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SYNTHESIS OF NANOCRYSTALLINE OLIVINE $LiNiPO_4$ POWDER PREPARED BY SOL-GEL METHOD: THERMAL ANALYSIS AND XRD STUDIES

(Penyediaan Serbuk Nanokristal $LiNiPO_4$ dengan Struktur Olivin Melalui Kaedah Sol-Gel: Analisis Terma dan Kajian XRD)

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Abstract

$LiMPO_4$ 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, $LiNiPO_4$ powder was prepared by sol gel method using LiOH, $Ni(CH_3COO)_2$, $NH_4H_2(PO_4)$ 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 $LiNiPO_4$ .The formation mechanism for the synthesis of $LiNiPO_4$ 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 $LiNiPO_4$. The precursors and the calcined powders were characterized by X-ray diffraction (XRD). Analysis of the synthesized $LiNiPO_4$ using XRD demonstrated the formation of a pure $LiNiPO_4$ phase powder.

Keywords: lithium nickel phosphate, sol-gel, mechanism

Abstrak

$LiMPO_4$ 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 $LiNiPO_4$ telah disintisis dengan mencampurkan LiOH, $Ni(CH_3COO)_2$, $NH_4H_2(PO_4)$ dan asid tartarik dengan menggunakan kaedah sol-gel. Analisis TGA telah dilakukan keatas prapenanda $LiNiPO_4$ untuk menetukan suhu pembakaran dan didapati suhu yang sesuai adalah 1000^0C. Unjuran persamaan bagi penguraian prapenanda $LiNiPO_4$ 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 $LiNiPO_4$ adalah tulin.

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

Introduction

In recent years, lithium metal phosphate ($LiMPO_4$) 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), $LiMPO_4$ does not liberate oxygen on decomposition. In addition, $LiMPO_4$ is cheaper, benign, and environmentally friendly and has greater stability than LMO. Various methods have been used to synthesize $LiMPO_4$ cathode material such as solid-state [1], sol-gel [2-4], hydrothermal [5-7] and aqueous precipitation [8].

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 $LiNiPO_4$ (lithium nickel phosphate) which belongs to the olivine structure. In this work, $LiNiPO_4$ 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 $LiMnPO_4$ nanocrystalline structured powders prepared by tartaric acid and calcined in air are rare.

The resulting $LiNiPO_4$ powders obtained were then characterized by thermogravimetric analysis (TGA),) and X-ray diffraction (XRD). The formation mechanism for the synthesis of $LiNiPO_4$ are also discussed in this paper.

Materials and Methods

Sample preparation

Stoichiometric amounts of lithium hydroxide ($LiOH.H_2O$, Ajax), nickel acetate ($Ni(CH_3COO)_2 . 4H_2O$, Ajax) and ammonium dihydrogen phosphate $NH_4H_2PO_4$(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 60^0C for 3 days.

Characterization of sample synthesized

Thermogravimetric analysis (TGA) and differential thernogravimetric analysis (DTGA) analysis of the $LiNiPO_4$ powders were performed in order to examine the thermal decomposition behaviour of the gel precursor. The heating rate was 10^0C min^{-1}and the precursor was heated at 30^0C-1000^0C 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 % ocurred slowly as the temperature was increased to about 150 ^oC, due to the evaporation of residual water which are still present in the sample. Rapid weight loss occurred around the temperature range between 150 ^oC -275 ^oC 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 gel formed in the experiment. The decomposition process of the precursor is also accompanied by a sharp peak at about 237 ^oC 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 ^oC. 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 ^oC to 725 ^oC. The weight loss is attributed to the decomposition of nickel acetate and lithium hydroxide. Nickel acetate steadily decomposed in the temperature range from 272 ^oC to 400 ^oC .

The DTGA thermogram reveals a sharp peak at 354 ^oC indicating the rapid decomposition of nickel acetate. The weight is constant after 725 ^oC indicating that no heat is used for evaporation or decomposition processes and that $LiNiPO_4$ can be obtained by firing the precursor at temperatures above 750 ^oC. 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.

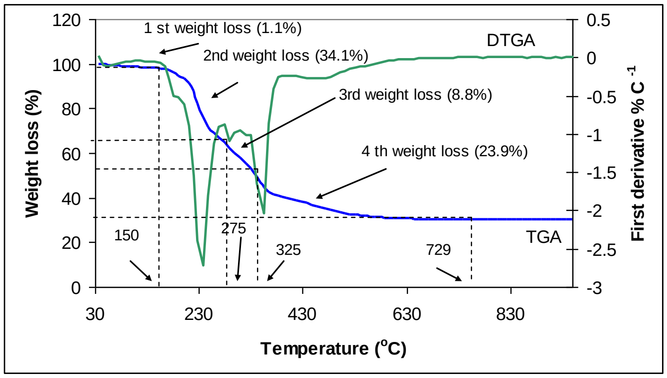

Figure 1. TG-DTGA curves of the precursor

Table 1. TG/DTGA results of the $LiNiPO_4$ precursor

Sample	**Temperature range**	**Weight loss(%)**	**Assignment**
$LiNiPO_4$ from LiOH, $Ni(CH_3COO)_2$ and $(NH_4)H_2PO_4$ with tartaric acid.	30-150	1.1	Evaporation of absorbed water.
	150-275	34.1	Decomposition of $(NH_4)H_2PO_4$ and evaporation of tartaric acid. Li-Ni acetate gel(precursor) decomposition
	275-325	8.8	Burning out organic residues resulted from the complex decomposition
	325-725	23.9	Decomposition of $Ni(CH_3COO)_2$. and LiOH. Structural OH bond broken
	725-900	-	Formation of $LiNiPO_4$
Total weight loss		67.9	

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 $(NH_4)H_2PO_4$ and LiOH according to the following equations:

$$2(NH_4)H_2PO_4 + C_4H_6O_6 \rightarrow H_3PO_4 + H_2PO_4^- + ((NH_4)_2C_4H_5O_6))^+ \quad (1)$$

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

LiOH also reacted with H_3PO_4 produced in equation (1) according to the following,

$$LiOH + H_3PO_4 \rightarrow LiH_2PO_4 + H_2O \quad (3)$$

On heating,

$$2(Ni(CH_3COO)_2) \quad + \quad 2\,C_4H_6O_6 \quad + \quad 8O_2 \quad \rightarrow \quad 2(Ni\,C_4H_4O_6) \quad + \quad 8CO_2 \quad + \quad 8H_2O \qquad (4)$$

and

$$H_2PO_4^- \quad + \quad ((NH_4)_2C_4H_5O_6)^+ \quad + \quad C_4H_6O_6 \quad + \quad {}^{5}\!/_{2}\,O_2 \quad \rightarrow \qquad (5)$$

$$((H_2PO_4)(NH_4)_2C_4H_5O_6) \quad + \quad 4CO_2 \quad + \quad 3H_2O$$

Therefore overall reaction is given as,

$$2(NH_4)\,H_2PO_4 \quad + \quad 2LiOH \quad + \quad (Ni(CH_3COO)_2) \quad + \quad 5C_4H_6O_6 \quad + \quad {}^{21}\!/_{2}\,O_2 \quad \rightarrow \qquad (6)$$

$$LiH_2PO_4 \quad + \quad Li(C_4H_5O_6) \quad + \quad ((H_2PO_4)(NH_4)_2C_4H_5O_6) \quad + \quad 2(NiC_4H_4O_6) \quad + \quad 12CO_2 \quad + \quad 13H_2O$$

Equation (6) suggests that the dried gel precursor is composed of $Li((H_2PO_4)_2(NH_4)_2C_4H_5O_6)\ LiC_4H_5O_6\,.\,(NiC_4H_4O_6)_2$

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

$$Li((H_2PO_4)_2(NH_4)_2C_4H_5O_6)\ Li\,C_4H_5O_6\,.\,(Ni\,C_4H_4O_6)_2 \quad + \quad 10O_2 \quad \rightarrow \qquad (7)$$

$$2LiNiPO_4 \quad + \quad 16CO_2 \quad + \quad 12H_2O \quad + \quad 2NH_3$$

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.

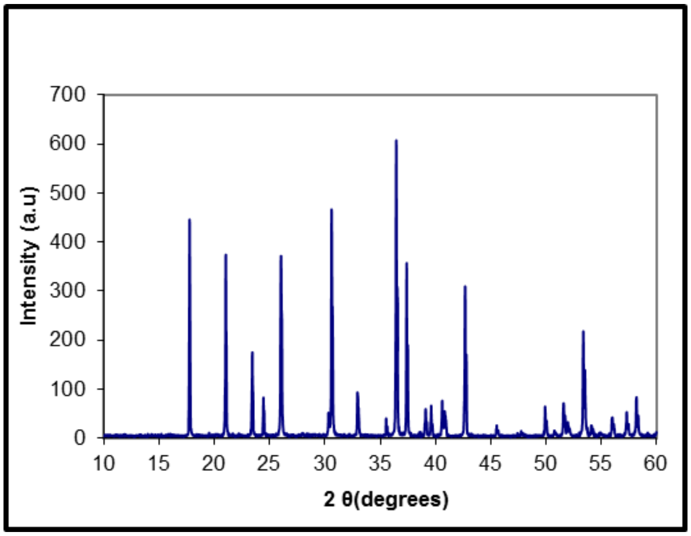

Figure 2. XRD Patterns of the $LiNiPO_4$ sample

The XRD pattern of the sample fired at 1000 °C for 24 hours exhibits the characteristic diffraction lines of $LiNiPO_4$ 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 $LiNiPO_4$ was successfully synthesized in the present work.

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

$$L = \frac{0.94\lambda}{B_r \cos\Theta} \tag{8}$$

Here λ 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 $LiNiPO_4$ is 66 nm**.**

Conclusion

The olivine $LiNiPO_4$ powders were successfully synthesized by the sol-gel method with tartaric acid as the chelating agent. TGA/DTGA results showed that the $LiNiPO_4$ 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 $LiNiPO_4$ is ~ 66 nm.

References

1. Liu, H., Li C., Zhang, H. P., Fu, L. Wu, Y. P., and H.Q. Wu (2006). Kinetic study on $LiFePO_4$/C nanocomposites synthesized by solid state technique, *Journal Power Sources* 159: 717-720.
2. Kuei-Feng H., Sun-Yuan T. and Bing-Joe H., (2005). Physical and electrochemical properties of LiFePO4/carbon composite synthesized at various pyrolysis periods, *Journal Power Sources* 146: 529-533.
3. Piana, M., Cushing, B. L., Goodenough, J. B. and Penazzi, N. (2004). A new promising sol–gel synthesis of phospho-olivines as environmentally friendly cathode materials for Li-ion cells, *Solid State Ion.* 175: 233-237.
4. Jingsi Y. and Jun John X, (2004). Nonaqueous Sol-Gel Synthesis of High-Performance $LiFePO_4$. Electrochem. *Solid-State Lett.* 7: 515-A518.
5. Jaewon L., and Amy S. T. (2006). Synthesis of $LiFePO_4$ Micro and Nanoparticles in Supercritical Water, *Mater Lett*, 60: 2105-109.
6. Jiajun C. and M Stanley W. (2006). Hydrothermal synthesis of lithium iron phosphate, *Electrochemistry Communications* 8: 855-858.
7. Shigehisa T., Yosuke I., Kazuyoshi U., Kenji T., Mineo S. (2004) Enhanced electrochemical performance of $LiFePO_4$ prepared by hydrothermal reaction, *Solid State Ion*. 175: 287-290.
8. Arnold, G. Garche, J., Hemmer, R., Strobe, S., Volgler, C., and Wohlfart-Mehrens M. (2003). Fine-particle lithium iron phosphate $LiFePO_4$ synthesized by a new low-cost aqueous precipitation technique, *Journal Power Sources* 119-121:247-251.