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SYNTHESIZING $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ CATHODE MATERIAL FOR LITHIUM-ION BATTERY

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ABSTRACT

Layered $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ cathode material was synthesized using glycine combustion method. The calcinations temperature effect is investigated in term of physical and electrochemical performance of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ as a cathode material. The synthesized $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ was calcine at 500^oC,600^oC,700^oC,800^oC and 900^oC respectively. The XRD analysis refine that a well formed layer structure exist as well as splitting of the peaks (006)/(102) and (108)/(110) showed by the samples. The synthesized cathode material presents as an agglomerated primary structure ranging from 30nm to 300nm. The charge discharge test was carried out under condition 0.14mA current in voltage range 3.0V to 4.2V. Not much differences on the structure of the samples although 800^oC delivered highest discharge capacity (211mAh/g) with good capacity retention. Layered $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ cathode material can be a promising option of $LiCoO_2$ as it can deliver higher capacity with good capacity retention at voltage range 3.0V to 4.2V.

INTRODUCTIONS

Recently, developed layered oxide $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ seems a very promising option for cathode material of lithium ion battery. The material which was introduced by Ohzuku and Makimura has a x=1/3 in $(LiNixCo1-2xMnx)O_2$ system can give specific capacity at 160mAh/g between 2.5V and 4.4V. Due to the complicated composition, the cathode properties of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ should be sensitively dependent on the microscopic features like the distribution of transition metal and the particle morphology[1]. This complex interactions between the three transition metal ions within the oxygen framework of layered $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ are not understood yet, and little literature exists on the details of the initial microstructure and its stability with electrochemical cycling[2].Thus the well care and optimum condition during synthesis is selected. Various methods have been employed to synthesis and study the performance of this material. Park [3] synthesis $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O2$ using hydroxide co-precipitate and gain capacity at 180mAh/g with agglomerated structure. Shin and co-workers investigate the microscopic features of layered $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ using three different methods including solid state, co-precipitation and combustion method. Their results also showed stable cycle retention with higher discharge capacity than $LiCoO_2$ depends on the synthesis method.

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The conventional methods (solid state, co-precipitation, sol-gel) is proved as a reliable route to synthesis $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$. However these methods are complicated, require multi-step reactions with a long reaction and synthesis routes[4]. A combustion method has attracted much interest recently as the technique is simple, quick, cost saving and straightforward technique. This method which also known as self propagating high temperature(SPHT) technique use nitrates mixture of respective salts and a nitrogenous fuel (urea or glycine). The glycine, in addition to complexion with the metal cations and increasing their solubility, serves as a fuel during charring. The key advantage of this method is that the thermal energy required for the reaction to occur is provided by the reaction itself and not by an external source. Here we study the temperature effect in term of physical and electrochemical performance of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ as a cathode material.

METHODS AND MATERIALS

Synthesis

The layered $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ was synthesized by a combustion technique as follows. The desired amount of lithium nitrate ($LiNO_3$), nickel nitrate ($Ni(NO_3)_2.6H_2O$), cobalt nitrate ($Co(NO_3)_2.6H_2O$), manganese nitrate ($Mn(NO_3)_2.6H_2O$) and glycine were mixed in a beaker and dissolved with distilled water. The ratio of $LiNO_3$/glycine used is calculated by the weight balanced which is the glycine amount is 100% from the $LiNO_3$. The aqueous solution is stirred to homogenize the material and the pH of the solution was controlled in the range of 6.5 to 7.0 by dropping ammonium hydroxide. The resulting solution is preheated at ~100^{o}C to remove the excess water. As the material becomes slurry the beaker was transfer into an aluminum box and heat at 450^{o}C to undergo self-sustaining combustion. The reaction is presented below as the usual product of combustion reaction are CO_2,H_2O and N_2[5]. The black ash powders resulting from this reaction is collected and calcine at 500^{o}C, 600^{o}C, 700^{o}C, 800^{o}C and 900^{o}C respectively for 12 hours to ensure complete combustion and modify the phase composition of the powders.

$LiNO_3 + 1/3Ni(NO_3)_2.6H_2O + 1/3Co(NO_3)_2.6H_2O + 1/3Mn(NO3)_2.6H2O + NH_2CH_2COOH \rightarrow Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2 + 37/2H_2O + 2CO_2 + 4N_2$

Electrode preparation and cell assembly

The positive electrode for the electrochemical studies was fabricated with active material and a mixture of acetylene black carbon and PTFE in the ratio of 2:1%. The sample was adhered onto the stainless steel mesh and dried at 100^{o}C for overnight. The electrode were fabricated in coin cell type 2032 with Li-metal as a negative electrode and immersed in an electrolyte of 1M $LiPF_6$ salt in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 v/v). The electrochemical testing was evaluated using Won A Tech Battery Cycler System (WBCS 3000) at voltage range 3.0 to 4.2V with current 1.40mA.

Analysis

The crystal structure of the powder samples of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ were characterized by x-ray diffraction (XRD) using a Bruker AXS powder diffractometer, equipped with

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Cu $K_{\alpha 1}$ radiation, λ = 1.5406Å. XRD was operated at 40kV and 30mA, at scanning rate of 2°/min, between 10° and 80° of 2θ angle. The microscopic surface morphology of the powder samples was examined by scanning electron microscopy (SEM), using Leo 1525 electron microscope. The electrochemical properties of the powder were evaluated using Won A Tech Battery Cycler System (WBCS 3000). The positive electrode for the electrochemical studies was fabricated with active material and a mixture of acetylene black carbon and PTFE in the ratio of 2:1%. The sample was adhered onto the stainless steel mesh and dried at 100°C for 12 hours. The electrode were fabricated in coin cell type 2032 with Li-metal as a negative electrode and immersed in an electrolyte of 1M $LiPF_6$ salt in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 v/v). The cell was tested at voltage range 3.0 to 4.2V with current 1.40mA.

RESULTS AND DISCUSSION

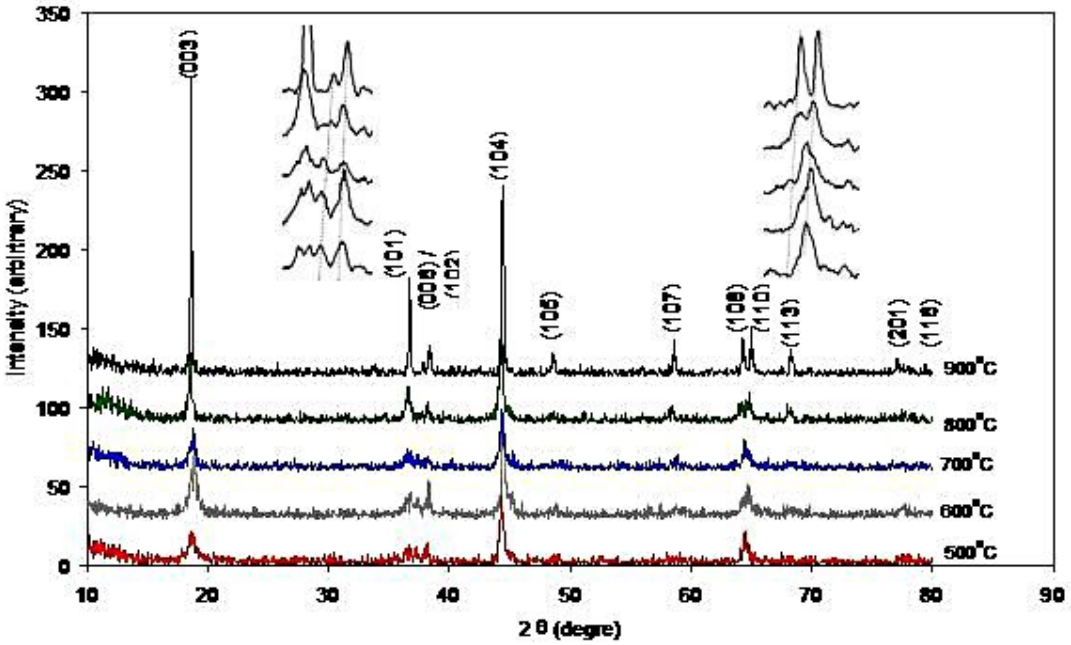

Figure 1 : X-ray diffactogram of the $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ using different calcinations temperature a) 500°C b)600°C c)700°C d)800°C e)900°C

Figure 1 shows the XRD pattern and refinement spectra for the synthesized $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ using different ratio of glycine. As prepared samples are indexed by assuming a layer manganese oxide structure based on a hexagonal α- $NaFeO_2$ structure (space group ; Rm166, R3*m*). The main peaks exist are (003), (104), (101), (006), (012), (018) and (110) with different intensity regarding to the calcinations temperature. The structural characterization clearly demonstrate that there is no superlattice peaks appear for all samples at 2θ between 20° and 25° which can act as an impurity in the synthesizing materials [7-8].The split of the peaks (006)/(102) and (108)/(110) are used to indicate the characteristic of the synthesized layered structure material[8-9]. Better splitting of the peaks give better layer formed of the structure. Initially the separation of the (006) and (102) seems difficult to differentiate and the

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splits become visible at temperature 700°C and above. Splitting of (108) and (110) peaks are visible at temperature 800°C and well split at 900°C. At 900°C, the diffraction peaks are narrow with high intensity indicating high crystalline structure. From the XRD result, a well complete layered structure of synthesized $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ is formed at temperature of 800°C and above.

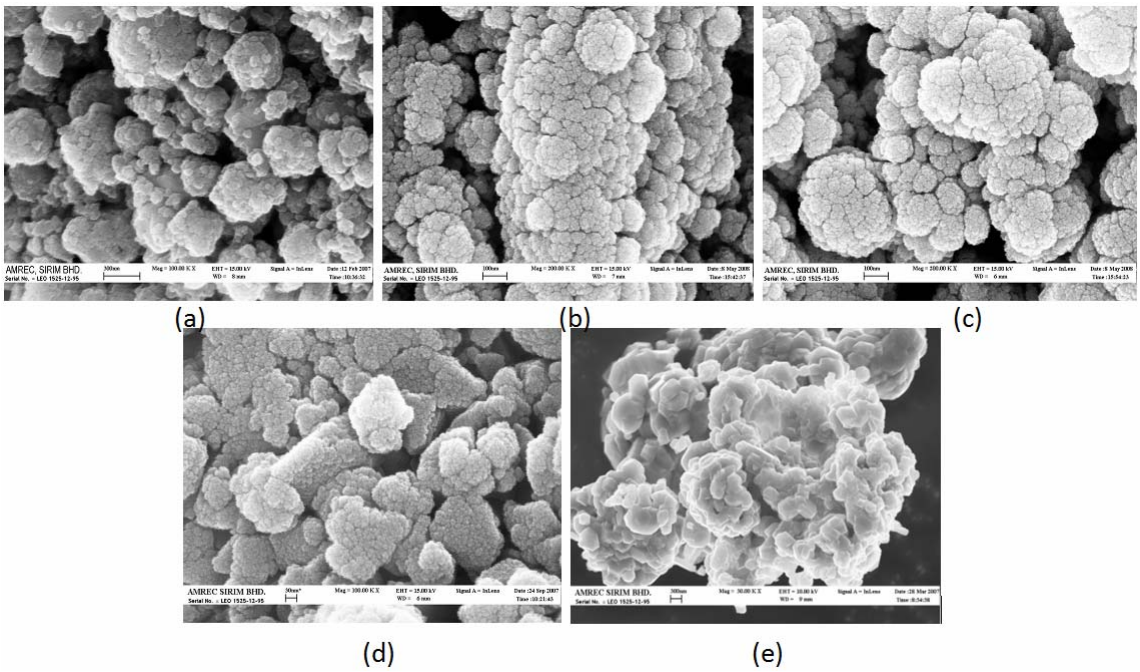

Figure 2: SEM micrographs of $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ calcined at temperature a) 500°C b)600°C c)700°C d)800°C e)900°C

Scanning electron microscopy (SEM) images of the synthesized $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ using different calcinations temperature are illustrated in Figure 2. The particles shape and size of cathode material directly affected the energy density of battery in practical usage. The samples exist as an agglomerated primary particles with semi-spherical powder shape and smooth surface. The morphology of the samples is similar and crystalzed at 900°C as shown in the XRD. The particle sizes are ranging from 30nm to 300nm. Shin[1] synthesized 300nm to 400nm crystallite grains using combustion method and 20µm sizes using solid state reaction. Bing-He[11] synthesis 6-10µm agglomerated structure with smaller primary particles. Thus, we consider that the cauliflower-like nano structure [10] with smaller primary particle illustrated will produce high specific area per volume to help improving the performance of the cathode $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ materials.

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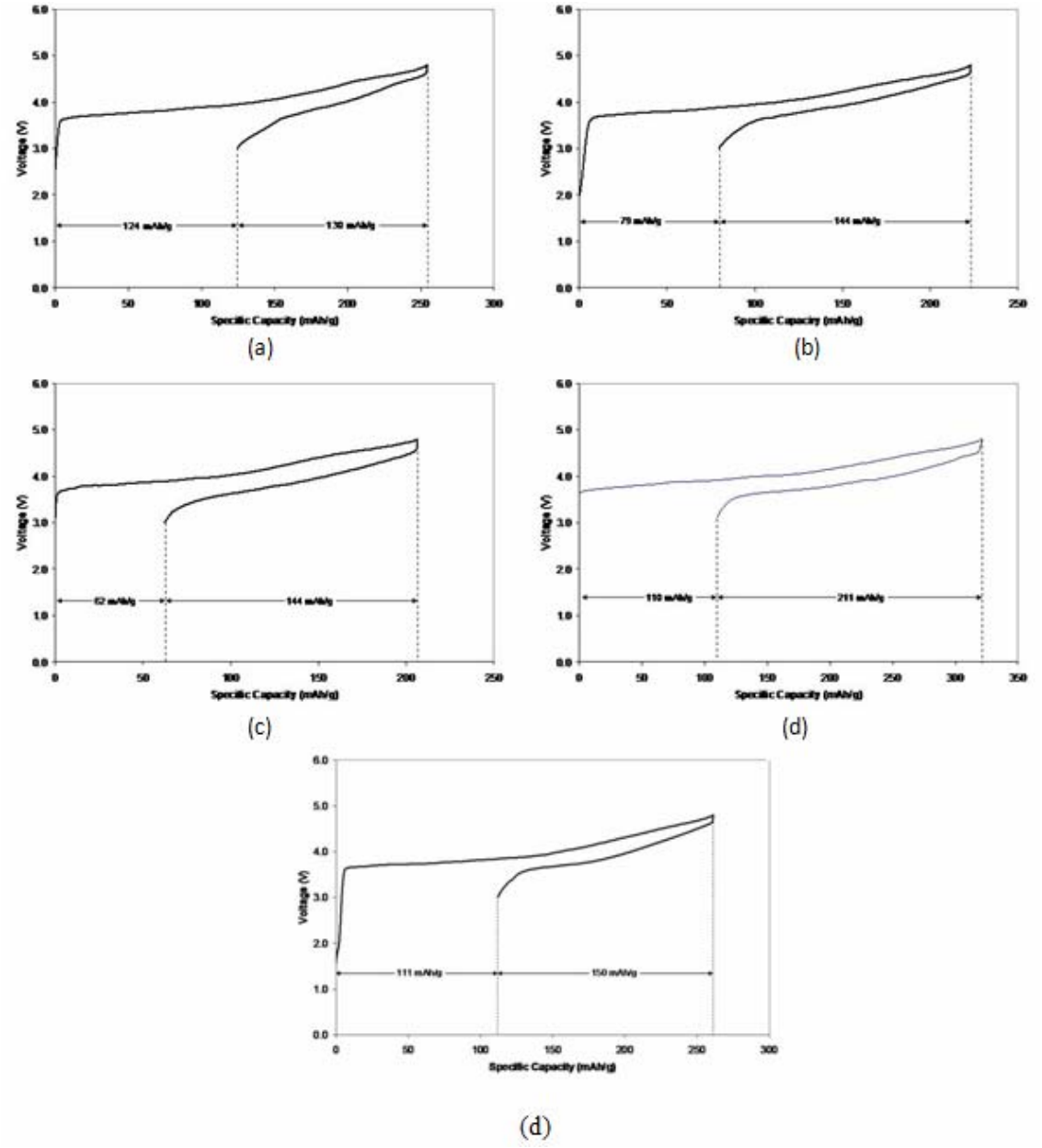

Figure 3: 1st cycle capacity of synthesized $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ with different calcination temperatures a) 500°C b) 600°C c)700°C d)800°C e)900°C

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Table 1 : Summary on 1st charge discharge capacity with different calcine temperature for synthesized $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$

Sample	Charge	Discharge	Columbic Efficiency (%)
500oC	254	130	51
600oC	223	144	62
700oC	206	144	70
800oC	321	211	66
900oC	261	150	57

Figure 3 show the first charge discharge capacity for calcined samples at 500°C, 600°C, 700°C, 800°C and 900°C of the synthesized $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ respectively. The samples were tested using 0.14mA current under voltage range of 3.0V to 4.2V. As the temperature increase, the discharge capacity increase to maximum 211mAh/g at 800°C before decreased to 150mAh/g for 900°C. At the first cycle all samples show great capacity fading as the columbic efficiency is about 50% to 70%. The initial fading of the first cycle can be assigned to the formation of a solid electrolyte interface (SEI) on the surface of the cathode active material [8]. On second cycle onwards, there is hardly any difference in charge and discharge capacity for 800°C although 700°C suffer great fading. Figure 4 shows the plot of discharge capacity (%) as a function of cycle number using current 0.14mA. The capacity retention of the sample 600°C, 800°C and 900°C is good with little fading. 800°C remain it capacity for 90% after 50 cycles. The figures show an optimum temperature condition gained with the best capacity at 800°C.

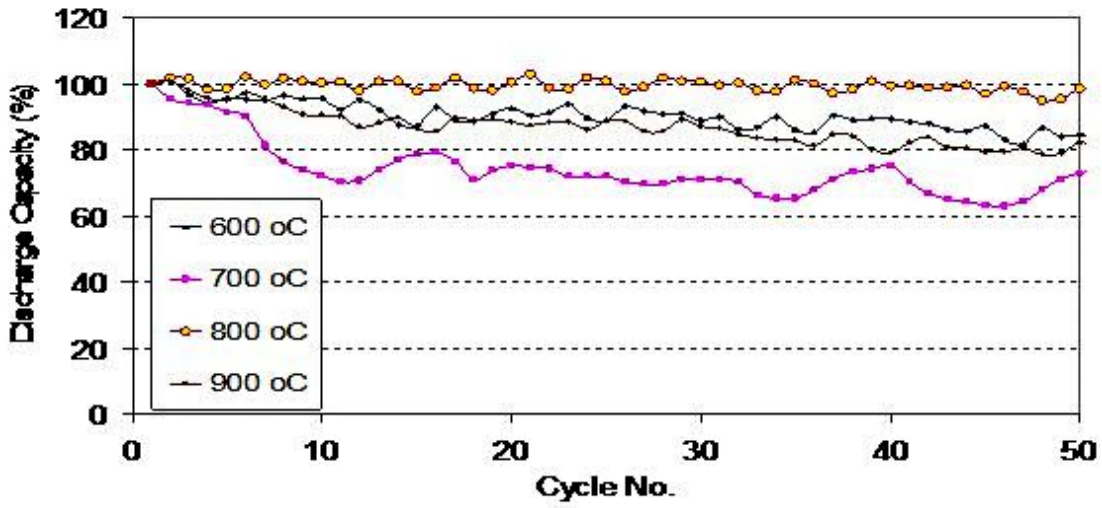

Figure 4: Discharge capacity(%) of synthesized $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ at different temperature

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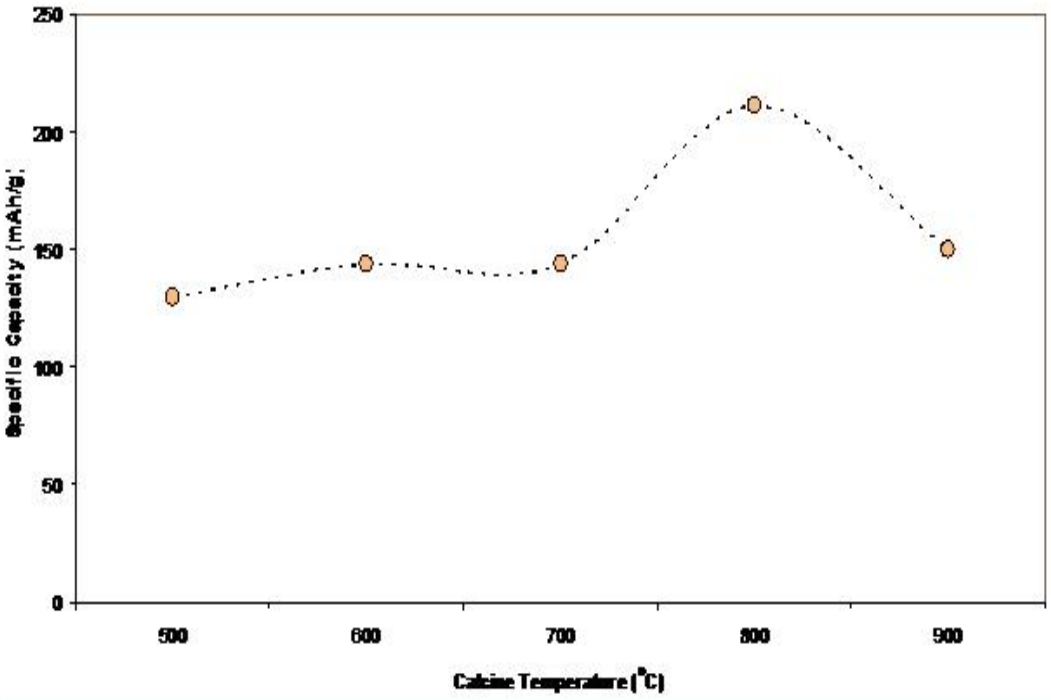

Figure 5: Correlation between discharge capacity and calcinations temperature.

Based on the XRD profile, good layered structure of $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ is formed at 700°C and above. The splitting of the peaks (006)/(102) and (108)/(110) which show good distribution transition ion metal in the layered structure is well defined for samples 800°C and 900°C. Scanning electron micrograph (SEM) screens the similar shape and morphology of the structure. Not much difference occurs as the samples were synthesized using same materials and method except 900°C show crystal structure as calcine at temperature 900°C. The electrochemical performance was affected most as the delivered capacity varied for each sample. Figure 5 show the correlation between the specific capacity with calcinations temperature. As the similar physical properties of the samples state above, the discharge capacity increases with the increase of the calcinations temperature. The capacity is highest for 800°C at 211mAh/g with good capacity retention indicating that calcine temperature gives huge effect in improving the cathode material capacity and influence the electrochemical performance of the samples.

CONCLUSION

Self propagating combustion method is successful in synthesizing layered $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ cathode material using glycine as a fuel. The XRD analysis confirmed that the products belong to a layered α- NaFeO2 structure. Splitting of peaks (006)/(102) and (108)/(110) which show good distribution transition ion metal in

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the layered structure was clearly visible in 800°C and above. The morphology of the samples is characterized as an agglomerated cauliflower-like nano structure with samller particles range from 30nm to 300nm. The particle becomes rougher with increasing calcine temperature and formed crystallite structure at temperature 900°C. For the electrochemical performance of the $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$, calcinations temperature is critical and selective as the sample calcine at 800°C shows highest specific capacity at 211mAh/g with good cycle retention.

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