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EFFECTS OF CALCINATION TEMPERATURES ON SYNTHESIS OF $LiMn_2O_4$ BY POLYMER MATRIX-BASED ALKALINE DEPOSITION METHOD

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Abstract

$LiMn_2O_4$ offers more affordable price than other cathode materials for lithium ion batteries. The other factors are the abundance of the Mn element in nature and its low level of toxicity. Therefore, this study aims to investigate the effects of calcination temperature on the synthesis of $LiMn_2O_4$to obtain better condition for calcination to produce $LiMn_2O_4$. In this study, cubic $LiMn_2O_4$ is synthesized by Polymer Matrix Deposition Method using hydrothermal technique. Precursors used were LiOH, ethylene glycol and $Mn(CH_3COO)_2$. The precursors were synthesized at 150^oC for 6 hours and calcined for 4 hours in different temperature variations in order to produce crystals with different sizes and crystalinity. The interval calcination temperature is 500-900^oC. The compound was characterized by XRD, TEM and then was analyzed by *U-Fit* program. It is found that at low calcination temperatures, impurities MnO_2 is present but it decreases along with the increase of calcination temperature. The lattice parameters and volume of $LiMn_2O_4$also increase with the increase in heating temperature.The optimum calcination temperature is 700^oC.

Keywords: $LiMn_2O_4$, polymer matrix-based alkaline deposition method, calcination temperature

INTRODUCTION

Today battery is almost inseparable from everyday life. Cell phones, digital cameras, laptops, hybrid cars, all require batteries as their energy source. Thus the prospect of battery asthe future energy source becomes strategic and economical. Among the many types of batteries,lithium battery has received great attention in research. In addition to having high power, lithium battery is lightand can be used many times (rechargeable). With the rapid development of technology, lithium battery is supposedly able to produce higher energy become indispensable (Thackeray, 1983).

Materials widely used as lithium battery cathode are $LiNiO_2$ and $LiCoO_2$ layered or the $LiMn_2O_4$ spinel structure (Howard *et al.*, 2003; Sarciaux, 1998). Compared to other lithium compounds such as $LiNiO_2$ and $LiCoO_2$, $LiMn_2O_4$ compound has more affordable price, abundance, and low toxicity level (Ritchie and Howard, 2005). $LiMn_2O_4$ has a spinel structure with the shape of the Li^+ ions fill the spinel tetrahedral cavities so that the flow of electricity or ion exchange electrons received from the anode (reduction reactions) can take place through these cavities (Van der ven *et al*, 2000).

Preparation of spinel $LiMn_2O_4$ is usually performed in a high temperature, between 700-900^oC, with the reaction in the form of solid materials including manganese oxide, nitrate or carbonate with lithium hydroxide, nitrate, or carbonate (Zhang, 2011). However, the final product of this reaction often contains too much impurities and the crystalline structure is not

well-shaped. To reduce it, various preparation methods such as sol-gel method, spray pyrolisis, hydrothermal (Hwang, 2001; Larcher, 1997; Sarciaux, 1998; Singh, 2010; Wang, 2002; He *at al*, 2003) have been developed.

In this study, we report the combination method using hydrothermal method and polymer matrix deposition techniques to synthesize $LiMn_2O_4$in various calcination temperatures to produce better $LiMn_2O_4$. Hydrothermal method using aqueous solvent takes place at a temperature and autogenous pressure of the bomb hydrothermal. Polymer Matrix Deposition technique uses ethylene glycol as polymer matrix. Precursors used in the synthesis process must be in the liquid phase. The polymers are used so that the precursors can be dispersed evenly in a polymer precursor that can be mixed homogeneously. Thus the reaction is expected to be running perfectly.

RESEARCH METHOD

The procedure was performed by making 50 mL of 0.4 M LiOH solution of LiOH crystals by weighing 0.2444 grams of crystalline LiOH using 50 mL volumetric flask. Then, 50 mL solution of $Mn(CH_3COO)_2$ 0.1 M of crystalline Mn $(CH_3COO)_2.4H_2O$ was prepared by weighing 1.2379 grams of crystalline $Mn(CH_3COO)_2.4H_2O$ using 50 mL volumetric flask. Both solutions were incorporated into a hydrothermal bomb, as much as 10 mL of ethylene glycol was added. The solution was then heated in an oven at 150°C for 6 hours. The resulting solid is then filtered and was put at room temperature for 24 hours. After that, the solid was calcined at 900^{o}C for 6 hours. The solid was then characterized by XRD and TEM. Similar calcination steps were also carried out to the temperature variations (T: 500.600, 700, 800, 900^{o}C).

RESULT AND DISCUSSION

This study was conducted to determine the effect of calcination temperature in the synthesis of $LiMn_2O_4$compounds using alkaline synthesis method based on the characteristics of $LiMn_2O_4$ polymer matrix. The polymer matrix-based alkaline deposition method can be categorized as a liquid phase reaction, which was part of soft chemical (*chimie douce*). This method is a combination of two methods: method of deposition and method of forming the base polymer matrix. The polymer matrix used in this study is ethylene glycol, which serves as a flocculant binder. Thus, after the addition of ethylene glycol, the bonds between the reactant compound will be disconnected and the polymer matrix will envelop the flocculant, so that the flocculants trapped in the matrix become more homogeneous.

The technique used in this study is hydrothermal technique as the formed crystalshave a high degree of purity, controllable stoichiometry, limitable particle size, controllable morphology, uniform and high crystallinity (Thackeray, 1983). Characteristics of $LiMn_2O_4$ compounds include the nature of crystallinity can be seen from the X-ray diffraction pattern.

Conducted at calcination temperature variations of 500, 600, 700, 800 and 900^{o}C,the reaction of $Mn(CH_3COO)_2$ and LiOH then yielded $LiMn_2O_4$. The synthesis performed at a temperature of 150^{o}C for 6 hours synthesis in aqueous solvent with hydrothermal method.

The resulting solidsare reddish black in color. Subsequently, the solids were characterized using X-ray diffraction, whose measurements were performed using an X-ray diffractometer in the region of $10° \leq 2\theta \leq 80°$ with a step size 0.0200 degrees, source of Cu Kα radiation (1.54060 Å), scan speed of 5.00 degrees per-minute, and irradiation performed continuously every 0.24 seconds. Smoothing process was conducted to clarify the X-ray diffraction pattern generated. *U - Fit* program is used to determine the space group and lattice parameters of the compound $LiMn_2O_4$,while TEM is used to determine the particle size of $LiMn_2O_4$.

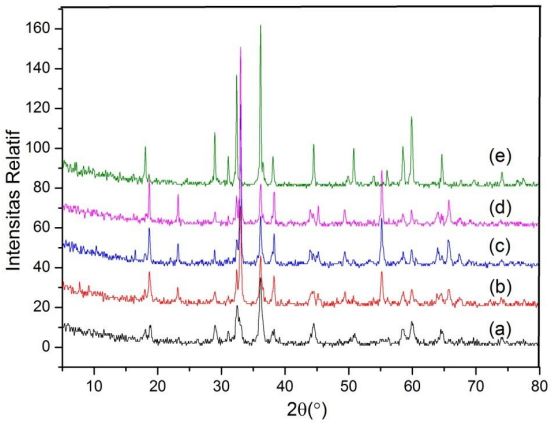

Figure1. X-ray diffraction pattern of solids produced in the calcination temperature variations of 500, 600, 700, 800 and 900°C

Table 1. Crystal plane (*hkl*) of solids generated at each temperature calcination

Solid produced at 500°C		**Solid produced at 600°C**		**Solid produced at 700°C**		**Solid produced at 800°C**		**Solid produced at 900°C**		***(h k l)***
2θ	I/Io	2θ	I/Io	2θ	I/Io	2θ	I/Io	2θ	I/Io	
18,723	21,9	18,699	29,2	18,698	20,3	18,660	22,7			(1 1 1)
								32.4	68.8	(2 2 1)
32,500	56,3					32,399	14,8			(3 0 0)
36,179	100	36,198	47,9	36,179	30,4			36.160	100	(3 1 1)
37,983	15,6									(2 2 2)
44,003	12,5			43,884	7,6	43,903	8			(4 0 0)
		45,198	10,4			45,184	9,1			(4 1 0)
								64.621	20	(4 4 1)
		48,140	6,3							(3 3 1)
		49.419	12,5	49,342	8,9	49,302	9,1			(4 2 0)
50,903	15,6	50,721	8,3	50,760	3,8					(4 2 1)
58,420	18,8									(3 3 3)
				63,943	10,1					(4 4 0)

Solid produced at 500°C		**Solid produced at 600°C**		**Solid produced at 700°C**		**Solid produced at 800°C**		**Solid produced at 900°C**		***(h k l)***
2θ	I/Io	2θ	I/Io	2θ	I/Io	2θ	I/Io	2θ	I/Io	
						65,772	13,6			(5 3 0)
				67,305	6,3					(5 3 1)
69,634	12,5									(6 1 0)
		72,205	6,3							(6 2 0)
74,00	9,4									(6 2 1)
								74.099	8.8	(6 3 0)
		77,620	6,3							(5 4 1)

Table 2. Crystal plane (*hkl*) of $LiMn_2O_4$at each calcinationtemperature

Solid produced at 500°C		**Solid produced at 600°C**		**Solid produced at 700°C**		**Solid produced at 800°C**		**Solid produced at 900°C**		***(h k l)***
2θ	I/Io	2θ	I/Io	2θ	I/Io	2θ	I/Io	2θ	I/Io	
18,723	21,9	18,699	29,2	18,698	20,3	18,660	22,7			(1 1 1)
36,179	100	36,198	47,9	36,179	30,4			36.160	100	(3 1 1)
37,983	15,6									(2 2 2)
44,003	12,5			43,884	7,6	43,903	8			(4 0 0)
		48,140	6,3							(3 3 1)
				63,943	10,1					(4 4 0)
				67,305	6,3					(5 3 1)

Based on the data presented in Fig. 1 and Table 2, there are differentpeaksin each calcination temperature. At 500°C,sharp peaks were formed showing that the calcination temperature forms crystalline solids with high peak intensity. At 600-800°C,the peaks become sharper but their intensity is lower compared to those at 500°C. Meanwhile, at 900°C there is only one peak corresponding to the *hk*l plane $LiMn_2O_4$ but has a high intensity. It can be concluded that the compound calcinated at 500 and 900°C has the best crystallinity compared to other temperatures. Of the five calcination temperatures, one which has the highest number of peaks with *hkl* plane corresponding to the standard $LiMn_2O_4$*hkl*plane is 700°C, i.e. with 5 peaks. Thus, the optimum temperature for the synthesis of $LiMn_2O_4$ by using polymer matrix based alkaline deposition method is 700°C.

In addition to the peaks of $LiMn_2O_4$ compound, the X-ray diffraction patterns also show peaks of impurities, largely in the forms of MnO_2compound. By using the *U-Fit* program and after matched with the standard of MnO_2compound data obtained 2θ and I / Io peaks of X-ray diffraction patterns of MnO_2compound impurity in Table 3.

Table 3. Crystal plane (*hkl*) of MnO_2at each calcinationtemperature

Solid produced at 500 °C		**Solid produced at 600 °C**		**Solid produced at 700 °C**		**Solid produced at 800 °C**		**Solid produced at 900 °C**		***(h k l)***
2θ	I/Io	2θ	I/Io	2θ	I/Io	2θ	I/Io	2θ	I/Io	
29,019	28,1	28,981	12,5	28,923	8,9	28,982	6,8	28.96	33	(3 0 0)
								31.097	16	(0 0 1)
		32,980	100	33,000	100	33,020	100			(1 0 1)
37,983	15,6									(0 1 1)
		40,655	6,3							(0 2 0)
44,500	12,5			43,884	7,6					(4 1 0)
		45,198	10.4	45,183	6,3	45,184	9,1			(2 2 0)
						49,302	9,1			(5 0 0)
		50,721	8,3	50,760	3,8			50.781	23	(4 0 1)
50,903	15,6									(3 2 0)
				53,280	2,5					(5 1 0)
						55,199	30,7			(4 1 1)
								56.003	9	(2 2 1)
		59,882	14,6	59,842	8,9	59,878	8	59.899	40	(6 0 0)
		65,740	14,6	65,640	15,2	65,722	13,6			(0 0 2)
69,634	12,5									(6 0 1)
74,000	9,4									(3 0 2)
77,445	9,4									(3 1 2)

Table 4. Lattice Parameter of $LiMn_2O_4$

Lattice Parameter and Volume of Crystal	**Calcination Temperatures**				
	500°C	**600°C**	**700°C**	**800°C**	**900°C**
a (Å)	8,187912	8,267488	8,230189	8,284771	8,302322
b (Å)	8,187912	8,267488	8,230189	8,284771	8,302322

Lattice Parameter and Volume of Crystal	Calcination Temperatures				
	500°C	**600°C**	**700°C**	**800°C**	**900°C**
b (Å)	8,187912	8,267488	8,230189	8,284771	8,302322
V (Å^3)	548,9332	565,0940	557,4802	568,6455	572,2670

Based on Table 4, it can be concluded that the lattice parameters of crystalline $LiMn_2O_4$ has a cubic structure *Fd3m*. The lattice parameters for the material prepared at 700°C for $LiMn_2O_4$ was almost identical to the standard value of 8. 245 Å, according to JCPDS card file No. 35-782. Table 4 shows that the lattice parameters of the crystal and the crystal volume have a tendency to rise in line with increasing calcination temperature. This indicates that the higher the calcination temperature,the bigger both the lattice parameters and the volume of the crystal. At low calcination temperatures, the resulting crystals have a relatively lower degree of crystallinity. In the crystal resulting from low temperatures, there are still many crystal defects. The higher the calcination temperature, the less the crystal defects will be and the higher the degree of crystallinity.

The larger the crystal volume and the better the crystallinity, the better the electrical conductivity of the crystal, as when the crystal volume gets bigger, the ions space will also get wider so that the ions will freely move in and out, making the resulting electrical conductivity better. It is therefore expected that the produced $LiMn_2O_4$ will be used as the more durable cathode material of lithium batteries.

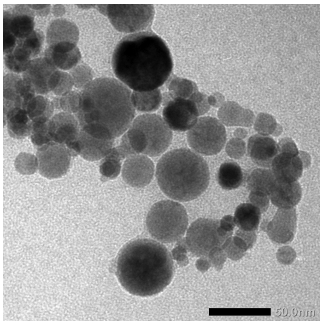

Figure2. TEM of $LiMn_2O_4$

Fig.2 shows that the $LiMn_2O_4$ solids generated from the polymer matrix-based alkaline deposition method with hydrothermal technique have good spherical morphology and uniform particle size between 20-50 nm.

CONCLUSION AND SUGGESTION

Based on the above discussion we can conclude the following:

1. Compound $LiMn_2O_4$ in various calcination temperature, T: 500, 600, 700, 800 and 900 °C can be synthesized with the polymer matrix deposition method using hydrothermal techniques.
2. Compounds synthesized $LiMn_2O_4$ (T: 500, 600, 700, 800 and 900 °C) has a cubic crystal structure with *Fd3m* phase alleged major and MnO_2 phase with minor phases with crystal structures orthorhombic.

A further research on the synthesis of compounds of Li with other methods to obtain the results that have single crystal structure.

REFERENCES

Armstrong, A.R. and Bruce, P.G. (1996) Synthesis of Layered $LiMnO_2$ as an Electrode for Rechargeable Lithium Batteries. *Nature*, 351, 499-500, doi: 10.1038/381499a0

Determination from Powder Diffraction Data. International Union of Crystallography, Oxford Science Publication

He, W.L., Zhang, Y.C., Zhang, X.X., Wang, H., Yan, H. (2003). Low temperature preparation of nanocrystalline Mn_2O_3 via ethanol-reduction of MnO_2, *Journal ofCrystal Growth*., 252, 285-288.

Hwang, B.J., Santhanam, R., Liu, D.G. (2001).Characterization of nanoparticles of $LiMn_2O_4$ syntesized by citric acid sol-gel method. *Journal of Power Source*. 98 : 443-446.

Larcher, D. (1997). Nouvelles voles de synthese et caracterisation de materiaux d'electrodes positives pour accumulateurs au lithium, *These de Doctorat*, L'Universite de Picardie Jules Verne, Perancis

R.C. Ropp. 2003. *Solid State Chemistry*. Netherlands: Elsevier.

Ritchie, A and Howard, W. (2005). Recent Development and Likely Advances in Lithium-ion Batteries. *Journal of Power Sources* 162 (2006) 809–812

Sarciaux. (1998) Les composes MnO2 γet LixMnO2 γ: influence des parameters structuraux et physic-chimiques sur l'insertion electrochimique du lithium. *These de Doctorat*. Universite de Nantes, Perancis

Singh, P., Sil, A., Nath, M., & Ray, S. (2010). Synthesis and Characterization of $Li[Mn_{2-x}Mg_x]O_4$ (x=0.0-0.3) Prepared by Sol-Gel Synthesis. *Original Papers Ceramics-Silikaty*. 54 (1) : 38-46Tarascon, J.M., Coowar F., Amatucci G.G., Shokoohi F., and Guyomard D., (1994). *J. Power Sources*, pp. 1421

Thackeray, M.M., David W.I.F., Bruce P.G., and Goodenough J.B., (1983) *Mat. Res. Bull.*, pp. 461

Van der ven, A., Marianetti, C., Morgan, D., & Ceder, G. (2000). Phase Transformations and Volume Changes in Spinel $Li_xMn_2O_4$. *Solid State Ionics*. 135 : 21-32.

Wang, X., Li, Y. (2002). Selected-Control Hydrothermal Synthesis of α- and β-MnO_2 Single Crystal Nanowires. *J. Am.Chem.Soc*. Vol. 124, No. 12, 2880-2881

Zhang, X., Zheng, H.,Battaglia, V., Axelbaum, R.L. (2011). Electrochemical performance of spinel $LiMn_2O_4$ cathode materials made by flame-assisted spray technology. *Journal of Power Sources*. 196 : 3640–3645.