SYNTHESIS AND ELECTRICAL CHARACTERISATION OF $Na_xCo_{(1-x)}O_2$, (x = 0.05, 0.1, 0.25, 0.5, 0.75, 0.9) and $Na_xni_{(1-x)}O_2$, (x = 0.1, 0.25, 0.5, 0.75) FOR THE CATHODE OF Na-ION RECHARGEABLE BATTERIES

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INTRODUCTION

Alternative rechargeable battery systems with transporting ions other than Li ion have attracted growing interests in recent years. Sodium is a cheap, nontoxic and abundant element that is uniformly distributed around the world and therefore would be ideal as a transporting ion for alternative rechargeable batteries.

Known for their commercial domination of the Li-ion battery market, layered oxides of the type AMO_2 (A = Li, Na; M = Co, Mn, Ni and combinations thereof) are sought after for their high intercalation potentials and energy densities. The alkali cation A is reversibly de/intercalated between the two-dimensional layers of transition metal MO_6 octahedra on electrochemical cycling (Ellis, 2012).

It is no wonder that sodium layered oxide compounds (Na_xMO_2) have drawn significant attention as cathode materials in Na-ion batteries (NIB) considering that their Li analogues have been comprehensively understood for the last two decades.

In this study, powder compositions of $Na_xCo_{(1-x)}O_2$, (x = 0.05, 0.1, 0.25, 0.5, 0.75, 0.9) and $Na_xNi_{(1-x)}O_2$, (x = 0.1, 0.25, 0.5, 0.75) were synthesized by Pechini method. This is a low cost synthesis technique but can result in powders with high purity, homogeneity and particle morphology (Wijayasinghe, 2006).

METHODOLOGY

$Na_xCo_{(1-x)}O_2$, (x = 0.05, 0.1, 0.25, 0.5, 0.75, 0.9) and $Na_xNi_{(1-x)}O_2$, (x = 0.1, 0.25, 0.5, 0.75) powder samples were synthesized using Pechini method. For this purpose, stoichiometric amount of metal Nitrates, $NaNO_3$, $Co(NO_3)_2.6H_2O$ and $Ni(NO_3)_2.6H_2O$ (BDH, England) 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 molar ratio of 4:1, because previous studies have proved that optimal gelling condition occur at this molar ratio. (Samarasinghe,*et al.,*2008).
The mixture of metal nitrates, citric acid and ethylene glycol were stirred for 24 hours and then heated while being stirred. The resultant powders were calcined at 800 ^oC for two hours in air in a box furnace.

Phase analysis of the compositions $Na_xCo_{(1-x)}O_2$ and $(Na_{0.1}Ni_{0.9})O_2$ was carried out with X-ray diffractometry and surface morphology of $Na_xCo_{(1-x)}O_2$ was investigated using scanning electron microscopy.The synthesized powders of $Na_xCo_{(1-x)}O_2$ and $Na_xNi_{(1-x)}O_2$ were uni-axially pressed at 150 MPa and the green pellets were subsequently sintered at 800 °C for two hours in static air. The electrical conductivity of these materials were determined by performing DC conductivity measurements on sintered pellets by the four-probe method. The conductivity measurements were performed in a cyclic manner on heating and cooling in air, in the temperature range 25 - 200 ^oC.

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RESULTS AND DISCUSSION

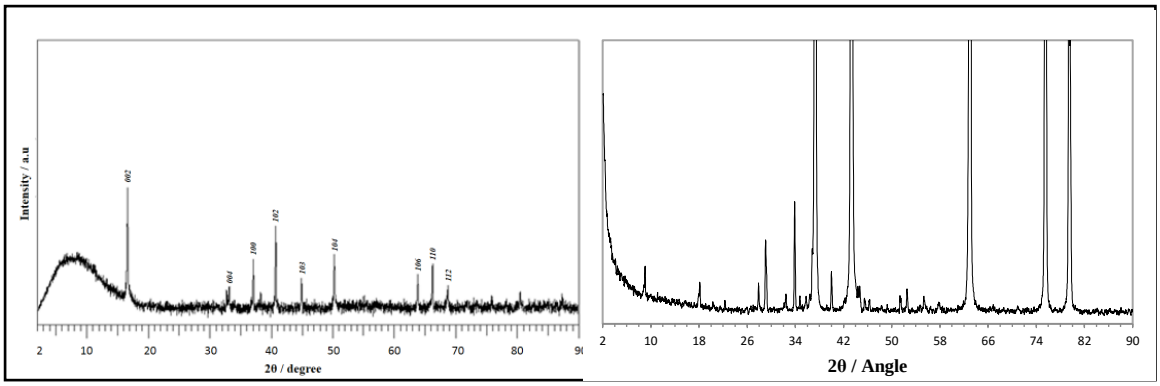

Figure 1. XRD Pattern of $(Na_{0.5}Co_{0.5})O_2$ (left) and $(Na_{0.1}Ni_{0.9})O_2$ (right)

Figure 1 (left) shows the XRD pattern of the $(Na_{0.5}Co_{0.5})O_2$ powder. The diffraction peaks at 2θ = 17.00°, 32.80°, 37.20°, 40.80°, 45.00°, 50.20°, 64.00°, 66.20°, 68.50° are in good agreement with the values reported for the required composition. These peaks could be well assigned to the reflection of crystal structure type of P2-phase with space group P63/mmc.

Figure 1 (right) shows the XRD pattern of the $(Na_{0.1}Ni_{0.9})O_2$ powder. It indicates the formation of the appropriate crystalline structure of the synthesized cathode material (De Silva, 2014*)*.

Figure 2 shows the SEM images of the powders $(Na_{0.1}Co_{0.9})O_2$ and $(Na_{0.25}Co_{0.75})O_2$. The images indicate a disordered morphology composed individual particles in the range of 0.2 - 0.5 μm with higher crystallinity. The small particles agglomerate together to form micro-sized irregular agglomerates.

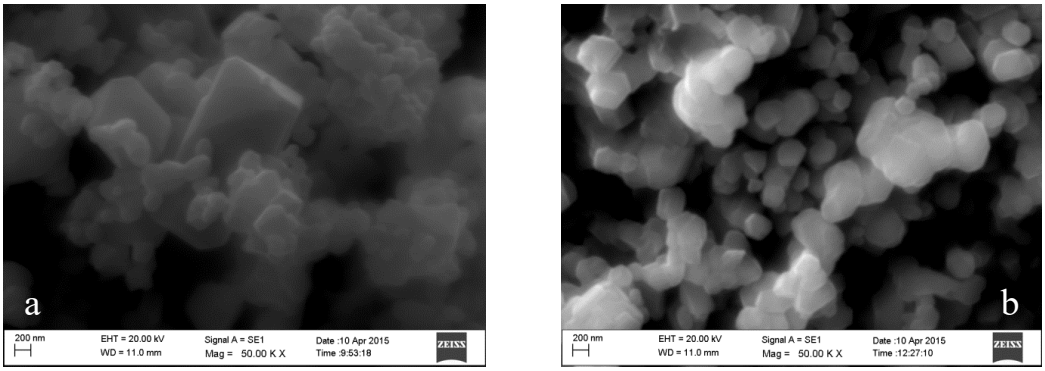

Figure 2. (a) SEM image of $(Na_{0.1}Co_{0.9})O_2$; (b) SEM image of $(Na_{0.25}Co_{0.75})O_2$.

Figure 3 shows the electrical conductivity behavior patterns observed from the prepared compositions of both Na-Co and Na-Ni systems. As seen in the figure, all these materials showed the increase of the conductivity in an exponential manner with the increase of ambient temperature. The electrical conductivity of these materials increases with increasing temperature, which is a good indication for the semiconducting nature and a prime requirement to be an electrode material. This is due to the excitation of the electrons over the band gap and occupying energy levels in conductivity band simultaneously creating holes in valence band. This process is thermally activated, so that conductivity increases with temperature.

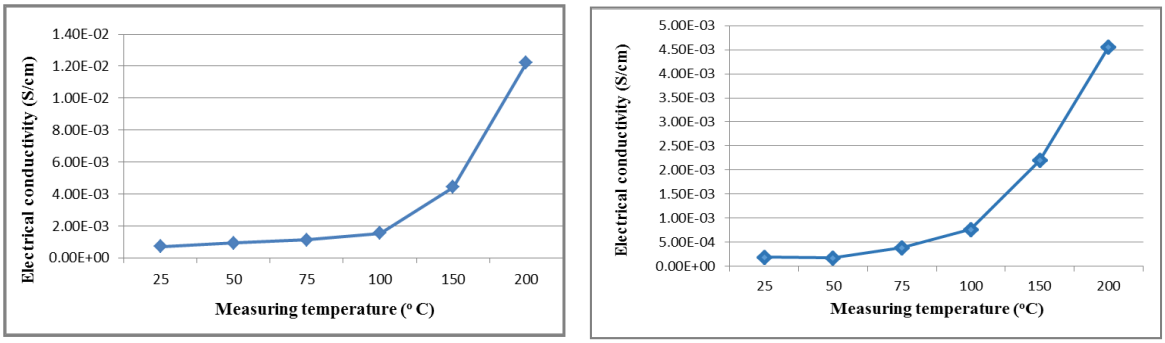

Figure 3. Variation of electrical conductivity of materials with measuring temperature, left: $Na_{0.5}Co_{0.95}O_2$ right: $Na_{0.25}Ni_{0.75}O_2$

The variation of the electrical conductivity of $Na_xCo_{1-x}O_2$ compositions is shown in the Figure 4(a). Increase of the Na content has drastically increased the conductivity and the composition with x = 0.75 has produced an electrical conductivity close to 1 S/cm at the room temperature. This is a significant achievement in electrical conductivity and this material can directly be used without any other additional conductivity enhancer, for electrode application

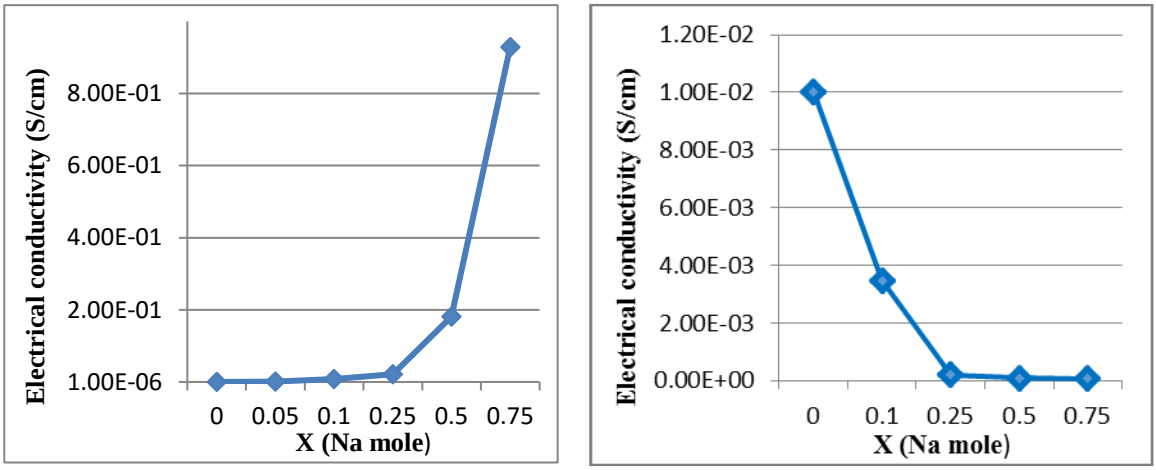

Figure 4. Variation of the electrical conductivity with composition $Na_xCo_{1-x}O_2$ (left), $Na_xNi_{1-x}O_2$ (right).

Similarly, Figure 4(b) shows the electrical conductivity behaviour of the $Na_xNi_{1-x}O_2$ compositions. The base composition NiO (with x = 0) shows an electrical conductivity of $1.0x10^{-2}$ S/cm and with each further addition of Na, it shows decrement down to $7.34x10^{-5}$ S/cm at x = 0.75. It needs further investigations especially with suitable conductive additives for enhancing electrical conductivity of these $Na_xNi_{1-x}O_2$ materials before using in cathodes for the NIB.

CONCLUSIONS

This study revealed the possibility of synthesizing $Na_xM_{1-x}O_2$, M = Co, Ni and x = 0 - 0.75 compositions by the Pechini wet chemical synthesis technique. All these prepared materials showed semiconducting behaviour. In the $Na_xCo_{1-x}O_2$ system, the electrical conductivity increased drastically to about 1 S/cm with the increase of Na content to 0.75. Among the $Na_xNi_{1-x}O_2$ system, the x = 0.1 composition showed the highest electrical conductivity of $3.47x10^{-3}$ S/cm at room temperature. In order to explain the observed effect in electrical conductivity after adding Na to these systems, these systems should be subjected to thorough electrical characterization. However, these significant achievements in electrical conductivity of this study indicate the potentiality of these $Na_xM_{1-x}O_2$, M = Co and Ni, compositions for the NIB cathode application.

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