

Synthesis And Characterization Of $\text{LiNi}_{1-x}\text{Zn}_x\text{VO}_4$

K. Rajammal, M.Z. Kufian, S.R. Majid and A.K. Arof*

Centre for Ionics University of Malaya, Department of Physics, Faculty of Science,
University Malaya, 50603 Kuala Lumpur, Malaysia

*Corresponding Author: akarof@um.edu.my

Abstract

$\text{LiNi}_{1-x}\text{Zn}_x\text{VO}_4$ was synthesized at $x = 0.0, 0.2, 0.4$ and 0.8 . by a polymer hybrid sol gel method. In this work acetates of lithium ($\text{C}_2\text{H}_3\text{O}_2\text{Li}$), nickel ($\text{C}_2\text{H}_3\text{O}_2\text{Ni}$) and zinc ($\text{C}_2\text{H}_3\text{O}_2\text{Zn}$) with ammonium metavanadate (NH_4VO_3) were used to synthesize the samples. These materials were dissolved in distilled water, stirred and heated continuously until a clear green solution was obtained. At this stage, a solution of chitosan in 1 % acetic acid was added. The solution was continuously stirred and heated until it dried. The obtained precursor powder was sintered at $700\text{ }^\circ\text{C}$ for 3 hours. The crystallite size, lattice constant and surface morphology has been studied for zinc substituted LiNiVO_4 . X-ray diffraction (XRD) exhibits peaks without impurities. Zinc substituted LiNiVO_4 shows decreasing crystallite size from $x = 0.0$ to $x = 0.4$. Crystallite size increases again from $x = 0.4$ to $x = 0.8$. Cyclic voltammetric (CV) studies were performed.

Keywords: substitution, cathode materials, sol-gel method

1. INTRODUCTION

Lithium ion batteries are given much attention due to its excellent properties such as high voltage, high energy density and good cycling charge characteristics [1]. LiNiVO_4 is known as potential cathode material for its use in the lithium ion batteries. It exhibits 4.8 V versus Li^+/Li in lithium ion cell. LiNiVO_4 is the first cathode material with an inverse spinel structure that has been used in Li-ion batteries [2]. The presence of nickel atoms in the spinel structure has found to be an important factor in the voltage behaviour of this material [3]. Substitution is one of the methods to improve the capacity of the batteries [4-6].

Doped cathode materials have shown improvements on the electrochemical performance of the battery. Examples include doped LiNiO_2 [5], LiCoO_2 [7], LiMn_2O_4 [8-11]. Structural and vibrational studies on Co substituted LiNiVO_4 has been carried out by Julien et al. [12]. This work focused mainly on the structural analysis. In

the present work, zinc substituted LiNiVO_4 was prepared by chitosan modified sol-gel method. The structure analyses were carried using XRD and TEM. Cyclic voltammetric studies were performed on zinc substituted LiNiVO_4 .

2. EXPERIMENTAL

2.1 The Preparation and Characterization of $\text{LiNi}_{1-x}\text{Zn}_x\text{VO}_4$

Chitosan modified sol-gel method was used to synthesize $\text{LiNi}_{1-x}\text{Zn}_x\text{VO}_4$ at $x = 0.0, 0.2, 0.4$ and 0.8 . Lithium acetate ($\text{C}_2\text{H}_3\text{O}_2\text{Li}$), nickel acetate ($\text{C}_2\text{H}_3\text{O}_2\text{Ni}$) and zinc acetate ($\text{C}_2\text{H}_3\text{O}_2\text{Zn}$) with ammonium metavanadate (NH_4VO_3) were used as starting materials to prepare $\text{LiNi}_{1-x}\text{Zn}_x\text{VO}_4$. The given starting materials were weighed for different compound ratios as x varies in $\text{LiNi}_{1-x}\text{Zn}_x\text{VO}_4$. These materials were dissolved in distilled water, stirred and heated continuously until a clear green solution was obtained. At this stage, a solution of

chitosan in 1 % acetic acid was added. The solution was continuously stirred and heated until it dried. The obtained solid was sintered at 700 °C for 3 hours to eliminate impurities.

The diffraction intensity at different glancing angles for LiNiVO_4 and zinc substituted LiNiVO_4 were measured by using X-ray diffractometer (Bruker AXS) with operating voltage and current of 40 kV and 40 mA respectively. The X-ray wavelength is 1.5406 Å and the glancing angles were in the range $5^\circ \leq 2\theta \leq 80^\circ$ with a step size of 0.04° . The samples were characterized using Leo Libra 120 transmission electron microscope (TEM) instrument. Electrochemical tests were performed at Autolab. Cathode was prepared by 20 mg active material with 8 mg TAB (Teflonized Acetylene Black). Lithium metal was used as anode. The electrolyte used was 1M LiPF_6 EC/DEC (1:2).

3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns for zinc substituted LiNiVO_4 samples. All the substituted samples were sintered at 700 °C to eliminate the impurities. The peaks are similar to LiNiVO_4 . All the peaks correspond to Fd3m space group with face centered cubic structure. The substitution with zinc did not change the structure of the material. There are no peaks that correspond to impurities such as NiO (at $2\theta = 43.5^\circ$) and Li_3VO_4 (at $2\theta = 16.2^\circ, 21.5^\circ, 22.8^\circ$ and 24.3°) which was found in some works on LiNiVO_4 [13-14]. This confirms that sintering at 700 °C enables elimination of impurities that could defect the structure of the product and result in poor performance of LiNiVO_4 .

Crystallite size (d) of the samples was calculated using Scherrer's equation [15-16]:

$$d = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where β is FWHM at the most intense diffraction peak (311) plane in radians, θ is wavelength of $\text{CuK}\alpha$ X- radiation. The results are presented in the Table 1.

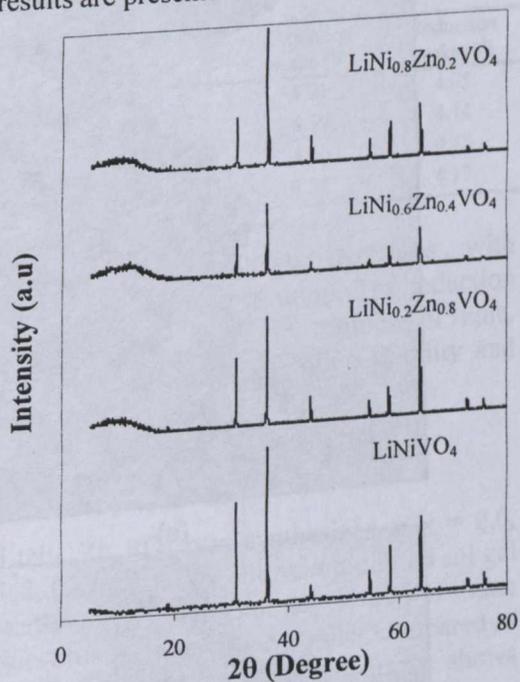


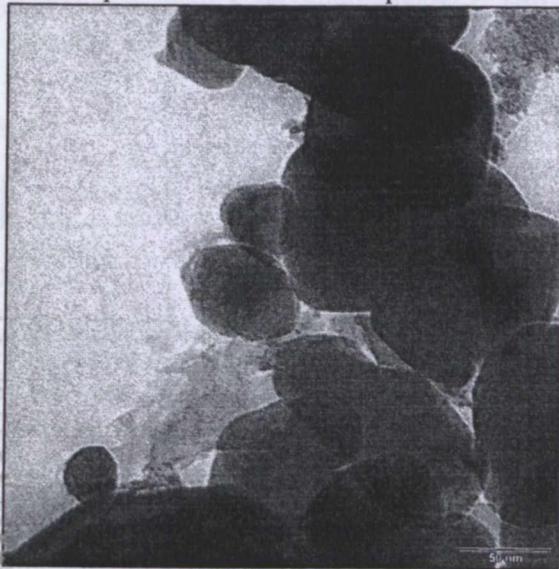
Fig. 3 X-ray diffraction of $\text{LiNi}_{1-x}\text{Zn}_x\text{VO}_4$ sintered at 700 °C

Table 1 Crystallite size of the Zn substituted LiNiVO_4

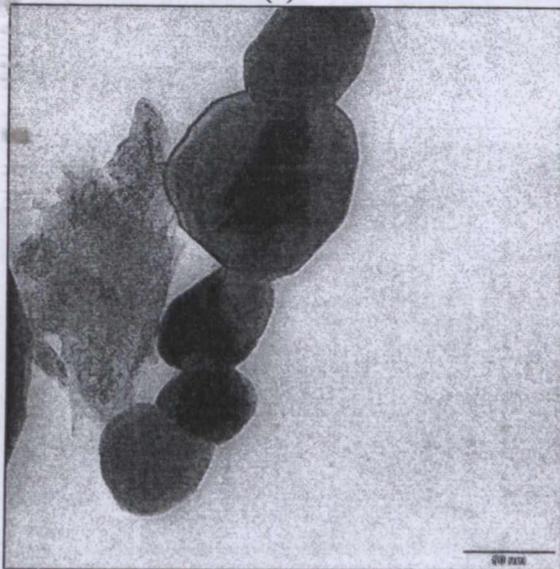
x in $\text{LiNi}_{1-x}\text{Zn}_x\text{VO}_4$	Crystallite size (nm)
0.0	97.2
0.2	86.1
0.4	49.1
0.8	65.8

Table 1 indicates that the changes of crystallite size with the zinc substitution in LiNiVO_4 . The crystallite size of the zinc substituted LiNiVO_4 decreased markedly from $x = 0.0$ to $x = 0.4$, and it is increasing from $x = 0.4$ and $x = 0.8$. The values of calculated crystallite size for every samples proved that the particles are in the size of nanometers. The crystallite size of cathode materials is another factor that plays an important role in the electrochemical properties. Smaller crystallites with larger surface area are able to reduce diffusion length of Li^+ ion. This results in better lithium ion intercalation which leads to improved electrochemical performance [17-

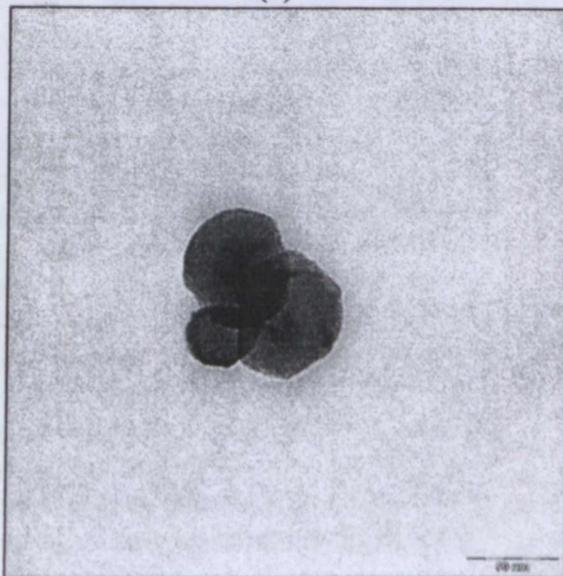
18]. TEM images as shown in Fig. 2 agree well with the calculated crystallite size. All the samples exhibit nanosized particles.



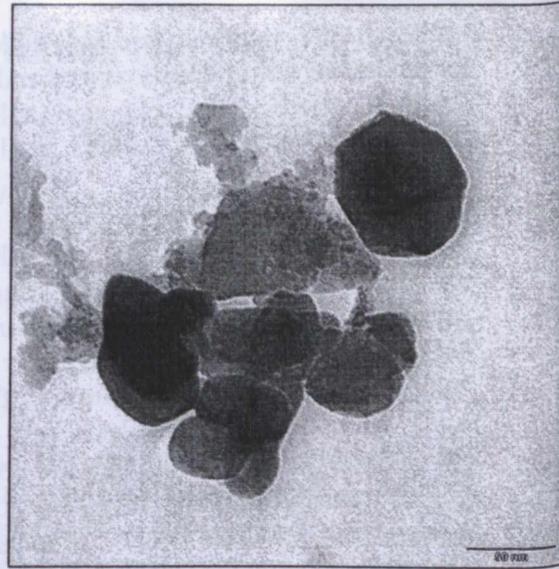
(a)



(b)



(c)



(d)

Fig. 2 TEM micrographs of (a) LiNiVO_4 , (b) $\text{LiNi}_{0.8}\text{Zn}_{0.2}\text{VO}_4$, (c) $\text{LiNi}_{0.6}\text{Zn}_{0.4}\text{VO}_4$ and (d) $\text{LiNi}_{0.2}\text{Zn}_{0.8}\text{VO}_4$

The sizes of particles are in the range of 50 nm to 90 nm for LiNiVO_4 . The particles of $\text{LiNi}_{0.8}\text{Zn}_{0.2}\text{VO}_4$ and $\text{LiNi}_{0.6}\text{Zn}_{0.4}\text{VO}_4$ are in the range of 40 nm to 70 nm and 30 nm to 50 nm respectively. The particles of $\text{LiNi}_{0.2}\text{Zn}_{0.8}\text{VO}_4$ are also nearly in the same range which is 30 nm to 60 nm.

Lattice constant showed a slight increase with substitution of zinc due to the different ionic radius of zinc and nickel [19]. When Zn^{2+} ion with larger ionic radius (0.88 Å) replaces Ni^{2+} ion with smaller ionic radius (0.83 Å), the lattice constant increased as tabulated in Table 2. Decrease of lattice constant at $\text{LiNi}_{0.8}\text{Zn}_{0.2}\text{VO}_4$ may be due to a different structure formed at higher zinc substitution [20].

Table 2 Lattice constant of zinc substituted LiNiVO_4

x in $\text{LiNi}_{1-x}\text{Zn}_x\text{VO}_4$	lattice constant (Å)
0.0	8.1964
0.2	8.1968
0.4	8.2140
0.8	8.2095

Cyclic voltammograms of the samples at scan rate 0.1 mV/s in the potential region of 3 to 4.8 V is shown in Fig 3.

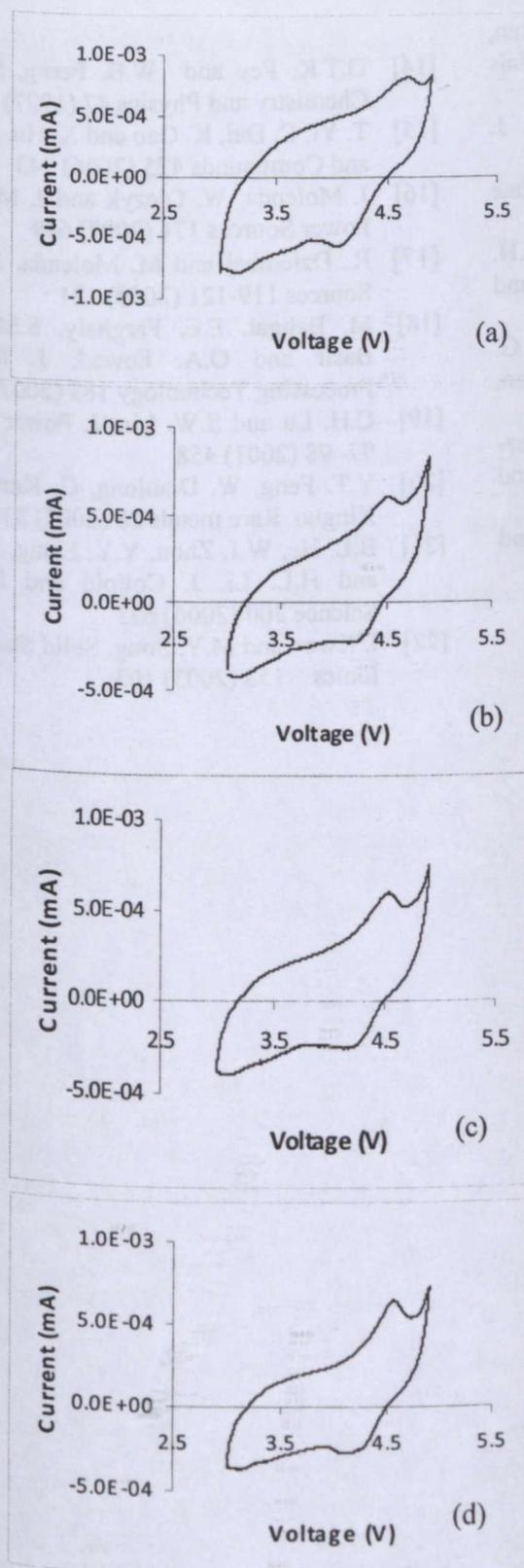


Fig. 3 Cyclic voltammograms of (a) LiNiVO₄, (b) LiNi_{0.8}Zn_{0.2}VO₄, (c) LiNi_{0.6}Zn_{0.4}VO and (d) LiNi_{0.2}Zn_{0.8}VO

Table 3 gives the values of oxidation and reduction peaks for substituted samples.

Table 3 Oxidation and reduction peaks of zinc substituted LiNiVO₄

x in LiNi _{1-x} Zn _x VO ₄	Oxidation peaks (V)	Reduction peaks (V)
0.0	4.71	4.05
0.2	4.59	4.14
0.4	4.56	4.15
0.8	4.54	4.17

The oxidation voltage decreases with increase in zinc substitution. The reduction peak increases with substitution of zinc. This shows improved cycling stability and reversibility [21].

4. CONCLUSIONS

LiNi_{1-x}Zn_xVO₄ was synthesized at x = 0.0, 0.2, 0.4 and 0.8 by chitosan modified sol gel method. The crystallite sizes of zinc substituted samples are smaller compared to LiNiVO₄. Cyclic voltammogram shows better cycling stability and reversibility.

ACKNOWLEDGEMENT

The author would like to thank University of Malaya for Graduate Research Assistant Scheme.

REFERENCES

- [1] D. Zhang, B.S. Haran, A. Durairajan, R.E. White, Y. Podrazhansky and B.N. Popov. *J. Power Sources* 91 (2000) 122
- [2] G.T.K. Fey and K.S. Chen. *J. Power Sources* 81-82 (1999) 467
- [3] G.T.K. Fey, K.S. Wang and S.M. Yang. *J. Power Sources* 68 (1997) 159
- [4] G.T.K. Fey, P. Muralidharan, C.Z. Lu, Y.D. Cho. *Solid State Ionics* 177 (2006) 877
- [5] M.Y. Song, C. Park, S. Yoon, H. Park and D.R. Mumm. *Ceramics International* 35 (2009) 1145
- [6] Y. Ding, P. Zhang, Y. Jiang, J. Yin, Q. Lu and D. Gao. *Materials Research Bulletin* 43 (2008) 2005

- [7] R. Sathiyamoorthy, R. Chandrasekaran, A. Gopalan and T. Vasudevan. *Materials Research Bulletin* 43 (2008) 1401
- [8] I.S. Jeong, J.U. Kim and H.B. Gu. *J. Power Sources* 102 (2001) 55
- [9] Z. Bakenov and I. Taniguchi. *Solid State Ionics* 176 (2005) 1027
- [10] Y.K. Yoon, C.W. Park, H.Y. Ahn, D.H. Kim, Y.S. Lee and J. Kim. *J. Physics and Chemistry of Solids* 68 (2007) 780
- [11] K. Suryakala, K.R. Marikkannu, G. Paruthimal Kalaignan and T. Vasudevan. *Ionics* 13 (2007) 41
- [12] C. Julien, M. Massot and C. Perez-Vicente. *Materials Science and Engineering B75* (2000) 6
- [13] G.T.K. Fey, J.R. Dahn, M. J. Zhang and W. Li. *J. Power Sources* 68 (1997) 549
- [14] G.T.K. Fey and W.B. Perng. *Materials Chemistry and Physics* 47 (1997) 279
- [15] T. Yi, C. Dai, K. Gao and X. Hu. *J. Alloys and Compounds* 425 (2006) 343
- [16] J. Molenda, W. Ojczyk and J. Marzec. *J. Power Sources* 174 (2007) 689
- [17] R. Dziembaj and M. Molenda. *J. Power Sources* 119-121 (2003) 121
- [18] M. Bahgat, F.E. Farghaly, S.M. Abdel Basir and O.A. Fowad. *J. Materials Processing Technology* 183 (2007) 117
- [19] C.H. Lu and S.W. Lin. *J. Power Sources* 97- 98 (2001) 458
- [20] Y.T. Feng, W. Dianlong, G. Kun and H. Xinguo. *Rare metals* 26 (2007) 330
- [21] B.L. He, W.J. Zhou, Y.Y. Liang, S.J. Bao and H.L. Li. *J. Colloid and Interface Science* 300 (2006) 633
- [22] I. Kwon and M.Y. Song. *Solid State Ionics* 158 (2003) 103