The Structural and Electrical Properties of $LiNi_{0.5}Mg_{0.5}VO_4$ Annealed at 450 ^oC and 550 ^oC

A.F.M.Fadzil[1*], S. I.Y.Saaid[1], A.Sanusi[2], M.Mohamad[3], and N.N.N.Ebrhiam[3]
[1]Centre for Foundation Studies, UiTM Puncak Alam Campus, [2]International Education College (INTEC), UiTM Section 17 Campus, [3]Chemistry Department, Faculty of Applied Science, UiTM Shah Alam.
*aidafazliza@ puncakalam.uitm.edu.my;sitiirma2902@puncakalam.uitm.edu.my;

***Abstract*-- In this work, cathode material $LiNi_{0.5}Mg_{0.5}VO_4$ was synthesized in a pure state by organic synthetic procedure known as sol-gel method. Tartaric acid was used as the complexing agent. The precursor sample was sent for Differential Scanning Calorimetry (DSC) as to determine the optimum temperature for annealing process. The annealing temperature was then defined at 450 ^oC and 550 ^oC for 5 hours. The structural properties of the compound were characterized by X-ray diffraction (XRD) using X'PERT PRO MRD XL analytical. It shows that both samples produced crystallinity phases but $LiNi_{0.5}Mg_{0.5}VO_4$ annealed at 450 ^oC shows more crystalline with sharp peaks. The electrochemical characterization was carried out by Solartron Impedance Spectroscopy measuring bulk resistance (R_B) and electrical conductivity of $LiNi_{0.5}Mg_{0.5}VO_4$ at various temperature of 25 ^oC, 35 ^oC, 45 ^oC, 55 ^oC and 65 ^oC. It was found that the bulk resistance (R_B) is proportional with temperature for both annealling temperature of 450 ^oC and 550 ^oC. However the conductivity is inversely proportional with temperature for both anealling temperature of 450 ^oC and 550 ^oC. At room temperature (25 ^oC) the conductivity of $LiNi_{0.5}Mg_{0.5}VO_4$ annealed at 450 ^oC was 1.58 x 10^{-4} S cm^{-1}while $LiNi_{0.5}Mg_{0.5}VO_4$ annealed at 550 ^oC was 1.40 x 10^{-4} S $cm^{-.1}$ This shows that $LiNi_{0.5}Mg_{0.5}VO_4$ annealed at 450 ^oC has greater electrical properties.**

***Index Term*-- $LiNi_{0.5}Mg_{0.5}VO_4$, Li-ion battery, cathode material, annealing temperature**

I. INTRODUCTION

Electrical energy is very important in our daily lives as our world evolved into the modern era where machineries, devices and motors require a lot of energy to generate them. Many alternative energy sources have been introduced in order to relieve the problem. One of the alternative ways to provide electrical supply is by introducing battery into our lives.

Today, we can find various types of batteries. One of the well known battery type is the Lithium-ion battery. Lithium-ion rechargeable battery was firstly introduced by Nagaura and Tozawa in portable telephones in June 1991. Lithium – ion battery is a type of rechargeable battery that is commonly used in the portable electronic devices [1]. This type of battery is very light causing it to become the most suitable rechargeable battery for hand phones, laptops and even in electric vehicles.

Cathode material of the battery plays major roles in the battery performance. Cathode materials are typically oxides of transition metal, which can undergo oxidation to higher valences when lithium is removed.

$LiNiVO_4$ was introduced in 1994 by Ting-kuo, Li, Zhang and Dahn and $LiNiVO_4$ was found to exhibit high voltage of 4.8 V with reasonable capacity and capability rate [2]. However, $LiNiVO_4$ is found to be less stable and exhibit poor cycleability than $LiCoO_2$. This leads to the concern of safety among the users. However, few reports stated the insertions of certain compounds into $LiNiVO_4$ are likely to introduce to a new good and safe lithium-ion battery [3].

In this work, the synthesis and characterisations of the cathode material called $LiNi_{0.5}Mg_{0.5}VO_4$ was done by using Sol-gel method. The structural properties were characterised by X-ray diffraction, while the conductivity of the compound was measured by Electrochemical Impedance Spectroscopy (EIS).

II. EXPERIMENTAL

$LiNi_{0.5}Mg_{0.5}VO_4$ compound was synthesized by the sol-gel method. The sample was prepared using $LiNO_3$ solution, $Ni(NO_3)_2$ solution, $Mg(NO_3)_2$ solution, V_2O_5 solution, and tartaric acid in molar ratio of 1:0.5:0.5:1. Each of the reagent solution was prepared at the concentration of 1 Molar. The expected yield of $LiNi_{0.5}Mg_{0.5}VO_4$ powder is 6 g. The final product was crushed into fine powders by using mortar and pestle. The thermal analysis was done on the precursor by using TGA-DSC High Temperature Thermogravimetry Analyzer (TGA-DSC) Setaram System Model LCT 10257-2 and further annealed at 450 ^oC and 550^{0}C for 5 hours to get a very crystalline $LiNi_{0.5}Mg_{0.5}VO_4$.

The XRD pattern was taken using model X'pert Pro analysis while the electrochemical property was characterised by the Electrochemical Impedance Spectroscopy (EIS) using Solartron Impedance SI 1260 Impedance/ Gain- Phase Analyzer and Solartron Electrochemical Interface SI 1287.

III. RESULTS AND DISCUSSION

A. Thermal Analysis

Differential Scanning Calorimetry (DSC) was carried out on the precursor of $LiNi_{0.5}Mg_{0.5}VO_4$ as to measure the thermal stability thus to determine the optimum annealing temperature. Fig. 1 shows the DSC thermogram of $LiNi_{0.5}Mg_{0.5}VO_4$ heated up from 0^{o}C to 800^{o}C and then cooled down to room temperature. The sample has

been heated at 10°C for every 10 minutes.

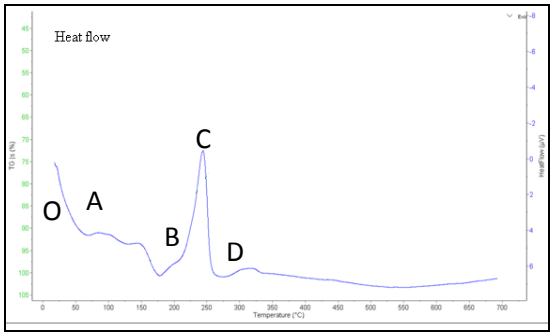

Fig. 1. DSC scan plot of $LiNi_{0.5}Mg_{0.5}VO_4$ precursor

The analysis for the heat flow from the thermogram of DSC can be divided into few groups. The mark O indicates the offset of the thermal analysis starting from 0˚C to 70˚C. It basically due to the imbalance in the thermal capacity of the sample. At A site is indicating the glass transition of the precursor. The glass transition usually occurs lower than the melting point temperature [4]. Because of the precursor contains the mixture between metals and organic compounds, the glass transition is a little lower which is approximately at 70˚C. The B site shows the enthalpy change where the heat flow decreases dramatically. This enthalpy change is an endothermic reaction. It is due to the absorption of the heat and the change in the heat capacity of the sample. This is the melting point for the sample precursor which is at 175-178˚C. The C site is where the sample starts to crystalline as the temperature increases. At this point, the molecules in the sample precursor start to arrange themselves spontaneously as they obtain enough freedom to move around themselves. This point is an exothermic reaction and also known as crystalline point which is at 240-245˚C. As the temperature increases, the crystalline precursor starts to melt again at D site. This endothermic reaction occurs at 260-270˚C. But after the point D, the molecules reach the stability as it start to crystalline and maintain the arrangement after 400˚C. So, the thermal stability for the sample was measured at 450˚C and 550˚C.

B.Structural studies

X-ray diffraction (XRD) was carried out on the precursor and the final product of $LiNi_{0.5}Mg_{0.5}VO_4$ annealed at 450 °C and 550 °C for 5 hours as to determine their crystalline structures. Fig. 2 shows the XRD pattern of precursor $LiNi_{0.5}Mg_{0.5}VO_4$ and Fig. 3 shows the XRD for the $LiNi_{0.5}Mg_{0.5}VO_4$ powder that was annealed at 550 °C for 5 hours. Meanwhile, Fig. 4 shows the XRD for the $LiNi_{0.5}Mg_{0.5}VO_4$ powder that was annealed at 450 °C for 5 hours.

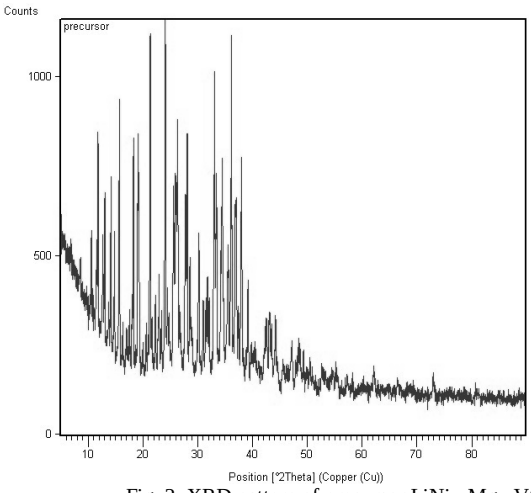

Fig. 2. XRD pattern of precursor $LiNi_{0.5}Mg_{0.5}VO_4$

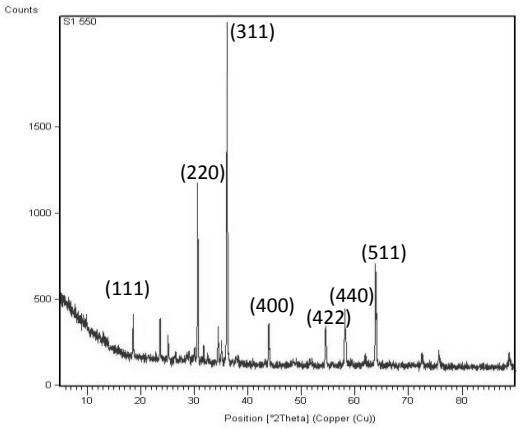

Fig. 3. XRD pattern of $LiNi_{0.5}Mg_{0.5}VO_4$ annealed at 550 °C for 5 hours

XRD for both annealed samples shows sharp lines indicating the crystalline nature of the sample prepared compared to the precursor. It shows that the sample prepared at temperature 450 °C gives sharper peak, indicating the crystallinity of the sample increases. It also shows narrowness of the diffraction peaks indicating a good crystallinity of $LiNi_{0.5}Mg_{0.5}VO_4$.

The crystalline structure for $LiNi_{0.5}Mg_{0.5}VO_4$ powder can be determined from the first two peaks that are very distinctive in the XRD pattern. In XRD pattern, peak [111] line and peak [220] line indicate that the structure of $LiNi_{0.5}Mg_{0.5}VO_4$ is inverse spinel structure [5].

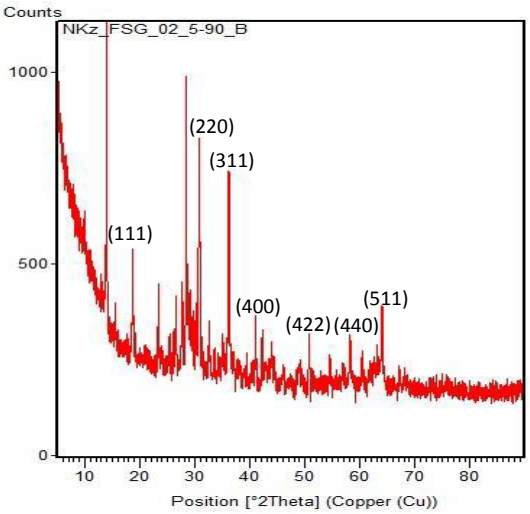

Fig. 4. XRD pattern of $LiNi_{0.5}Mg_{0.5}VO_4$ annealed at 450 °C for 5 hours

The decrease ratio intensity of [220] line with [311] line and increase of intensity ratio of [311] line with [400] line from $LiNiVO_4$ to $LiNi_{0.5}Mg_{0.5}VO_4$ annealed at 450 °C and 550 °C for 5 hours attribute to the incorporation of the magnesium with the cathode material at the nickel (Ni) sites of $LiNiVO_4$ structure [6]. Hence, proved that Mg was successfully substituted with the parental compound of $LiNiVO_4$ for both samples.

Table I shows the comparisons between $LiNiVO_4$, $LiNi_{0.5}Mg_{0.5}VO_4$ annealed at 450 °C and 550 °C for 5 hours, the Intensity ratio $I[220]/I[311]$ and Intensity ratio $I[311]/I[400]$.

TABLE I
COMPARISON TABLE BETWEEN $LiNiVO_4$, $LiNi_{0.5}Mg_{0.5}VO_4$ ANNEALED AT 450 °C AND 550 °C FOR 5 HOURS, THE INTENSITY RATIO $I[220]/I[311]$ AND INTENSITY RATIO $I[311]/I[400]$

Intensity ratio	I[220]/ I[311]	I[311]/ I[400]
$LiNiVO_4$	0.51	2.91
$LiNi_{0.5}Mg_{0.5}VO_4$ Annealed at 550°C	0.41	4.60
$LiNi_{0.5}Mg_{0.5}VO_4$ Annealed at 450°C	0.31	7.43
Observations	Decrease	Increase

B. Electrochemical Characterisation of $LiNi_{0.5}Mg_{0.5}VO_4$

The conductivity of $LiNi_{0.5}Mg_{0.5}VO_4$ was measured by Solartron Impedance SI 1260 Impedance/ Gain-Phase Analyzer and Solartron Electrochemical Interface SI 1287 with the initial and final frequencies were at 3.2×10^7 Hertz (Hz) and 0.1 Hz. The AC amplitude was applied at 200 mV. The conductivity of $LiNi_{0.5}Mg_{0.5}VO_4$ was measured with the temperature dependences with various temperatures from 25 °C to 65 °C.

The conductivity of the sample is particularly measured by the measurement and analysis of Z (impedance), Y (admittance) and plotting of these functions in the complex plane which is known as Nyquist plot [7].

The bulk electrical resistance value (R_B) can be obtained from the Nyquist plot where the intercept at the higher frequency side is on x-axis or Z_{real}. From the plot, the conductivity is calculated by using the formulae;

$$\sigma = \frac{t}{R_B A} \qquad (1)$$

Where, σ = conductivity ($S.cm^{-1}$), R_B = Bulk resistance (Ω), A = area of the sample (m^2),
t = thickness of the sample (m).

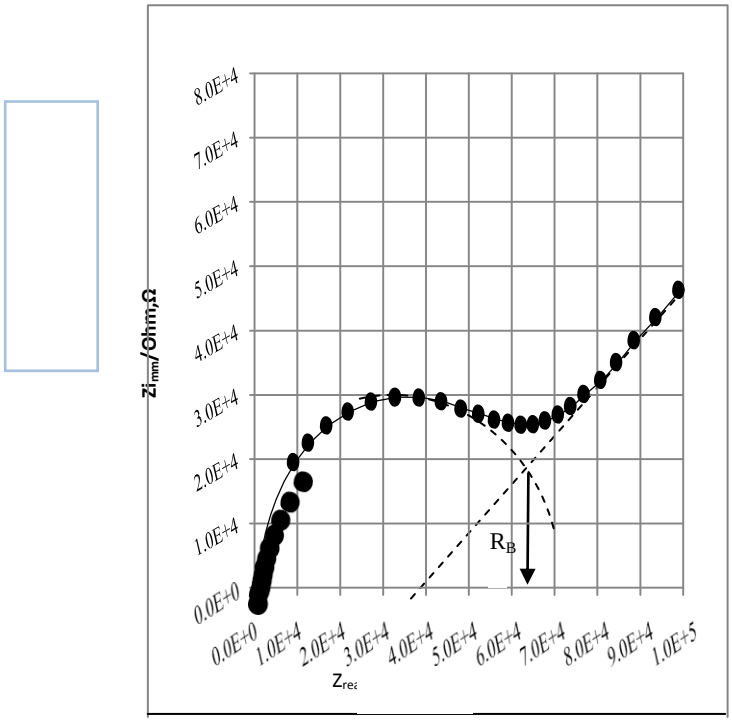

Fig. 5. Nyquist Plot of $LiNi_{0.5}Mg_{0.5}VO_4$ at 25˚C aneal at 550 ºC

The Nyquist plot obtained at room temperature 25 ºC for $LiNi_{0.5}Mg_{0.5}VO_4$ anneal at 550 ºC (Fig. 5) and 450 ºC (Fig. 6) gave the Bulk Resistance (R_B) values which are 6.36 X 10^4 Ω and 5.54 X 10^4 Ω respectively. The conductivities of both $LiNi_{0.5}Mg_{0.5}VO_4$ anneal at 550 ºC and 450 ºC were calculated using equation (4) and the values are 1.40 x 10^{-4} S cm^{-1} and 1.58 x 10^{-4} S cm^{-1} respectively.

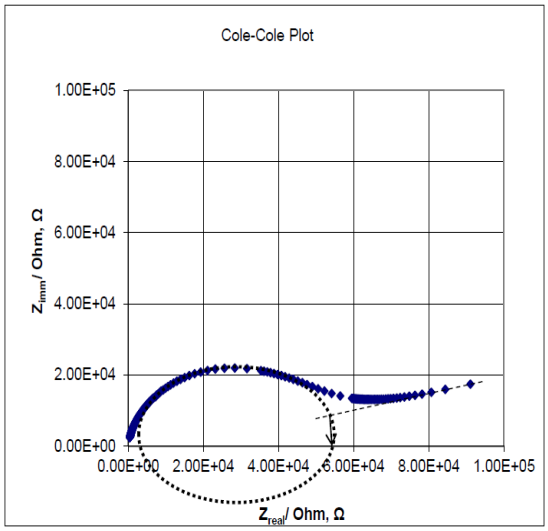

Fig. 6. Nyquist plot for $LiNi_{0.5}Mg_{0.5}VO_4$ aneal at 450 ºC

The same method was used to determine bulk resistance (R_B) and conductivity for temperature dependence studies and the values are recorded in Table II and Table III. Table II shows the temperature dependence on bulk resistance (R_B) and Table III shows the temperature dependence on the electrical conductivity.

TABLE II
TEMPERATURE DEPENDENCE ON BULK RESISTANCE FOR $LiNi_{0.5}Mg_{0.5}VO_4$ ANNEALED AT 450 ºC AND 550 ºC

Temperature (ºC)	Bulk Resistance, R_B (Ω)	
	450 ºC	550 ºC
25	5.54 x 10^4	6.36 x 10^4
35	1.17 x 10^5	2.45 x 10^5
45	1.86 x 10^5	4.00 x 10^5
55	2.09 x 10^5	6.18 x 10^5
65	2.17 x 10^5	2.08 x 10^6

From Table II, it can be seen that the bulk resistance (R_B) increases with increasing temperature. This is due to the velocity of the electrons in the material. As temperature increases, the particles gain more heat energy and fasten the mobility of the particles, thus increases the probability of the particles to collide with each other. The collision has diverted the electrons from forward transport thus increases the resistance in the material. Increasing in the bulk resistance (R_B) leads to decreasing in conductivity of the material [8] as shown in Table III. However $LiNi_{0.5}Mg_{0.5}VO_4$ annealed at 450 ºC give higher resistance values (Fig. 7).

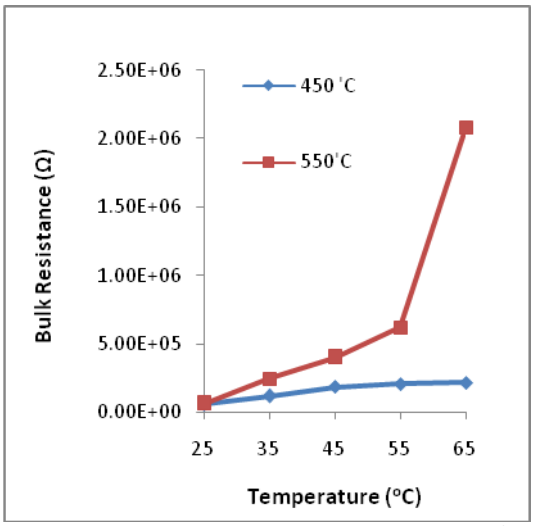

Fig. 7. Temperature dependence on bulk resistance (RB) for $LiNi_{0.5}Mg_{0.5}VO_4$ annealed at 450 °C and 550 °C

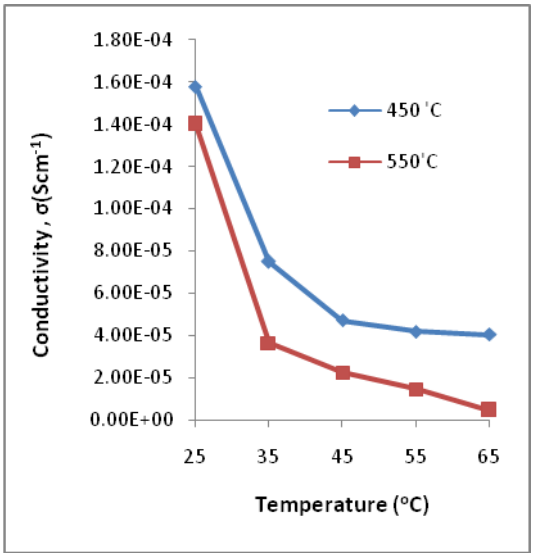

Fig. 8. Temperature dependence on conductivity for $LiNi_{0.5}Mg_{0.5}VO_4$ annealed at 450 °C and 550 °C

Temperature can also influence the conductivity of $LiNi_{0.5}Mg_{0.5}VO_4$ by the relationship between temperature and conductivity quantified from the Wiedemann Franz law;

$$\frac{\kappa}{\sigma} = LT \qquad \sigma = \frac{\kappa}{LT} \qquad (2)$$

where, κ = thermal conductivity, σ = conductivity ($S.cm^{-1}$), T = Temperature (K),L = Lorenz number, 2.44 x 10^{-8} $W.\Omega.K^2$ take out

From the formula (2), conductivity shall decreases with increasing temperature since this study is on the ionic conductors and it is proven in Table III. The conductivity decreases as the temperature increases.

TABLE III
TEMPERATURE DEPENDENCE OF CONDUCTIVITY FOR $LiNi_{0.5}Mg_{0.5}VO_4$ ANNEALED AT 450 °C AND 550 °C

Temperature (°C)	Conductivity,σ ($S.cm^{-1}$)	
	450 °C	550 °C
25	1.58 x 10^{-4}	1.40 x 10^{-4}
35	7.49 x 10^{-5}	3.63 x 10^{-5}
45	4.71 x 10^{-5}	2.22 x 10^{-5}
55	4.19 x 10^{-5}	1.44 x 10^{-5}
65	4.00 x 10^{-5}	4.28 x 10^{-6}

Although the conductivity of $LiNi_{0.5}Mg_{0.5}VO_4$ annealed at 450 °C and 550 °C show the same conductivity decreasing pattern but $LiNi_{0.5}Mg_{0.5}VO_4$ annealed at 450 °C produced higher conductivity values (Fig. 8).

The phenomenon happened in the transition metals, $LiNi_{0.5}Mg_{0.5}VO_4$ is different from what happened in electrolyte. In electrolyte, the resistance decreases with the increasing temperature leads to increasing conductivity [9,10,11] because the electrons are not packed tightly in the electrolyte and the electrons are freely as compared to the solid form metal where the electrons are packed closely and tightly together [12]. Therefore, the electrical conductivity will increase with increasing temperature in electrolyte but the electrical conductivity will drop with increasing temperature in transition metals, $LiNi_{0.5}Mg_{0.5}VO_4$.

CONCLUSION

$LiNi_{0.5}Mg_{0.5}VO_4$ synthesized by the sol-gel method with different annealing temperature of 450 °C and 550 °C gave different structural and electrical properties. The chosen temperatures were due to TGA results showing thermal stability achieved at temperature over 400 °C. The XRD pattern for both $LiNi_{0.5}Mg_{0.5}VO_4$ annealed at 450 °C and 550 °C shown crystalline with FCC structure. However $LiNi_{0.5}Mg_{0.5}VO_4$ annealed at 450 °C shows more crystalline.The electrical conductivity for both $LiNi_{0.5}Mg_{0.5}VO_4$ annealed at 450 °C and 550 °C is found to be decreasing with the increasing temperature. However, the conductivity values for $LiNi_{0.5}Mg_{0.5}VO_4$ anneal at 450 °C are slightly greater than $LiNi_{0.5}Mg_{0.5}VO_4$ anneal at 550 °C. The conductivity obtained at room temperature (25 °C) for both $LiNi_{0.5}Mg_{0.5}VO_4$ anneal at 450 °C and 550 °C are 1.58 x 10^{-4} and 1.40 x 10^{-4} respectively. It can be conclude that $LiNi_{0.5}Mg_{0.5}VO_4$ annealed at 450 °C has better structural and electrical properties as compared to $LiNi_{0.5}Mg_{0.5}VO_4$ annealed at 550 °C. It can be said that $LiNi_{0.5}Mg_{0.5}VO_4$

annealed at 450 ^{o}C can be a potential cathode material in Li-ion batteries.

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BIBLIOGRAPHY

A.F.M.Fadzil was born in Alor Setar, Kedah on April 29, 1982. She graduated her first degree in Nuclear Science from Universiti Kebangsaan Malaysia (UKM) Bangi, Selangor, Malaysia in 2004. Then, she graduated her Masters Degree in Advanced Material and Nanotechnology from UiTM Shah Alam, Selangor, Malaysia (2007).

She was one a RESEARCH ASSISTANT (RA) in UiTM Shah Alam, Selangor, Malaysia (2005-2006) supervised by Prof. Dr. Norlida Kamaruzzaman. Then, she worked as A-Level PHYSICS LECTURER (2006-2011) in International Education College (INTEC), UiTM. She is currently working as Physics Lecturer at Center of Foundation Studies, UiTM Puncak Alam Campus, Selangor, Malaysia. She has published 3 international journal papers as following;

i. "Characterization and Microstructural Studies of $LiFe_5O_8$ Synthesized by the Self Propagating High Temperature Combustion Method", Journal of Ionics (11), pp 446-450 (2005). Publications: Institute of Ionics, Stuttgard, Germany.

ii. "Comparative Study of Substituted $LiMn_{(2-x)}Fe_xO_4$ via Sol-Gel Route" (2007), pp153. AIP Conf. Proc. 1217, pp. 33-36.

iii. "Synthesis and Characterization of Lithium Ferrite ($LiFe_5O_8$) Powders By Sol-Gel Method" (2007), pp152. AIP Conf. Proc. 1217, pp. 370-374.

Currently, her research interest are in cathode material, Li-ion batteries and nanotechnology.

Madam Aida Fazliza Mat Fadzil has won Gold Medal for Selangor Young Scientist Award 2007 in Innovation Category, Bronze Medal for Innovation, Invention & Design Competition (IID-2008) and the latest is Bronze Medal for Research Innovation, Invention & Design Competition (RIID-2013).

S.I.Y.Saaid was born in Gelugor, Penang on January 08, 1983. She graduated her Diploma in Science from UiTM Arau Campus, Perlis, Malaysia in 2004. Then, she graduated her Bachelor Degree (Hons) in Physics from UiTM Shah Alam, Selangor, Malaysia in 2007. After that, she graduated her Masters Degree in Advanced Material (Solid State Ionics) from UiTM Shah Alam, Selangor, Malaysia (2010).

She was one a RESEARCH ASSISTANT (RA) in UiTM Shah Alam, Selangor, Malaysia (2007) supervised by Prof. Dr. Muhd Zu Azhan Yahya. Then, she worked as PHYSICS LAB DEMONSTRATOR (2009-2010) in Universiti Malaya (UM). She is currently working as PHYSICS LECTURER at Center of Foundation Studies, UiTM Puncak Alam Campus, Selangor, Malaysia. She has published a journal paper which is "Solid State Proton Battery Using Plastisized Cellulose-Salt Complexes Electrolyte", Material Research Innovations (13), pp 252-254 (2009).Currently, her research interests are in proton batteries, polymer electrolyte and biopolymer.

Madam S.I.Y Saaid has won Bronze Medal for Research Innovation, Invention & Design Competition (RIID-2013).