\circ\text{C}$  for 48 h. For simplicity, from hereon we will refer to  $\text{LiNi}_y\text{Co}_{1-y}\text{VO}_4$  as 'topic compounds'.

Scanning electron microscopy (SEM) was carried out using a Hitachi S-2300 microscope. An ion coater was used for vacuum gold plating. Powder X-ray diffraction (XRD) measurements were made with a Siemens D500 diffractometer equipped with a diffracted beam monochromator and  $\text{Cu K}\alpha$  radiation.

Glass test cells were constructed as described previously [11] and they were galvanostatically cycled to the desired depths (usually from 3.0–4.5 V or up to 4.7 V) using an Amel Model 545 galvanostat–electrometer at a current density of  $0.1\text{ mA/cm}^2$ . Two electrolytes were used in charge/discharge tests: a 1 M  $\text{LiClO}_4\text{-EC+PC}$  (1:1) and 1 M  $\text{LiBF}_4\text{-EC+PC+DMC}$  (1:1:4). Numbers in parentheses denote a volume ratio of the solvents used in the electrolyte.

### 3. Results and discussion

Figs. 1 and 2 show that the XRD patterns of HT- $\text{LiNi}_y\text{Co}_{1-y}\text{VO}_4$  ( $0 \leq y \leq 1$ ) prepared by a HT solid-state method were very similar to those of corresponding LT- $\text{LiNi}_y\text{Co}_{1-y}\text{VO}_4$  prepared by a LT coprecipitation method. For  $0 < y < 1$ , both HT- and LT- $\text{LiNi}_y\text{Co}_{1-y}\text{VO}_4$  compounds are essentially single-phase and have inverse spinel-like XRD patterns identical to those of their parent compounds,  $\text{LiNiVO}_4$  and  $\text{LiCoVO}_4$ . Furthermore, we calculated the cubic lattice constant  $a$  for the whole series of  $\text{LiNi}_y\text{Co}_{1-y}\text{VO}_4$  ( $0 \leq y \leq 1$ ) based on the available XRD data and found that the lattice constant  $a$  is a linear function of stoichiometry  $y$  in  $\text{LiNi}_y\text{Co}_{1-y}\text{VO}_4$  ( $0 \leq y \leq 1$ ). This linear relationship plotted in Fig. 3 confirmed that a solid solution of  $\text{LiNiVO}_4$  and  $\text{LiCoVO}_4$  with an inverse spinel structure had been obtained in the whole  $0 < y < 1$  range. The calculated  $a$  values of  $\text{LiNiVO}_4$  and  $\text{LiCoVO}_4$  in Fig. 3 were 8.220 and 8.279 Å, respectively, which were consistent with their corresponding literature values of 8.215 and 8.276 Å [10].

A comparison of inductively-coupled plasma–atomic emission spectroscopy (ICP–AES) analytical results of  $\text{LiNi}_y\text{Co}_{1-y}\text{VO}_4$  ( $y=0$  to  $y=1.0$ ) prepared by the HT method and the LT method is given in Table 1. The quantitative results from ICP–AES analysis showed that lithium stoichiometry in both the LT- and the HT- $\text{LiNi}_y\text{Co}_{1-y}\text{VO}_4$  samples was slightly deficient ranging from 0.932 to 0.950

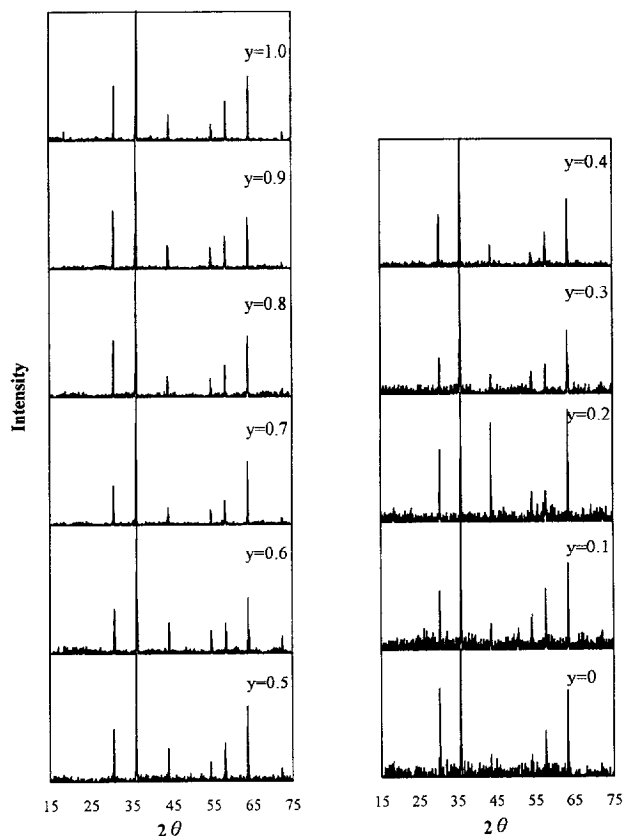


Fig. 1. XRD patterns of  $\text{LiNi}_y\text{Co}_{1-y}\text{VO}_4$  ( $y=0$  to  $y=1.0$ ) prepared by reacting  $\text{Li}_2\text{CO}_3$ ,  $\text{NiO}$ ,  $\text{Co}_3\text{O}_4$  and  $\text{V}_2\text{O}_5$  at  $800^\circ\text{C}$  for 12 h.

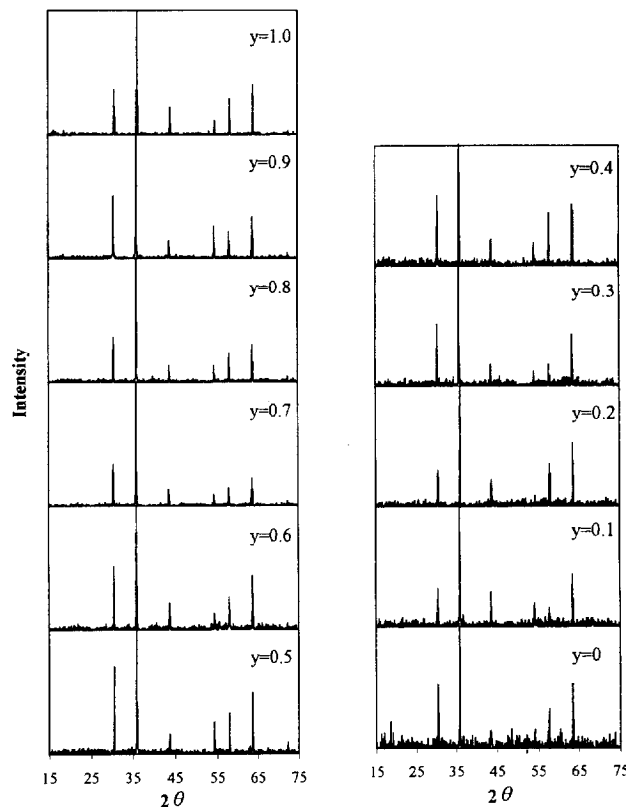


Fig. 2. XRD patterns of  $\text{LiNi}_y\text{Co}_{1-y}\text{VO}_4$  ( $y=0$  to  $y=1.0$ ) prepared by reacting  $\text{LiOH}\cdot\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ , and  $\text{NH}_4\text{VO}_3$  at  $500^\circ\text{C}$  for 48 h.

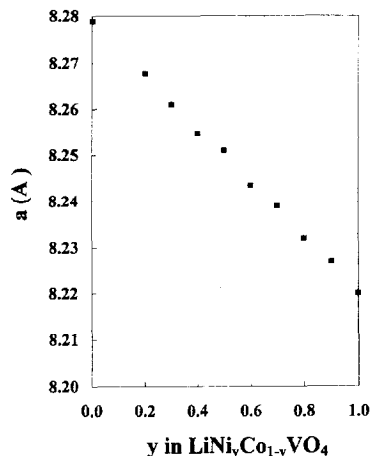


Fig. 3. The cubic lattice constant  $a$  for  $\text{LiNi}_y\text{Co}_{1-y}\text{VO}_4$  as a function of stoichiometry  $y$  in  $\text{LiNi}_y\text{Co}_{1-y}\text{VO}_4$ .

and from 0.910 to 0.925 for LT- and HT-samples, respectively. The results indicated that all topic compounds were lithium deficient, and deviated from their theoretical value,  $x = 1$ , revealing that some lithium mass loss occurred during the heating process. The topic compounds prepared by the LT method had higher lithium content than those prepared by the HT method.

The SEM micrographs in Figs. 4 and 5 show the grain size of the topic compounds prepared by the HT and LT methods. These micrographs indicated that the grain size of the topic compounds prepared by the HT method increased as the

cobalt content increased. Grain sizes ranged from 5 to 30  $\mu\text{m}$  and were not uniform. On the other hand, the grain size of the topic compounds prepared by the LT method were quite small, ranging from 0.1 to 1  $\mu\text{m}$ . The advantages of the LT method are: (i) less lithium stoichiometric loss, and (ii) small grain-size powders. From SEM results, the grain-size distribution of LT- $\text{LiNi}_y\text{Co}_{1-y}\text{VO}_4$  was in the 0.1–1  $\mu\text{m}$  range whereas that of HT- $\text{LiNi}_y\text{Co}_{1-y}\text{VO}_4$  was in the 5–30  $\mu\text{m}$  range.

For preliminary tests on the cell performance of these LT- and HT- $\text{LiNi}_y\text{Co}_{1-y}\text{VO}_4$  cathode materials, it was very difficult to cover all topic compounds from  $y = 0.1$  to 0.9 because a large number of samples and tests were involved. In order to get representative results,  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$  was selected since it is in the middle of the series.

Fig. 6 displays the effect of charge voltage on the cell capacity of a Li/1 M  $\text{LiBF}_4\text{-EC + PC + DMC (1:1:4)}$  /  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$  cell. Cell performance results in Table 2 show that cell capacity strongly depends upon charge voltage. The optimum charge voltage was found to be 4.7 V for cells where the maximum charge capacity of 43.8 mAh/g and discharge capacity of 34.8 mAh/g were obtained. At 4.8 V or higher, cell capacity greatly decreased probably due to electrolyte decomposition. A charge voltage of 4.5 V was used in regular tests instead of the optimum charge voltage of 4.7 V to achieve a compromise between capacity and cycle life.

Table 1

Comparison of the ICP-AES analytical results of  $\text{LiNi}_y\text{Co}_{1-y}\text{VO}_4$  ( $y = 0\text{--}1.0$ ) prepared by high temperature solid state and low temperature coprecipitation methods

Theoretical values	Experimental ICP-AES values	
	High temperature solid state method	Low temperature coprecipitation method
$\text{LiNiVO}_4$	$\text{Li}_{0.916}\text{Ni}_{0.937}\text{VO}_4$	$\text{Li}_{0.950}\text{Ni}_{0.938}\text{VO}_4$
$\text{LiNi}_{0.9}\text{Co}_{0.1}\text{VO}_4$	$\text{Li}_{0.922}\text{Ni}_{0.926}\text{Co}_{0.099}\text{VO}_4$	$\text{Li}_{0.938}\text{Ni}_{0.864}\text{Co}_{0.099}\text{VO}_4$
$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{VO}_4$	$\text{Li}_{0.916}\text{Ni}_{0.814}\text{Co}_{0.201}\text{VO}_4$	$\text{Li}_{0.945}\text{Ni}_{0.773}\text{Co}_{0.190}\text{VO}_4$
$\text{LiNi}_{0.7}\text{Co}_{0.3}\text{VO}_4$	$\text{Li}_{0.917}\text{Ni}_{0.723}\text{Co}_{0.291}\text{VO}_4$	$\text{Li}_{0.944}\text{Ni}_{0.673}\text{Co}_{0.292}\text{VO}_4$
$\text{LiNi}_{0.6}\text{Co}_{0.4}\text{VO}_4$	$\text{Li}_{0.911}\text{Ni}_{0.624}\text{Co}_{0.384}\text{VO}_4$	$\text{Li}_{0.942}\text{Ni}_{0.596}\text{Co}_{0.384}\text{VO}_4$
$\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$	$\text{Li}_{0.920}\text{Ni}_{0.538}\text{Co}_{0.486}\text{VO}_4$	$\text{Li}_{0.948}\text{Ni}_{0.465}\text{Co}_{0.477}\text{VO}_4$
$\text{LiNi}_{0.4}\text{Co}_{0.6}\text{VO}_4$	$\text{Li}_{0.916}\text{Ni}_{0.412}\text{Co}_{0.604}\text{VO}_4$	$\text{Li}_{0.944}\text{Ni}_{0.324}\text{Co}_{0.665}\text{VO}_4$
$\text{LiNi}_{0.3}\text{Co}_{0.7}\text{VO}_4$	$\text{Li}_{0.918}\text{Ni}_{0.309}\text{Co}_{0.694}\text{VO}_4$	$\text{Li}_{0.941}\text{Ni}_{0.242}\text{Co}_{0.639}\text{VO}_4$
$\text{LiNi}_{0.2}\text{Co}_{0.8}\text{VO}_4$	$\text{Li}_{0.910}\text{Ni}_{0.203}\text{Co}_{0.795}\text{VO}_4$	$\text{Li}_{0.944}\text{Ni}_{0.182}\text{Co}_{0.807}\text{VO}_4$
$\text{LiNi}_{0.1}\text{Co}_{0.9}\text{VO}_4$	$\text{Li}_{0.925}\text{Ni}_{0.111}\text{Co}_{0.893}\text{VO}_4$	$\text{Li}_{0.950}\text{Ni}_{0.093}\text{Co}_{0.933}\text{VO}_4$
$\text{LiCoVO}_4$	$\text{Li}_{0.923}\text{Co}_{0.971}\text{VO}_4$	$\text{Li}_{0.932}\text{Co}_{0.946}\text{VO}_4$

Table 2

Results of charge voltage vs. specific capacity of a Li/1 M  $\text{LiBF}_4\text{-EC + PC + DMC (1:1:4)}$  /  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$  cell

Charge voltage (V)	Charge capacity (mAh/g)	Discharge capacity (mAh/g)	Cycle efficiency (%)
4.50	33.8	26.2	78
4.60	34.1	28.3	83
4.70	43.8	34.8	79
4.80	37.7	12.1	32
4.85	22.2	8.7	39

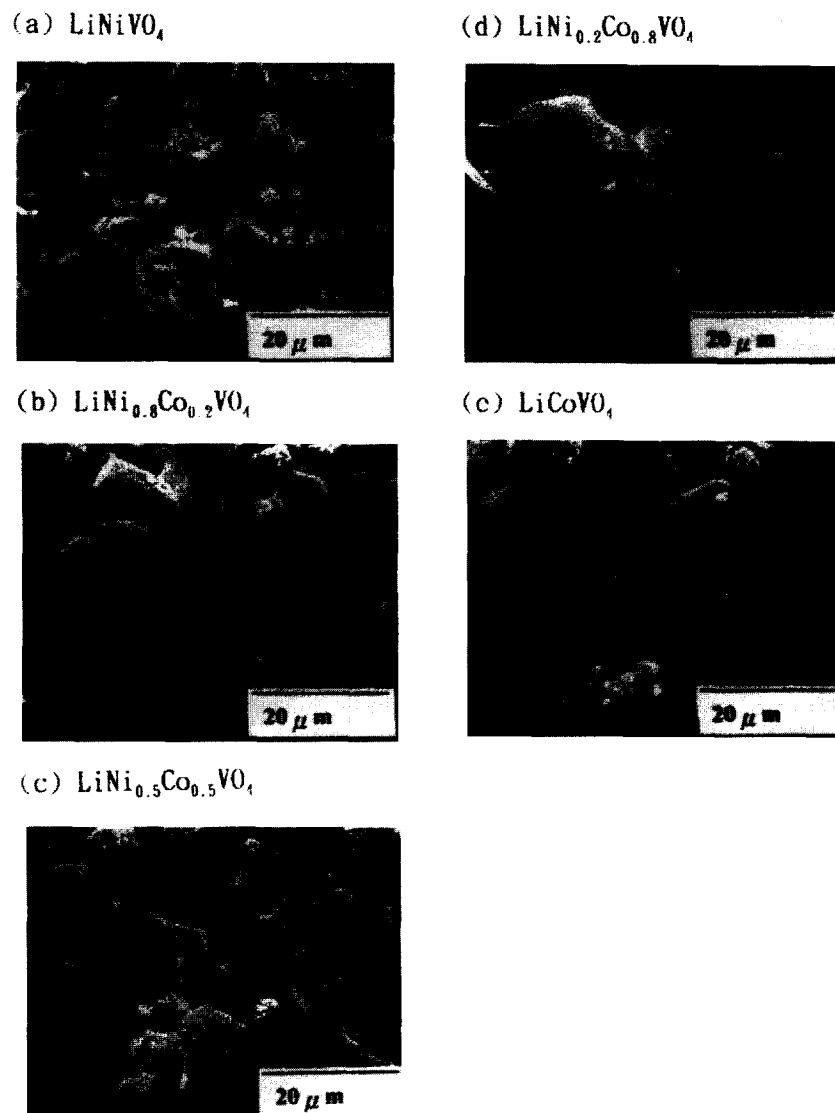


Fig. 4. SEM micrographs of  $\text{LiNi}_x\text{Co}_{1-y}\text{VO}_4$  prepared by a high temperature solid-state method.

Table 3

Comparison of selected capacity data of  $\text{Li}/1\text{ M LiBF}_4\text{-EC + PC + DMC (1:1:4)}/\text{LiNi}_x\text{Co}_{1-y}\text{VO}_4$  cells (where  $y=0$  or  $0.5$ ) with cathode materials prepared by either the high temperature or low temperature method

Cycle	$y=0.5$			$y=0$		
	Charge capacity (mAh/g)	Discharge capacity (mAh/g)	Cycle efficiency (%)	Charge capacity (mAh/g)	Discharge capacity (mAh/g)	Cycle efficiency (%)
<b>a) High temperature solid-state method</b>						
1	50.4	34.9	69.1	62.7	40.0	63.8
2	39.7	33.9	85.4	44.1	37.9	85.9
3	36.7	33.0	90.1	32.5	28.5	87.6
4	33.6	30.6	90.9	38.3	34.5	90.2
5	39.7	36.9	90.7	33.3	29.3	88.1
<b>b) Low temperature coprecipitation method</b>						
1	66.9	43.6	65.1	69.2	46.6	67.3
2	33.8	30.1	89.1	36.0	31.8	88.2
3	28.9	26.4	91.5	31.1	27.9	89.8
4	27.0	24.6	90.9	29.7	26.1	88.1
5	26.7	24.5	91.9	27.5	24.4	88.5

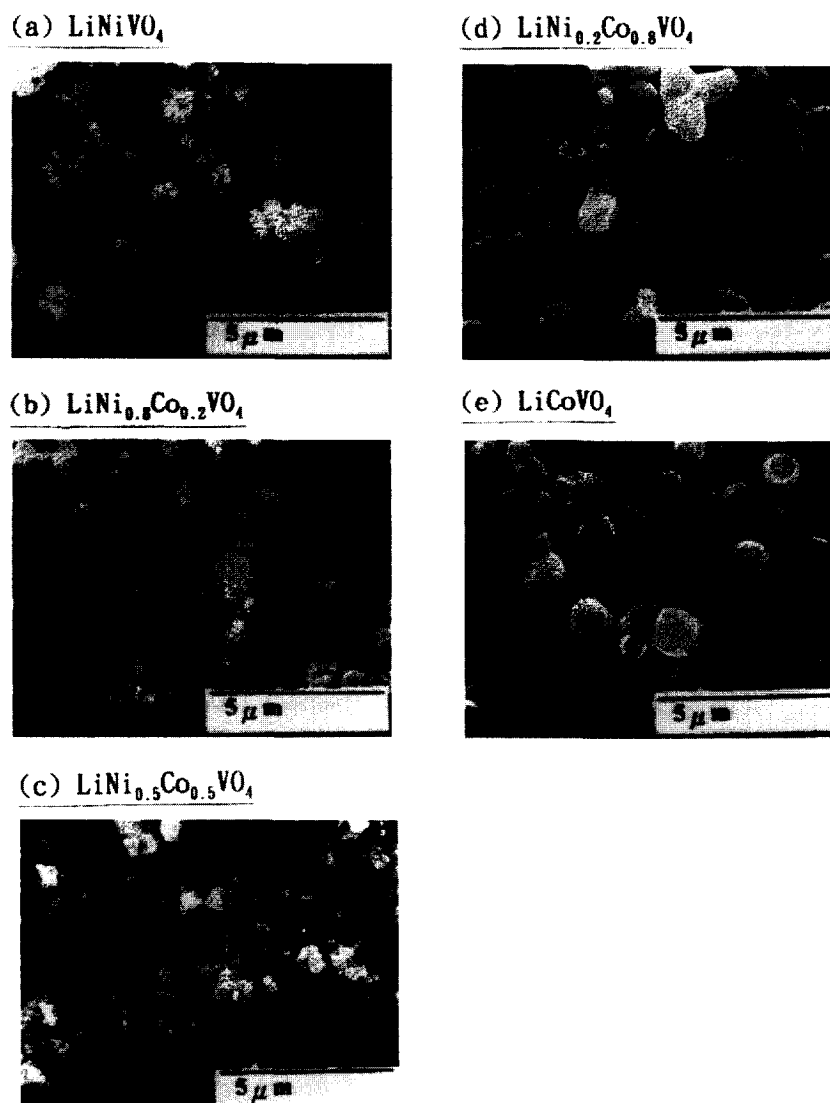


Fig. 5. SEM micrographs of  $\text{LiNi}_x\text{Co}_{1-y}\text{VO}_4$  prepared by a low temperature solution coprecipitation method.

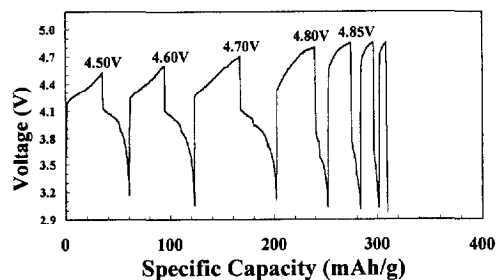


Fig. 6. Effect of charge voltage on the cell capacity of a  $\text{Li}/1 \text{ M LiBF}_4\text{-EC+PC+DMC (1:1:4)}/\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$  cell.

Typical charge/discharge curves and selected capacity data for  $\text{Li}/1 \text{ M LiClO}_4\text{-EC+PC (1:1)}/\text{LiNi}_y\text{Co}_{1-y}\text{VO}_4$  cells (where  $y=0$  or  $y=0.5$ ) are shown in Fig. 7 and Table 3. Both cathode materials were prepared by the HT method. These cells initially delivered about 38 mAh/g and a cycle efficiency of roughly 60%. The capacity of the cells using  $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{VO}_4$  and  $\text{LiCoVO}_4$  as the cathodes slowly declined with cycling and remained at 31.1 and 21.5 mAh/g

in the fifth cycle, respectively. It is significant that the former cell showed a two-step discharge curve with a deflection potential at 3.9 V. A similar situation occurred at near 4.1 V with the cell using a 1 M  $\text{LiBF}_4\text{-EC+PC+DMC (1:1:4)}$  electrolyte, but it did not occur with the cells whose cathode materials were prepared by the LT method. The structural basis of this two-step process is not yet known.

Fig. 8 shows a comparison of the charge/discharge characteristics of a 1 M  $\text{LiBF}_4\text{-EC+PC+DMC (1:1:4)}$  electrolyte using  $\text{LiNi}_y\text{Co}_{1-y}\text{VO}_4$  (where  $y=0, 0.2, 0.5, \text{ or } 0.7$ ) and  $\text{LiCoVO}_4$  as cathode materials, all prepared by the HT method. As the nickel stoichiometry  $y$  was increased to 0.8 or above, the cell had to be charged higher than 4.8 V. Undoubtedly, some electrolyte oxidation occurred at such a high voltage, causing a rapid decline in capacity. As a result, we were unable to get satisfactory cycle performance for cells with  $y=0.8, 0.9$  and 1.0.

Fig. 9 displays the charge/discharge curves of  $\text{Li}/1 \text{ M LiBF}_4\text{-EC+PC+DMC (1:1:4)}/\text{LiNi}_y\text{Co}_{1-y}\text{VO}_4$  cells

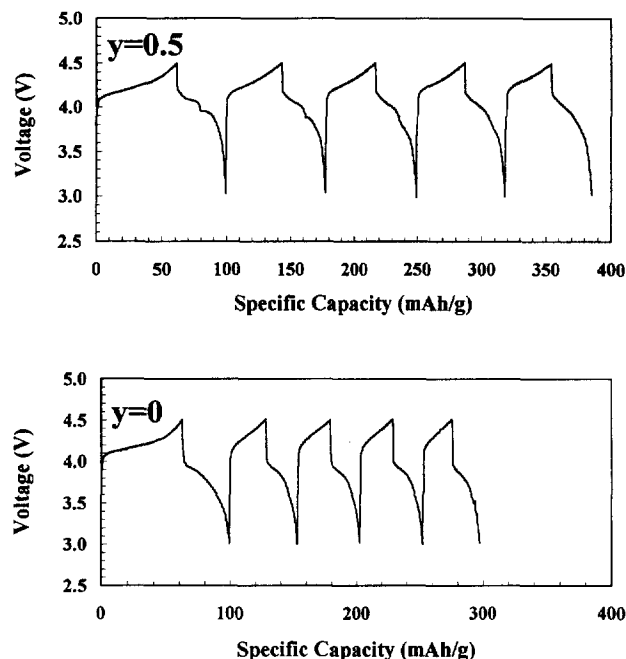


Fig. 7. Charge/discharge curves for Li/LiClO<sub>4</sub>-EC+PC (1:1)/LiNi<sub>y</sub>Co<sub>1-y</sub>VO<sub>4</sub> cells (where y=0 or 0.5) with cathode materials prepared by the high temperature method.

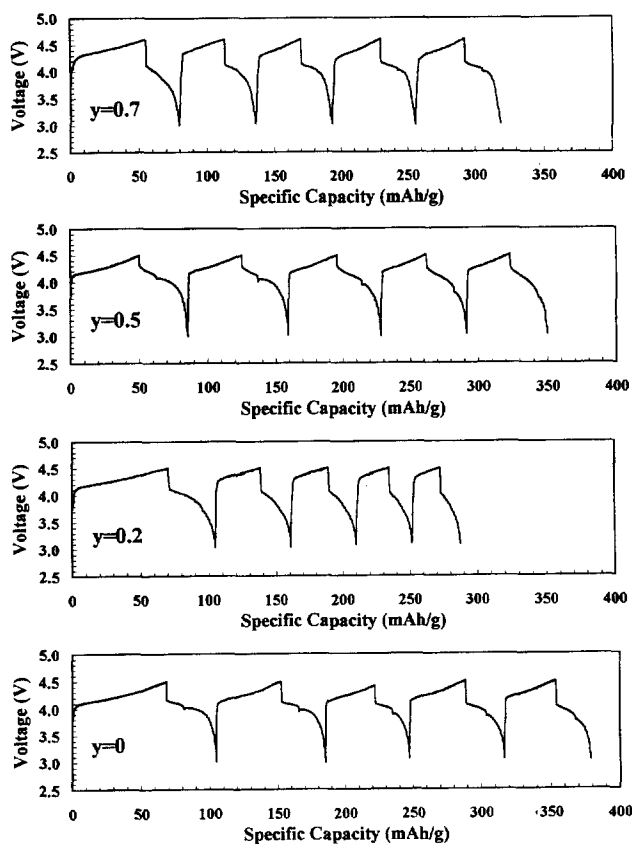


Fig. 8. Charge/discharge curves for Li/LiBF<sub>4</sub>-EC+PC+DMC (1:1:4)/LiNi<sub>y</sub>Co<sub>1-y</sub>VO<sub>4</sub> cells (where y=0, 0.2, 0.5 or 0.7) with cathode materials prepared by the high temperature method.

(where y=0 or 0.5), whose cathode materials were prepared by the LT method. To simplify comparing the cell performance of cathode materials with different preparation methods,

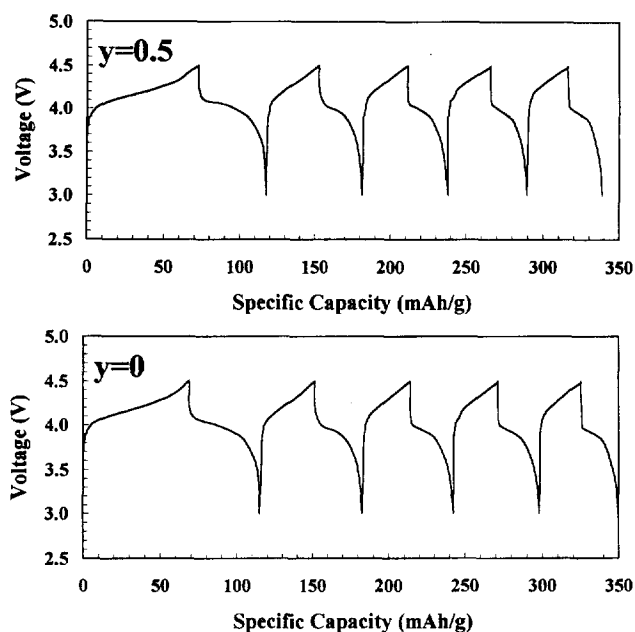


Fig. 9. Charge/discharge curves for Li/LiBF<sub>4</sub>-EC+PC+DMC (1:1:4)/LiNi<sub>y</sub>Co<sub>1-y</sub>VO<sub>4</sub> cells (where y=0 or 0.5) with cathode materials prepared by the low temperature method.

some capacity data of Li/1 M LiBF<sub>4</sub>-EC+PC+DMC (1:1:4)/LiNi<sub>y</sub>Co<sub>1-y</sub>VO<sub>4</sub> cells (where y=0 or 0.5) selected from Figs. 8 and 9 are listed in Table 3. In general, the charge/discharge capacity of an Li/LiNi<sub>0.5</sub>Co<sub>0.5</sub>VO<sub>4</sub> cell is comparable with that of an Li/LiCoVO<sub>4</sub> cell. In terms of cathode preparation, the LT method offers a small advantage in capacity over the HT method. All cells suffered a large irreversible loss in overall capacity in the first cycle and became stable in terms of cycle efficiency during cycling.

#### 4. Conclusions

A series of LiNi<sub>y</sub>Co<sub>1-y</sub>VO<sub>4</sub> (y=0.1–0.9) compounds with an inverse spinel structure were successfully synthesized and characterized as the potential new cathode materials for lithium/lithium-ion batteries. Preliminary cell performance when LiNi<sub>y</sub>Co<sub>1-y</sub>VO<sub>4</sub> (0 ≤ y ≤ 1) was used as a cathode did not measure up to the cell capacity of the Li/LiNiVO<sub>4</sub> coin cell we tested in a previous study. Possible causes are a low lithium-stoichiometry product and the differences in test cell configuration, preparation method, charge cut-off voltage, and electrolyte source. Several studies on the improvement of synthesis, determination of structure, and development of oxidation-resistant electrolytes are currently being carried out to improve lithium cycling capacity and reversibility. At present, these new materials do not seem capable of delivering capacities comparable with those of the best cathodes for lithium or lithium-ion cells. With sufficient efforts and delicate work, they may turn out to be useful cathode materials.

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