SYNTHESIS OF NANOCRYSTALLINE OLIVINE LiNiPO₄ 
POWDER PREPARED BY SOL-GEL METHOD: THERMAL ANALYSIS AND XRD STUDIES

(Penyediaan Serbuk Nanokristal LiNiPO₄ dengan Struktur Olivin Melalui Kaedah Sol-Gel: Analisis Terma dan Kajian XRD)

Azlin Sanusi¹²³*, Shanti Navaratnam²³, Wan Jeffrey Basirun⁴

¹INTEC Education College, Jalan Senangin Satu 17/2A, Seksyen 17, 40200 Shah Alam, Selangor, Malaysia
²Faculty of Applied Sciences, Institute of Science, Universiti Teknologi Mara,40450 Shah Alam, Selangor Malaysia
⁴Chemistry Department, Faculty of Science, University of Malaya,50732 Kuala Lumpur, Malaysia

*Corresponding author: azlin457@salam.uitm.edu.my

Abstract
LiMPO₄ have attracted much attention as potential cathode material as it does not liberate oxygen on decomposition unlike lithium transition metal oxides (LMO). In this work, LiNiPO₄ powder was prepared by sol gel method using LiOH, Ni(CH₃COO)₂, NH₄H₂(PO₄) and tartaric acid as chelating agent. The precursor powders were studied by thermogravimetric analysis (TGA). Based on the TGA results, the sample was calcined at 1000°C in air. The TGA/DTGA studies have been employed to analyse the reaction of raw materials during the formation of LiNiPO₄. The formation mechanism for the synthesis of LiNiPO₄ and the overall decomposition equation for the precursor were proposed from the TGA/DTGA analysis. The calculated total weight loss from the overall proposed decomposition process which is 66.4% shows agreement with the percentage weight loss from the TGA curves which is 68%. The X-ray diffraction analysis was carried out to confirm the formation of LiNiPO₄. The precursors and the calcined powders were characterized by X-ray diffraction (XRD). Analysis of the synthesized LiNiPO₄ using XRD demonstrated the formation of a pure LiNiPO₄ phase powder.

Keywords: lithium nickel phosphate, sol-gel, mechanism

Abstrak
LiMPO₄ telah menarik banyak minat terhadap potensinya sebagai bahah katod untuk bateri litium. kerana tidak seperti litium oksida logam peralihan (LMO) bahan ini tidak melepaskan oksigen ketika proses penguraian. Didalam kajian ini LiNiPO₄ telah disintisis dengan mencampurkan LiOH, Ni(CH₃COO)₂, NH₄H₂(PO₄) dan asid tartarik dengan menggunakan kaedah sol-gel. Analisis TGA telah dilakukan keatas prapenanda LiNiPO₄ untuk menetukan suhu pembakaran dan didapati suhu yang sesuai adalah 1000°C. Unjuran persamaan bagi penguraian prapenanda LiNiPO₄ telah diperolehi dengan menggunakan lekok TGA/DTGA. Pengiraan peratus penurunan berat menggunakan persamaan unjuran (66.4%) dan lekok TGA (68%) adalah hampir sama. Spektrum belauan sinar –X (XRD) menunjukkan bahan sampel LiNiPO₄ adalah tulin.

Kata kunci: litium nikel fosfat, kaedah sol-gel, mekanisme

Introduction
In recent years, lithium metal phosphate (LiMPO₄) with the olivine structure has received a lot of attention to be a potential candidate for cathode materials in lithium ion batteries [1-4]. Unlike lithium transition metal oxides (LMO), LiMPO₄ does not liberate oxygen on decomposition. In addition, LiMPO₄ is cheaper, benign, and environmentally friendly and has greater stability than LMO. Various methods have been used to synthesize LiMPO₄ cathode material such as solid-state [1], sol-gel [2-4], hydrothermal [5-7] and aqueous precipitation [8].

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Many of the sol-gel method reported used citric acid as chelating agent and argon or nitrogen ambient during calcinations of precursor powders.

This paper reports the synthesis and characterization of LiNiPO₄ (lithium nickel phosphate) which belongs to the olivine structure. In this work, LiNiPO₄ was prepared by the sol-gel method with tartaric acid and calcined in air. Sol-gel has considerable advantages of good mixing of the starting materials and good chemical homogeneity of the product. To the best of our knowledge, reports on LiMnPO₄ nanocrystalline structured powders prepared by tartaric acid and calcined in air are rare.

The resulting LiNiPO₄ powders obtained were then characterized by thermogravimetric analysis (TGA), and X-ray diffraction (XRD). The formation mechanism for the synthesis of LiNiPO₄ are also discussed in this paper.

Materials and Methods

Sample preparation
Stoichiometric amounts of lithium hydroxide (LiOH·H₂O, Ajax), nickel acetate (Ni(CH₃COO)₂·4H₂O, Ajax) and ammonium dihydrogen phosphate NH₄H₂PO₄ (AR grade) were weighed and dissolved in distilled and deionised water separately with 1:1:1 mole ratio. The aqueous solutions were mixed together and stirred constantly. A 1.0 M tartaric acid solution was slowly added to the mixture as the chelating agent. Ammonium hydroxide was added carefully into the mixture until a pH value of 5-7 was achieved. The mixtures were mixed and stirred thoroughly until a greenish gel was obtained. The gels were left for drying in an oven at 60°C for 3 days.

Characterization of sample synthesized
Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTGA) analysis of the LiNiPO₄ powders were performed in order to examine the thermal decomposition behaviour of the gel precursor. The heating rate was 10°C min⁻¹ and the precursor was heated at 30°C-1000°C in nitrogen atmosphere.

The structure and phase of the product was identified by X-ray powder diffraction (XRD) analysis. The measurements were made with Siemens D5000 X-ray diffractometer with CuKα radiation at room temperature.

Results and Discussion

The TGA/DTGA analysis of the greenish gel obtained in this work is shown in Fig 1. The TGA thermogram of the precursors revealed that there are four significant weight loss regions as shown in Figure 1. A weight loss about 1.1% occurred slowly as the temperature was increased to about 150°C, due to the evaporation of residual water which are still present in the sample. Rapid weight loss occurred around the temperature range between 150°C - 275°C and is associated with a 34.1% weight loss. The decomposition process is attributed to the decomposition of unreacted ammonium dihydrogen phosphate as it was one of the reactant materials in the sample. The removal of tartaric acid is also assigned to this region. The weight loss is also due to the decomposition of the Li-Ni acetate complex formed in the experiment. The decomposition process of the precursor is also accompanied by a sharp peak at about 237°C as seen on the DTGA thermogram in Figure 1. The peak is probably due to the decomposition of ammonium dihydrogen phosphate which is an endothermic process.

The third weight loss occurred at the temperature range from 275 to 325°C. This decomposition was associated with a weight loss of 8.8% and can be attributed to the burning out of organic residues which resulted from the Li-Ni acetate complex decomposition. The final decomposition step which is associated with 23.9% weight loss occurred in the temperature range from 325°C to 725°C. The weight loss is attributed to the decomposition of nickel acetate and lithium hydroxide. Nickel acetate steadily decomposed in the temperature range from 272°C to 400°C.

The DTGA thermogram reveals a sharp peak at 354°C indicating the rapid decomposition of nickel acetate. The weight is constant after 725°C indicating that no heat is used for evaporation or decomposition processes and that LiNiPO₄ can be obtained by firing the precursor at temperatures above 750°C. The tartaric acid is likely to act as a fuel in the pyrolysis and expedite the process of decomposition of acetate ions. The corresponding weight loss, temperature ranges and their assignment are summarized in Table 1.
The reaction mechanism for the synthesis of LiNiPO$_4$ has been proposed as shown below. When tartaric acid ($C_4H_6O_6$) was added to the mixture, it reacted with (NH$_4$)$_2$H$_2$PO$_4$ and LiOH according to the following equations:

\[
2(NH_4)H_2PO_4 + C_4H_6O_6 \rightarrow H_3PO_4 + H_3PO_4^- + ((NH_4)C_4H_5O_6)^+ \quad (1)
\]

\[
LiOH + C_4H_6O_6 \rightarrow Li(C_4H_5O_6) + H_2O \quad (2)
\]

LiOH also reacted with H$_3$PO$_4$ produced in equation (1) according to the following,

\[
LiOH + H_3PO_4 \rightarrow LiH_2PO_4 + H_2O \quad (3)
\]
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On heating,

\[
2(\text{Ni} (\text{CH}_3\text{COO})_2) + 2 \text{C}_6\text{H}_6\text{O}_6 + 8 \text{O}_2 \rightarrow 2(\text{Ni C}_4\text{H}_4\text{O}_6) + 8\text{CO}_2 + 8\text{H}_2\text{O}
\] (4)

and

\[
\text{H}_3\text{PO}_4^- + ((\text{NH}_4)_2\text{C}_2\text{H}_5\text{O}_6)^+ + \text{C}_6\text{H}_6\text{O}_6 + \frac{5}{2} \text{O}_2 \rightarrow
\] (5)

\[
((\text{H}_3\text{PO}_4)(\text{NH}_4)_2\text{C}_2\text{H}_5\text{O}_6) + 4\text{CO}_2 + 3\text{H}_2\text{O}
\]

Therefore overall reaction is given as,

\[
2(\text{NH}_4)_2\text{H}_2\text{PO}_4 + 2\text{LiOH} + (\text{Ni} (\text{CH}_3\text{COO})_2) + 5\text{C}_6\text{H}_6\text{O}_6 + \frac{21}{2} \text{O}_2 \rightarrow
\] (6)

\[
\text{LiH}_2\text{PO}_4 + \text{Li}(\text{C}_6\text{H}_6\text{O}_6) + ((\text{H}_2\text{PO}_4)(\text{NH}_4)_2\text{C}_2\text{H}_5\text{O}_6) + 2(\text{NiC}_4\text{H}_4\text{O}_6) + 12\text{CO}_2 + 13\text{H}_2\text{O}
\]

Equation (6) suggests that the dried gel precursor is composed of \( \text{Li}((\text{H}_2\text{PO}_4)_{2}\text{NH}_4)_2\text{C}_4\text{H}_5\text{O}_6 \). \( (\text{NiC}_4\text{H}_4\text{O}_6)_2 \)

Therefore the overall proposed decomposition equation for the precursor in air atmosphere i.e. during firing is,

\[
\text{Li}((\text{H}_2\text{PO}_4)_{2}\text{NH}_4)_2\text{C}_4\text{H}_5\text{O}_6 \rightarrow \text{LiC}_4\text{H}_5\text{O}_6. (\text{Ni C}_4\text{H}_4\text{O}_6)_2 + 10\text{O}_2
\] (7)

\[
2\text{LiNiPO}_4 + 16\text{CO}_2 + 12\text{H}_2\text{O} + 2\text{NH}_3
\]

Based on equation (7), the percentage weight loss is 66.4 %. The total weight loss of the decomposition process from the TGA curves as shown in Table 1 is 67.9 % which agrees closely with the calculated values based on Equation (7). The discrepancy could be due to the absorbed water from the ambient.

Figure 2. XRD Patterns of the LiNiPO₄ sample
The XRD pattern of the sample fired at 1000 °C for 24 hours exhibits the characteristic diffraction lines of LiNiPO₄ without any impurities and matches the orthorhombic structure listed in JCPDS pattern number 32-0578. The XRD of this sample also agrees with the results of Ruffo and co-workers (2005). The above observations confirmed that a pure compound of LiNiPO₄ was successfully synthesized in the present work.

The crystallite size (L) was estimated using the conventional Scherrer equation below.

\[ L = \frac{0.94 \lambda}{B_r \cos \Theta} \]  

Here \( \lambda \) is the X-ray wavelength 1.5406 Å and \( B_r \) is the FWHM of the peak representing the (111) plane. The full width at half maximum (FWHM) of the (111) reflection plane was determined since the peak at \( 2\theta = 25.9^0 \) has the highest intensity. The average crystallite size of the prepared pure LiNiPO₄ is 66 nm.

**Conclusion**

The olivine LiNiPO₄ powders were successfully synthesized by the sol-gel method with tartaric acid as the chelating agent. TGA/DTGA results showed that the LiNiPO₄ powders can be obtained by calcining the precursor at temperature above 750°C. The sample prepared at 1000°C showed that the position of peaks and the variation in intensity matches the pattern shown in the standard JCPDS data. The weight loss obtained from the thermogram supports the mechanism of reactions proposed. The percentage weight loss is 66.4% while the total weight loss of the decomposition process from the TGA curves is 67.9% which agrees closely with the calculated values based on the proposed equation. By using information obtained from the FWHM, the crystallite size of the LiNiPO₄ is ~ 66 nm.

**References**


