# Synthesis, characterization, and cell performance of LiNiVO$_4$ cathode materials prepared by a new solution precipitation method

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## Abstract

LiNiVO$_4$ was prepared by a new solution precipitation process using acetylacetonate as a reagent. The effects of pH value on the purity, grain size, lithium stoichiometry, and cycling behavior of LiNiVO$_4$ were studied. Solution precipitation performed in an acidic medium of pH = 3 with heat-treatment at 450°C for 12 h yielded pure and fine LiNiVO$_4$ powders which showed lithium stoichiometry of 0.971 and narrow grain-size of 0.34 μm. Under neutral and basic conditions, the LiNiVO$_4$ particles were contaminated with NiO and formed aggregates with a larger grain size in the 0.36–0.54 μm range. The resulting LiNiVO$_4$ powders were characterized by TGA, XRD, ICP-AES, SEM, and AFM techniques. Moreover, the cycle behavior of LiNiVO$_4$ products synthesized by a high temperature solid state method and this new solution precipitation method was compared and discussed. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Lithium–nickel orthovanadate; Solution precipitation; Acetylacetonate; Cathode materials; Nickel; Vanadium; Lithium batteries

## 1. Introduction

Lithium–nickel orthovanadate, LiNiVO$_4$, is an interesting intercalation compound, because it displays a high voltage of 4.8 V and is the first cathode material with an inverse spinel structure that has been proposed for Li and Li-ion battery applications [1]. Various synthesis methods of solid state reactions for preparing LiNiVO$_4$ [2–4] and its related inverse spinel compounds [5] have been reported. The products of LiNiVO$_4$ prepared by these solid state methods showed a large grain distribution in the 10–30 μm range and a large irreversible capacity loss in the first cycle. Particle size has been shown to play an important role in the cycling behavior of LiCoO$_2$ and LiMn$_2$O$_4$ [6–8].

A solution precipitation method provides an alternative route for the synthesis of finely dispersed oxide powders at lower reaction temperatures and offers better control over the morphology and texture of solid particles. Recently, we successfully developed a new solution precipitation method, using acetylacetonate as a reagent for synthesizing ultrafine LiCoO$_2$ powders [9], which showed higher reversible capacity than the samples prepared by conventional HT- and LT-solid state methods.

This paper is concerned with the application of this new solution precipitation method to the preparation of LiNiVO$_4$. We investigated suitable pH conditions for synthesizing LiNiVO$_4$. The resulting LiNiVO$_4$ powders were further characterized by TGA, XRD, ICP-AES, SEM, and AFM techniques. The effects of pH value during processing on the purity, grain size, lithium stoichiometry, and cell performance of LiNiVO$_4$ products are discussed.

## 2. Experimental

LiNiVO$_4$ was prepared by the solution precipitation process using LiNO$_3$ (Ferak, 99%), Ni(NO$_3$)$_2$ · 6H$_2$O (Ferak, 99%), and V(C$_5$H$_7$O$_2$)$_3$ (Aldrich, 99%) as starting reactants, where the mole ratio was 1:1:1 for lithium nitrate, nickel nitrate, and vanadium(III) acetylacetonate, respectively. Each starting reactant was dissolved in *n*-butanol (Ferak, 99%) at 60°C. The initial reaction took place by mixing these *n*-butanol solutions at 60°C and stirring well. The pH value of the resulting solution was adjusted to the desired one (e.g., pH = 3, 7, or 11) by adding diluted nitric acid or NH$_4$OH solution. The solution was left open in a fume hood at room temperature. After the solvent evaporated, the black slurry residue obtained was first dried at 80°C for 2 h, and then transferred to an alumina boat and heated at 450°C for 12 h. A brownish

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yellow solid product of LiNiVO$_4$ was obtained with a yield of 91.5%. To compare the cycling behavior of LiNiVO$_4$ made by a high temperature (HT) solid state method, a sample was prepared by the solid state reaction of Li$_2$CO$_3$, NiO and V$_2$O$_5$ at 730°C for 12 h.

Powder XRD measurements were made with a Siemens D-500 diffractometer equipped with a diffracted beam monochromator and Cu K$\alpha$ radiation of 1.5406 Å. TGA and ICP-AES determinations were performed using a Seiko SSC-5000 analyzer and Jarrell-Ash ICPA-9000 spectrometer, respectively. The details of SEM and AFM instrumental analysis were reported in Ref. [10]. A Maccor S-4000 Battery Test System controlled the cell cycling tests. Cathode preparation was similar to that described in Ref. [11]. Coin-type-2325 cell hardware used for the cycling tests was similar to that described in Ref. [12]. The test cells containing 1 M LiPF$_6$-EC-DEC (1:1 volume ratio) were charged usually to 4.9 V and discharged to 3.0 V at a 0.15 C rate. $V_c$, $V_d$, $V_{i.d.}$ denote charge voltage, discharge voltage, and initial discharge voltage, respectively.

## 3. Results and discussion

In Fig. 1, the four peaks registered by all precursor samples obtained from the reaction of LiNO$_3$, Ni(NO$_3$)$_2$ · 6H$_2$O and V(C$_5$H$_7$O$_2$)$_3$ under various pH conditions near 110°C, 230°C, 305°C and 420°C resemble each other. These peaks are not as well-defined or as sharp as those reported in Ref. [9] due to multiple phase transitions which occurred during the thermal decomposition of acetylaceto-
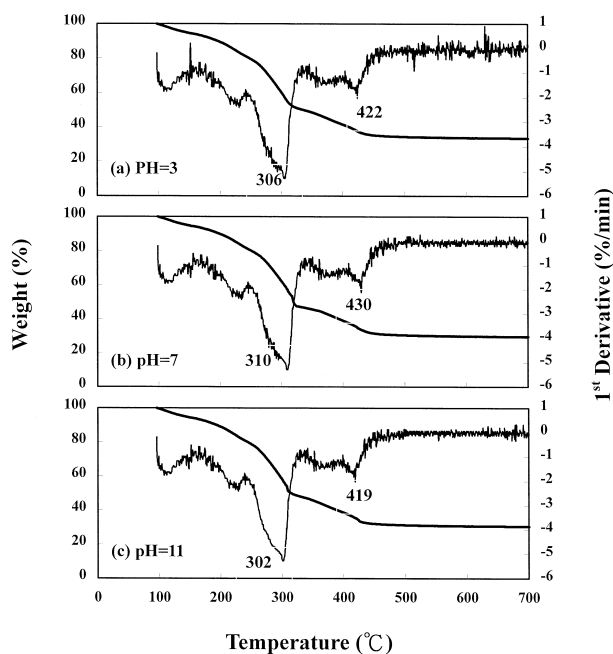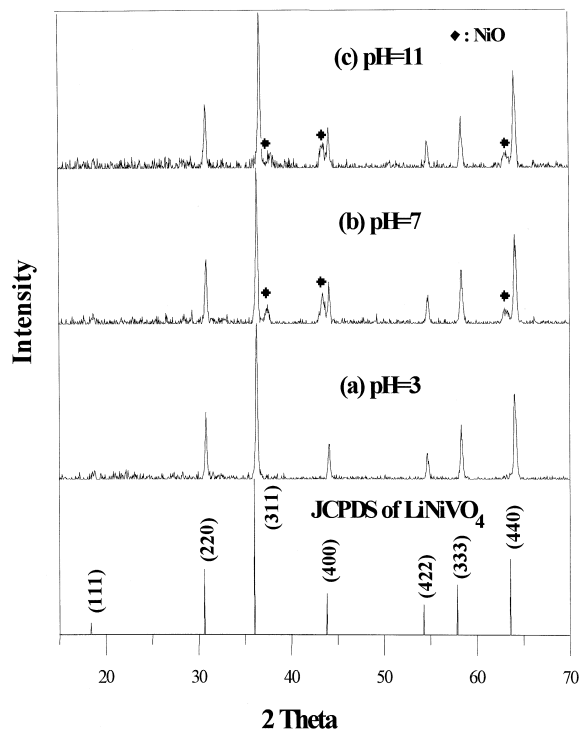


Fig. 2. XRD patterns of LiNiVO$_4$ prepared by the solution precipitation method: (a) pH = 3; (b) pH = 7; (c) pH = 11.

nate. The assignments of these related peaks were also discussed in Ref. [9]. The minimum heat-treatment temperature of the black residues for preparing LiNiVO$_4$ was chosen to be 450°C because their TG and DTG curves from solution precipitation processing under various pH conditions, as shown in Fig. 1, clearly indicated that the weight loss of the specimens remained almost constant above 450°C. Total weight loss was 70%, compared to the calculated value of 74%, which was based on the proposed reaction equation in argon atmosphere: LiNO$_3$ + Ni(NO$_3$)$_2$ 6H$_2$O + V(C$_5$H$_7$O$_2$)$_3$ → LiNiVO$_4$ + 2NO + NH$_3$ + 15H$_2$ 15CO.

Fig. 2 displays the XRD patterns of LiNiVO$_4$ powders prepared by the solution precipitation method at 450°C for 12 h under acidic, neutral and basic conditions, and compares them to the JCPDS' patterns of a LiNiVO$_4$ standard. A pure LiNiVO$_4$ product can be obtained only in an acidic medium of pH = 3, when XRD patterns closely match that of the JCPDS' LiNiVO$_4$ standard. Under neutral and basic conditions, the LiNiVO$_4$ products were contaminated with NiO.

The lithium stoichiometry of LiNiVO$_4$ products depends upon the preparation method and the pH values of the precursors in solution precipitation processing. Table 1 compares the ICP-AES analytical results of the lithium stoichiometry number, $x$, in Li$_x$NiVO$_4$ prepared under various pH conditions or by the HT-solid state method. These results show that all LiNiVO$_4$ products were lithium-deficient and deviated from their theoretical value,



Fig. 1. TG and DTG curves of the precursor samples from the reactions of LiNO$_3$, Ni(NO$_3$)$_2$·6H$_2$O, and V(C$_5$H$_7$O$_2$)$_3$ under various pH conditions: (a) pH = 3; (b) pH = 7; (c) pH = 11.

$x = 1$, revealing that the tunnels present in normal spinels are absent or insufficient in the inverse spinel. As a result, insufficient Li atoms can diffuse in and out of this compound. Among the three pH conditions, the $LiNiVO_4$ samples prepared in acidic media had higher lithium content than those prepared in neutral or basic media or by the HT-solid state method.

Fig. 3 displays the SEM micrographs of $LiNiVO_4$ samples prepared by the HT solid state method (called Sample A herein) and by the solution precipitation process at 450°C under various pH conditions (called Samples B, C, D herein). The grain-size distribution of Sample A is broader and in the 10–15 μm range whereas Samples B–D are narrower and in the 0.3–0.5 μm range. We noticed that samples prepared under acidic conditions (i.e., Sample B) were fine powders around 0.3 μm with the least amount of aggregates, while under basic conditions (i.e., Sample D), clusters of particles were most readily formed. This result was probably due to acid-catalyzed condensation promoted by the acetylacetonate precursor [9]. Because high acid concentration severely impeded condensation kinetics, grain growth kinetics of $LiNiVO_4$ in the solution precipitation process were less favoured under acidic conditions.

The AFM results were consistent with those from the aforementioned SEM analysis. Again, grain size was the smallest for samples made in an acidic medium of pH = 3 and heated at 450°C for 12 h. The grain sizes measured by tapping mode AFM were 343, 366, and 544 nm, for samples processed in acidic, neutral, and basic media, respectively.
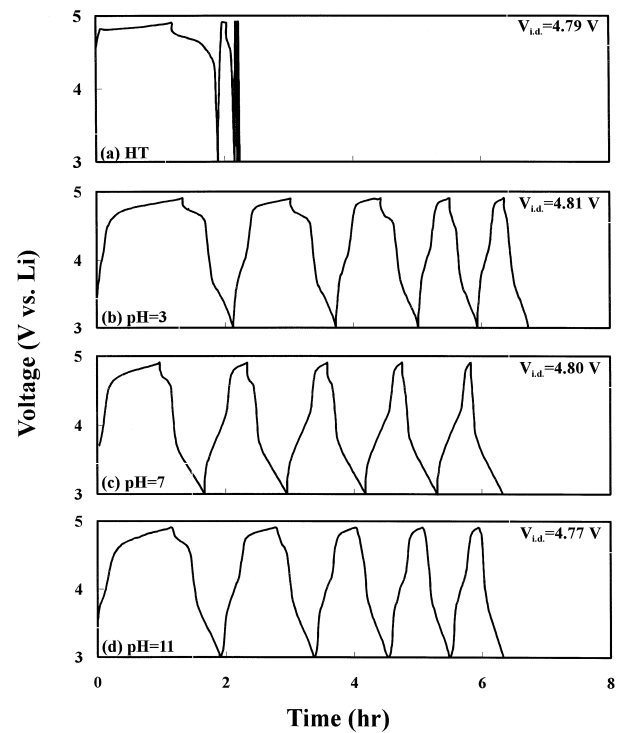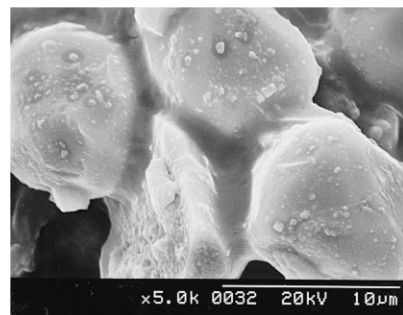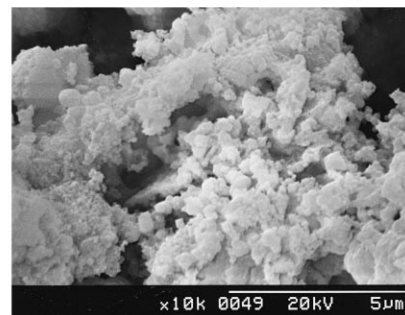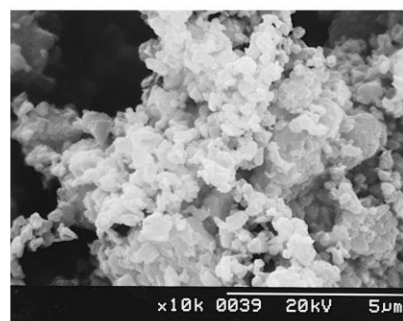


Fig. 4. The cycling behavior of cells with $LiNiVO_4$ prepared by various methods. (a) HT-solid state method and the solution precipitation method: (b) pH = 3; (c) pH = 7; (d) pH = 11.
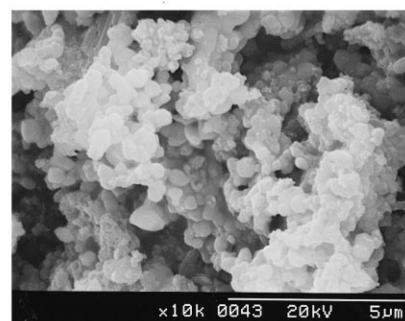


(a) HT-solid method



(b) pH=3



(c) pH=7



(d) pH=11

Fig. 3. SEM micrographs of $LiNiVO_4$ prepared by (a) HT-solid state method and the solution precipitation method: (b) pH = 3; (c) pH = 7; (d) pH = 11.

Table 1
Comparison of the ICP-AES analytical results of $LiNiVO_4$ prepared by various methods

| Process | Reaction condition | | Theoretical value | ICP-AES analytical results |
|---|---|---|---|---|
| Solution precipitation method | $LiNO_3 + V(C_5H_7O_2)_3 + Ni(NO_3)_2 \cdot 6H_2O$ (450°C, 12 h) | pH = 3 | $Li_xNiVO_4$ ($x = 1$) | $Li_{0.971}Ni_{0.962}VO_4$ |
| | | pH = 7 | | $Li_{0.967}Ni_{0.937}VO_4$ |
| | | pH = 11 | | $Li_{0.960}Ni_{0.948}VO_4$ |
| Solid state method | $Li_2CO_3 + 2NiO + V_2O_5$ (730°C, 12 h) | | | $Li_{0.948}Ni_{0.938}VO_4$ |

Table 2
Comparison of selected capacity data of cells with $LiNiVO_4$ prepared by the HT-solid state method and the solution precipitation method under various pH conditions

| Process | | Cycling behavior | | | | | |
|---|---|---|---|---|---|---|---|
| | | First cycle | | | Second cycle | | |
| | | C.C. (mA h/g) | D.C. (mA h/g) | C.E. (%) | C.C. (mA h/g) | D.C. (mA h/g) | C.E. (%) |
| Solid state method | | 36 | 21 | 58.3 | 4 | 3 | 75.0 |
| Solution precipitation method | pH = 3 | 39 | 24 | 61.5 | 26 | 22 | 84.6 |
| | pH = 7 | 30 | 19 | 63.3 | 21 | 18 | 85.7 |
| | pH = 11 | 34 | 23 | 67.6 | 24 | 16 | 66.6 |

C.C., D.C. and C.E. denote charge capacity, discharge capacity and cycle efficiency, respectively.

The cycling behavior of cells with $LiNiVO_4$ prepared under different pH conditions and by the HT-solid state method is shown in Fig. 4. The initial discharge voltages were 4.81, 4.80, and 4.77 V for $LiNiVO_4$ prepared at pH = 3, 7, and 11, respectively. Among the various pH conditions studied, the cell with $LiNiVO_4$ prepared at pH = 3 showed the lowest polarization effect between charge and discharge processes, since it had the highest $V_{i.d.}$ With increasing pH value, cell polarization increased, as expected since increasing the grain size slowed the kinetics of lithium diffusion, producing larger differences between the voltages on charge and discharge.

The charge–discharge curves in Fig. 4b–d display a voltage plateau around 4.6–4.8 V, along with a shoulder around 3.7 V under various pH conditions. The plateau corresponds to Li insertion/extraction, whereas the shoulder may be related to structural phase transitions. In our previous studies [1–3], cells with single-phase $LiNiVO_4$ prepared by other synthesis methods exhibited only the plateau around 4.6–4.8 V. Thus, there is no qualitative explanation for such structural phase transitions. Similarly, the cell with $LiNiVO_4$ prepared by the HT-solid state method shows a plateau around 4.4–4.8 V in Fig. 4a, but it almost disappears in the second cycle, indicating very low capacity. Selected capacity data from the first two cycles in Fig. 4 are presented in Table 2. All cell capacity values from this work are low compared to those from our previous investigations [1–4]. Cell charge capacity dropped significantly after the first cycle in all cases. The cell with $LiNiVO_4$ prepared in a medium of pH = 3 delivered the best cell performance: the highest capacity during charge and discharge which was 39 and 24 mA h/g, respectively. However, these are just preliminary results and further studies on the synthesis of $LiNiVO_4$ under various acidic pH conditions and heat-treatment temperatures by this new solution precipitation method will be discussed in a forthcoming paper.

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