The Structural and Electrical Properties of LiNi$_{0.5}$Mg$_{0.5}$VO$_4$ Annealed at 450 °C and 550 °C

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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 °C and 550 °C 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 °C 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 °C, 35 °C, 45 °C, 55 °C and 65 °C. It was found that the bulk resistance ($R_b$) is proportional with temperature for both annealing temperature of 450 °C and 550 °C. However the conductivity is inversely proportional with temperature for both annealing temperature of 450 °C and 550 °C. At room temperature (25 °C) the conductivity of LiNi$_{0.5}$Mg$_{0.5}$VO$_4$ annealed at 450 °C was 1.58 x 10$^{-4}$ S cm$^{-1}$ while LiNi$_{0.5}$Mg$_{0.5}$VO$_4$ annealed at 550 °C was 1.40 x 10$^{-4}$ S cm$^{-1}$. This shows that LiNi$_{0.5}$Mg$_{0.5}$VO$_4$ annealed at 450 °C has greater electrical properties.

Index Term— LiNi$_{0.5}$Mg$_{0.5}$VO$_4$, Li-ion battery, cathode material, annealing temperature

I. INTRODUCTION

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 Nagauru and Tzawa 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$_2$O$_5$ 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 6.1 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 10297.2 and further annealed at 450 °C and 550°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°C to 800°C and then cooled down to room temperature. The sample has
been heated at 10°C for every 10 minutes.

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.

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_{1.5}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_{1.5}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_{1.5}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>
<thead>
<tr>
<th>Intensity ratio</th>
<th>I[220]/</th>
<th>I[311]/</th>
<th>I[311]/I[400]</th>
</tr>
</thead>
</table>

**B. Electrochemical Characterisation of LiNi_{1.5}Mg_{0.5}VO_4**

The conductivity of LiNi_{1.5}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 x 10^5 Hertz (Hz) and 0.1 Hz. The AC amplitude was applied at 200 mV. The conductivity of LiNi_{1.5}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;

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

Where, $\sigma$ = conductivity (S.cm^-1), $R_B$ = Bulk resistance (Ω), $A$ = area of the sample (m^2), $t$ = thickness of the sample (m).
The Nyquist plot obtained at room temperature 25 °C for LiNi$_{0.5}$Mg$_{0.5}$VO$_4$ anneal at 550 °C (Fig. 5) and 450 °C (Fig. 6) gave the Bulk Resistance ($R_B$) values which are 6.36 $\times$ 10$^4$ $\Omega$ and 5.54 $\times$ 10$^4$ $\Omega$ respectively. The conductivities of both LiNi$_{0.5}$Mg$_{0.5}$VO$_4$ anneal at 550 °C and 450 °C were calculated using equation (4) and the values are 1.40 $\times$ 10$^{-4}$ S cm$^{-1}$ and 1.58 $\times$ 10$^{-4}$ S cm$^{-1}$ respectively.

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 °C give higher resistance values (Fig. 7).

**TABLE II**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Bulk Resistance, $R_B$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>450 °C</td>
</tr>
<tr>
<td>25</td>
<td>5.54 $\times$ 10$^4$</td>
</tr>
<tr>
<td>35</td>
<td>1.17 $\times$ 10$^5$</td>
</tr>
<tr>
<td>45</td>
<td>1.86 $\times$ 10$^5$</td>
</tr>
<tr>
<td>55</td>
<td>2.09 $\times$ 10$^5$</td>
</tr>
<tr>
<td>65</td>
<td>2.17 $\times$ 10$^5$</td>
</tr>
</tbody>
</table>
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:

\[
\frac{k}{\sigma} = LT \\
\sigma = \frac{k}{LT}
\]

where, \(k\) = thermal conductivity, \(\sigma\) = conductivity (S cm\(^{-1}\)), \(T\) = Temperature (K), \(L\) = Lorenz number, \(2.44 \times 10^{-8}\) W Ω 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 |

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Conductivity, (\sigma) (S cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>450 °C</td>
</tr>
<tr>
<td>25</td>
<td>(1.58 \times 10^4)</td>
</tr>
<tr>
<td>35</td>
<td>(7.49 \times 10^5)</td>
</tr>
<tr>
<td>45</td>
<td>(4.71 \times 10^5)</td>
</tr>
<tr>
<td>55</td>
<td>(4.19 \times 10^5)</td>
</tr>
<tr>
<td>65</td>
<td>(4.00 \times 10^5)</td>
</tr>
</tbody>
</table>

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 showed 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 °C can be a potential cathode material in Li-ion batteries.

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REFERENCES

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