SYNTHESIS AND ELECTRICAL CHARACTERIZATION OF Li ($Ni_{1/3}Co_{1/3-x}Mn_{1/3}M_x$)$O_2$, (M=Fe, Al, Mg, Cu and X=0.04, 0.08) FOR THE CATHODE OF LI-ION RECHARGEABLE BATTERIES

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INTRODUCTION

Energy can be stored in many forms, among which batteries are the most versatile energy storing method to be used in almost all portable devices, where a power source is required. When we consider popular rechargeable batteries, the Li-ion battery (LIB) has twice the specific energy compared to Ni metal hydride battery and four times that of Ni-Cd battery.
In searching for alternative cathode materials to replace the costly $LiCoO_2$in LIB, the layer structured NMC compositions, which contains the transition metal elements of Ni, Mn and Co, such as Li ($Ni_yCo_{1-2y}Mn_y$)O_2 system has extensively been studied. Li($Ni_{1/3}Co_{1/3}Mn_{1/3}$)$O_2$is an important member of this system (Whittingham, 2004).The electrochemical performances and safety of these materials are analogous or even superior to that of $LiCoO_2$(Xu, 2012).

Further development of this Li ($Ni_{1/3}Co_{1/3}Mn_{1/3}$)O_2system by substituting Co by other cheaper metal oxides, Li($Ni_{1/3}Co_{1/3x}Mn_{1/3}M_x$)$O_2$, (M=Fe, Al, Mg, Cu and x = 0.11, 0.22, 0.33),has recently been investigated by this group (Samarasingha, 2013). The outcome of it indicated the importance of studying the lower level substitutions ($x < 0.11$). Therefore this work was based on investigations of ($Ni_{1/3}Co_{1/3x}Mn_{1/3}M_x$)$O_2$(M=Fe,Al,Mg,Cu and x= 0.04 and 0.08) synthesized by the Pechini method. This is a low cost synthesis technique but can result in powders with high purity, homogeneity and particle morphology (Wijayasinghe, 2006) that are greatly preferred for the rechargeable Li-ion battery cathodes.

METHODOLOGY

Li($Ni_{1/3}Co_{1/3x}Mn_{1/3}M_x$)$O_2$, (M=Fe,Al,Mg,Cu and x= 0.04 and 0.08) powders were synthesized using Pechini method. In this, stoichiometric amount of metal Nitrates, $LiNO_3$, $Ni(NO_3)_2.6H_2O$,$Co(NO_3)_2.6H_2O$,$Mn(NO_3)_2.4H_2O$,$Fe(NO_3)_3.9H_2O$,$Al(NO_3)_2.9H_2O$,$Mg(NO_3)_2$. $6H_2O$,$Cu(NO_3)_2.3H_2O$ of analysis grade were used as starting materials with the organic precursor solutions of citric acid (CA) and ethylene glycol (EG). Powders were prepared with the EG/CA ratio of 4:1, because the previous studies have proved that optimal gelling condition occur at this ratio (Samarasinghaet*al.*,2008*)*.The mixture of nitrates, citric acid, and ethylene glycol was stirred for 20 hours and then heated while being stirred (Samarasingha *et al, 2013)*.The resultant powders were calcined at 900 °C inair in a box furnace. The phase analysis was carried out with X-ray diffractometry (XRD, Siemens D5000 using monochromatic Cu Kα radiation). The calcined powders were pressed in to green pellets of 12 mm in diameter, followed by sintering at 1000 °C in a box furnace in static air. The d.c. electrical conductivity measurements were performed on gold pasted sintered pellets, on heating and cooling in the temperature range between room temperature (25°C) and 200°C.

RESULTS AND DISCUSSION

The calcined powders were subjected to XRD phase analysis and Figure1 shows the X-ray diffractograms obtained on these powders calcinated at 1000^0C for four hours. As seen in the figure, all these materials show the peak pattern corresponding to the α–$NaFeO_2$ layered

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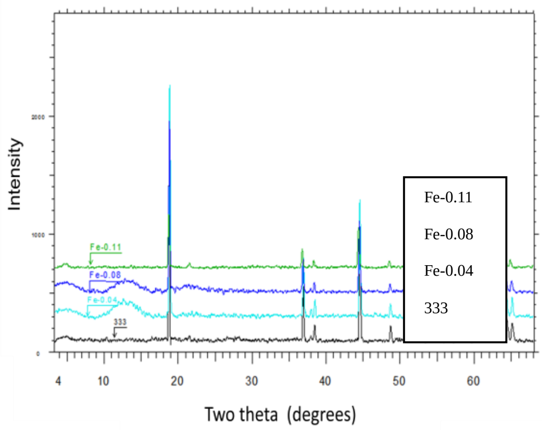
structure of R3*m* phase, indicating the formation of the appropriate $Li(Ni_{1/3}Co_{(1/3x)}Mn_{1/3}M_x)O_2$(M=Fe,Al,Mg,Cu) in all the materials investigated in this study.



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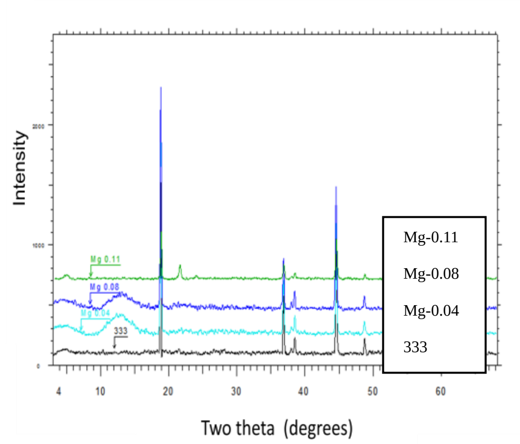

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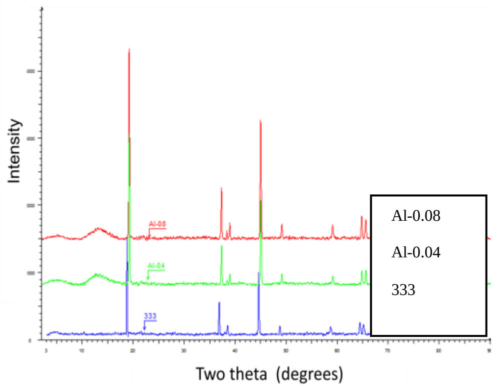

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Figure 1: The X-ray diffratograms obtained on prepared Li ($Ni_{1/3}Co_{(1/3-x)}Mn_{1/3}M_x)O_2$ materials (a). Fe substituted materials (b). Al substituted materials (c). Mg substituted materials

Figure 2 shows the variation of the measured electrical conductivity with the temperature. As seen in the figure, the electrical conductivity of these materials increased exponentially with measured temperature, therefore, indicating a semiconductor behavior for these materials. Table 01 shows the corresponding room temperature (25 °C) electrical conductivity varies with the composition of the prepared materials

All of these materials (except 0.04 mole% of Mg substituted material) show comparable or even better electrical conductivity than that of the base material (Pushpaka Samarasingha *et al., 2013)*.Further, the Cu substituted materials, Li ($Ni_{1/3}Co_{1/3-x}Mn_{1/3}Cu_x$) O2(X=0.04, 0.08) show a significantly increased conductivity. As a whole, this study reveals the possibility of synthesizing these materials by Pechini method with appropriate phase purity and considerable electrical conductivity for the LIB cathode application.

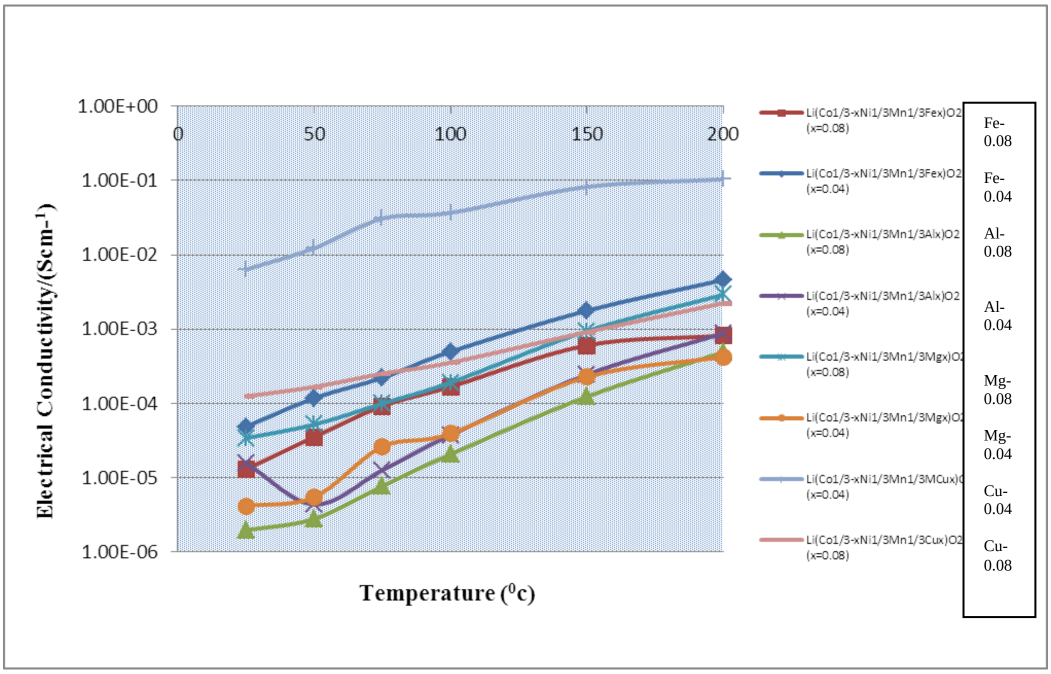

Figure 2: Variation of the d. c. electrical conductivity of synthesized powders with temperature.

Table 1: The d.c. electrical conductivity of synthesized powders at room temperature (25 °C)

Composition of synthesized powders	**X (mole %)**	**DC electrical conductivity(S/cm) at room temperature (25^{0}C)**
Li ($Ni_{1/3}Co_{(1/3-x)}Mn_{1/3}$)$O_2$ (The base material)	0.00	7.85 x 10^{-05}
Li ($Ni_{1/3}Co_{(1/3-x)}Mn_{1/3}Fe_x$)$O_2$	0.08	1.31 x 10^{-05}
	0.04	4.88 x 10^{-05}
Li ($Ni_{1/3}Co_{(1/3-x)}Mn_{1/3}Al_x$)$O_2$	0.08	1.98 x 10^{-06}
	0.04	1.58 x 10^{-05}
Li ($Ni_{1/3}Co_{(1/3-x)}Mn_{1/3}Mg_x$)$O_2$	0.08	3.43 x 10^{-05}
	0.04	4.20 x 10^{-06}
Li ($Ni_{1/3}Co_{(1/3-x)}Mn_{1/3}Cu_x$)$O_2$	0.08	1.26 x 10^{-04}
	0.04	6.36 x 10^{-03}

CONCLUSIONS

The XRD phase analysis performed on Li ($Ni_{1/3}Co$ $_{(1/3-x)}$ $Mn1_{/3}M_x$) O2 (M=Fe,Al,Mg,Cu),(x=0.04,0.08) materials prepared by the Pechini method in this study, revealed the formation of only the appropriate layered R3m structure in all the synthesized and caicined at 900 ^{O}C.

The measured conductivity at 25 ^{0}C is varies according to the material composition. The Cu substituted materials show the highest electrical conductivity, which was 6.36 x 10^{-03} Scm^{-1}at room temperature. Accordingly, this study shows the possibility of synthesizing Li($Ni_{1/3}Co_{(1/3-x)}Mn_{1/3}M_x$)$O_2$ (M=Fe,Al,Mg,Cu) materials by the Pechini method with appropriate phase purity and electrical conductivity for the LIB cathode application.

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