INVESTIGATIONS ON SYNTHESIS OF $LI(NI_{1/3}CO_{1/3}MN_{1/3})O_2$ BY GLYCINE NITRATE COMBUSTION TECHNIQUE

A.D.B.D.Senarathna[1, 2],T.H.N.G.Amaraweera[2, 3],H.W.M.A.C. Wijayasinghe[2]

[1]*Department of Physics, The Open University of Sri Lanka*
[2]*Institute of Fundamental Studies (IFS),Hantana Road, Kandy, Sri Lanka*
[3]*Department of Science and Technology, Uva Wellassa University of Sri Lanka, Badulla*

INTRODUCTION

As far as the world energy consumption is concerned, switching to new sources of energy such as wind power, tidal power, geothermal energy, solar cells, fuel cells and energy storing devices as batteries are important. The batteries are given a major importance due to its wide range of usage in almost all portable and house hold-devices, without which, perhaps, people cannot fulfill their necessities at present. From an overall perspective rechargeable Li-ion batteries undoubtedly represent the most promising energy storage system and certain aspects of its principles of operation deserve particular attention (Xu *et al.,* 2012). The performance of a battery is mainly related to the intrinsic property of the materials of the positive and negative electrodes and the electrolyte. $LiCoO_2$ has most widely been used. However, the high cost is a main obstacle for reaching it to the common mass as a cheaper and reliable material for potable power source (Whittingham,2004).

$Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ has recently been investigated as an alternative for cathode materials in secondary lithium ion batteries with better cycling performance and stability at high potential windows (Samarasingha *et al.,* 2008*)*. It has been reported that the electrochemical performance of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ is strongly affected by the synthesis condition due to the difference in homogeneity. However, its optimum synthesis conditions and material characteristics, especially electrical properties, have not been systematically investigated. By considering them, this work was based on investigation of synthesis and electrical conductivity of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ material prepared by Glycine-Nitrate Combustion (GNC) methods (Wijayasingh,.2004), which is a low cost technique but can result in powders with high purity, homogeneity and particle morphology that are highly desired for Li-ion battery cathodes.

METHODOLOGY

$Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ powder was synthesized by GNC method. Stoichiometric amount of metal nitrates, $LiNO_3$, $Ni(NO_3)_2.6H_2O$, $Co(NO_3)_2.6H_2O$ and $Mn(NO_3)_2.4H_2O$ were mixed with distilled water. Glycine fuel was added to the nitrate solution and the new powder compositions were prepared with various glycine (G) to nitrate (N) ratios to investigate the effect of G:N ratio on the powder synthesis.The powder obtained after the combustion was ground and calcined at 1000 ^{0}C for four hours. The phase analysis of powder was carried out with X-ray diffractometry (XRD, Siemens D5000 using monochromatic Cu Kα radiation).

The calcined powders were uni-axially pressed at different pressure to find the optimum pressing condition to prepare solid pellets. Then the green pellet of 12 mm diameter and 0.5 mm length was prepared. After that the green pellets were subsequently sintered at 1000^{0}C for 2 hours under air. The d.c. four probe electrical conductivity measurements of gold pasted pellets were performed on heating and cooling in the temperature range between room

[1]Correspondences should be addressed to A.D.B.D.Senarathna[1], Department of Physics, The Open University of Sri Lanka

temperature (25°C) and 200 °C, keeping the specimens in a specially designed sample holder.

RESULTS AND DISCUSSION

The calcined powders were subjected to phase analysis by XRD. Figure 1 shows the x-ray diffractograms obtained on these powders prepared with different G:N ratios, calcinated at 10000C. In this figure, the corresponding diffraction pattern of the Li(Ni1/3Co1/3Mn1/3)O2 base material is labeled as 333 (Samarasingha et al., 2008). Accordingly, the existence of the same R3m phase of □□-NaFeO2 layered structure of Li (Ni1/3Co1/3Mn1/3)O2 can be seen in all these materials prepared in this study with different G:N ratio.

Furthermore, as seen in Figure 1, this study shows the possibility of obtaining the appropriate $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ material even with a very low G:N ratio, such as 0.2. However, the higher G:N ratios have improved the structural behavior of the materials, by narrowing the peaks in the peak pattern as seen in Figure 1. Accordingly, the optimum G:N ratio of around 0.6 can be suggested from this study to synthesize these $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ powders by the GNC method.

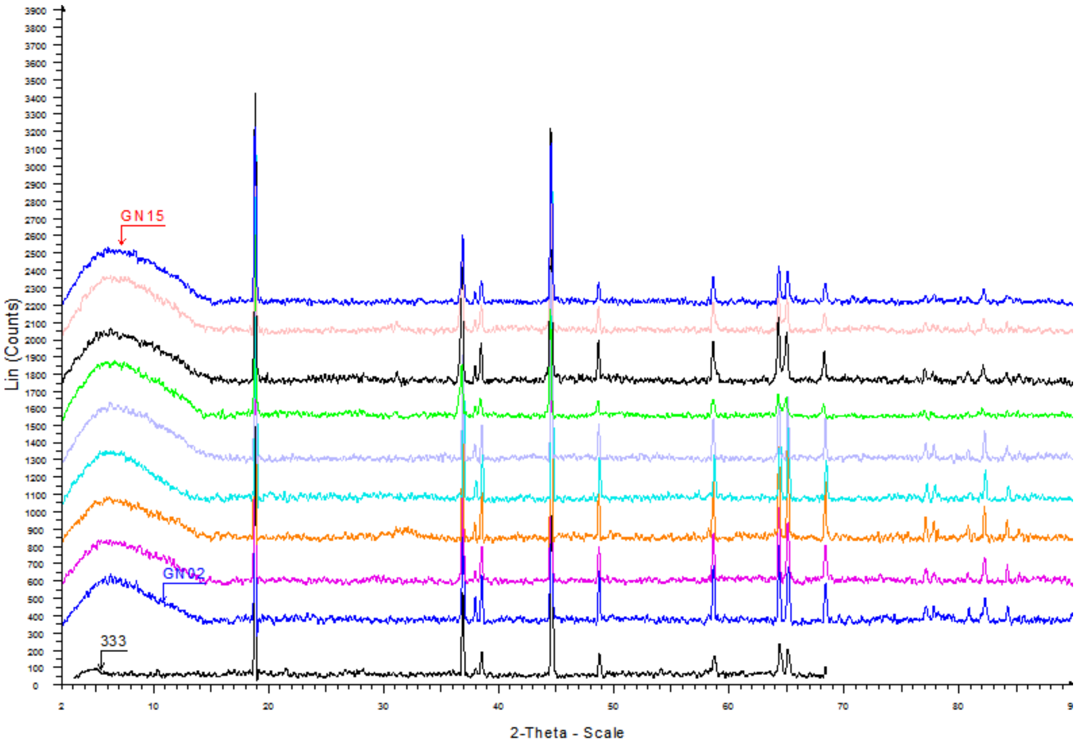

Figure 1: The X-ray diffractograms obtained on the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ materials prepared with different G:N ratios. The corresponding diffraction pattern of the Li $(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ base material is labeled as 333 (Samarasingha *et al.*, 2008).

Figure 2 shows the variation of the pellet density (both green density and sintered density) with the pressing pressure. This study was performed to find the optimum pressing pressure in order to obtained dense pellets with highest possible sintered density, hence with lowest possible porosity in the solid pellets.

As seen in the figure, the green density (density before sintering) was continuously increasing with the pressing pressure. However, the behavior of the sintered density with pressure was significantly different. With the increase of the pressing pressure, the sintered density increased to a maximum and further increase of the pressure has decreased the sintered density. Hence this indicated that an optimum pressing pressure around 250 MPa is necessary to obtain well sintered solid pellets with highest possible density.

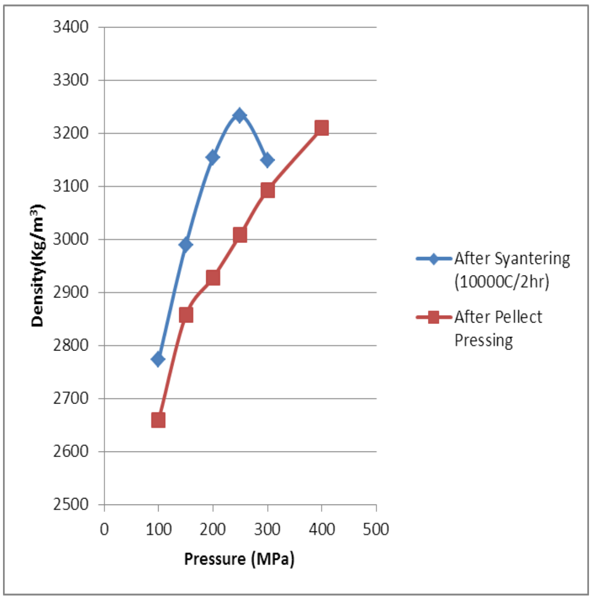

Figure 2: Variation of density with the pressure applied in uni-axial pressing of the pellets.

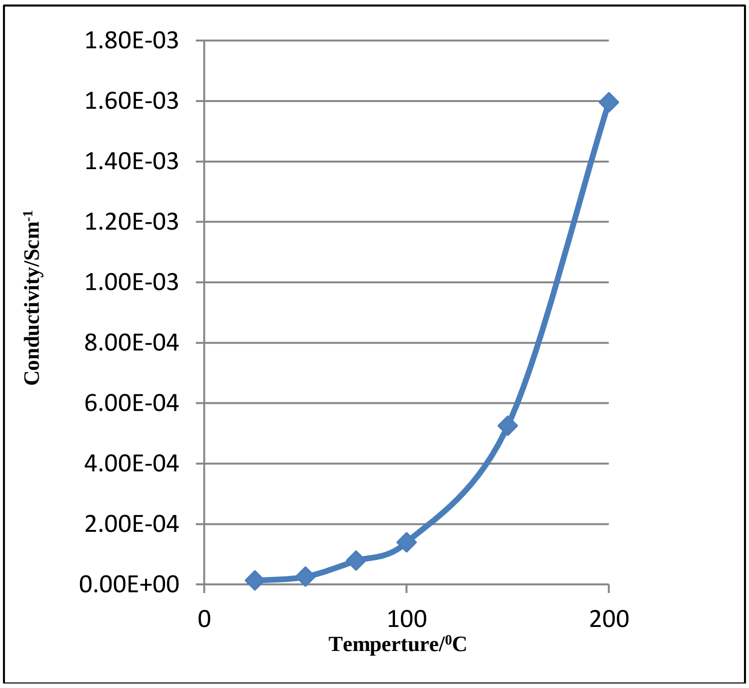

Figure 3: The variation of the DC electrical conductivity of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ material with temperature.

As seen in Figure 3, the measured electrical conductivity of these materials increased exponentially with measuring temperature, indicating semicondutor behaviour in these materials. The measured electrical conductivity of the material prepared with G:N = 0.5

shows a room temperature (25 ^{0}C) electrical conductivity of 1.25 x 10^{-5} S/cm, indicating a sufficient electrical conductivity for the intended application in LIB cathode.

Accordingly, this study reveals the possibility of synthesizing these materials by the glycine nitrate combustion technique with appropriate phase purity and electrical conductivity for the cathode application in the lithium ion rechargeable batteries.

CONCLUSIONS

The XRD phase analysis on the Li $(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ materials prepared by the glycine nitrate combustion technique revealed the formation of only the appropriate layered R3*m* structure in all the prepared materials with different G:N ratios from 0.2 to 1.5. Higher G:N ratios can improve the structural behavior of the materials to an optimum ratio of 0.6.

According to this study, the optimum pressing pressure is 250MPa to obtain a dense solid material with the highest density. Further, the material prepared with G:N= 0.5 showed a considerable electrical conductivity of 1.25 x 10^{-5} S/cm at room temperature (25 ^{0}C) .

In conclusion, this study shows the possibility of preparing Li(Ni1/3Co1/3Mn1/3)O2 materials by the glycine nitrate combustion technique with phase purity and electrical conductivity required for the cathodes of the rechargeable Li-ion batteries.

REFERENCES

Samarasingha, P., Tran-Nguyen, D., Behm, M., and Wijayasinghe, A. (2008). $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ synthesized by the pechini method for the positive electrode in Li-ion batteries: Material characteristics and electrochemical behavior electrochemical Acta, 53: 7995-8000.

Whittingham, S. (2004). Lithium Batteries and Cathode Materials. Chemical Review 104: 4271- 430.

Wijayasinghe, A.(2004). Development and Characterisation of Cathode Materials for the Molten Carbon Fuel Cell. Doctoral Thesis, Department of Material Science and Engineering, Royal Institute of Technology, Stockholm, Sweden.ISBN91-7283-746-2.

Xu,B., Qian D., Wang, Z., and Meng Y.S., (2012). Recent progress in cathode materials research for advanced lithium ion batteries. Materials Science and Engineering. 73: 51-65

ACKNOWLEDGMENTS

Mr. W. G. Jayasekara of the Institute of Fundamental Studies, Sri Lanka and Mr. Pushpaka Samarasinghe of the Department of Chemistry, University of Oslo, Norway.
.