

# UTILIZATION OF THERMALLY SYNTHESIZED $\text{NaCoO}_2$ IN CATHODES OF SODIUM-ION RECHARGEABLE BATTERIES

R.C.L. De Silva<sup>1</sup>, V.P.S. Perera<sup>1</sup> and S.R.D. Rosa<sup>2</sup>

<sup>1</sup>*Department of Physics, The Open University of Sri Lanka*

<sup>2</sup>*Department of Physics, University of Colombo*

## INTRODUCTION

It is found that 1.4 billion people live without access to electricity out of which 67% live in Asia (World Energy Issues, 2012). The storage of energy is another dimension in the energy problem. Where electrical energy storage batteries are concerned, research on lithium and sodium-ion rechargeable batteries started in the early 1980s. Comparatively the lithium ion rechargeable battery was chosen to be developed first because of its higher energy density (Kim *et al.*, 2006). The cost concern of lithium metal caused sodium metal to be looked at again for rechargeable batteries (Terasaki, 2003; Shin, et al., 2002). Research and development aspect of sodium-ion batteries are now on the move globally. At present the challenge for materials design exist in the field of sodium-ion batteries, and in the past couple of years, several reports on new sodium-ion technologies and electrode materials have emerged. They range from new layered oxides, polyanion-based materials, carbons and other insertion materials for sodium-ion batteries, many of which hold the promise for future sodium-based energy storage applications. As sodium resided lower to the Li in reactive series, the size suffers when it resides in the cathode material structure.

This study utilizes sodium cobalt oxide as the cathode material of sodium ion rechargeable batteries due to its remarkable physical and chemical properties. But in previous studies this material has been synthesized to be used in lithium ion rechargeable batteries. Therefore,  $\text{NaCoO}_2$  is synthesized, characterized and utilized in sodium ion rechargeable batteries to evaluate its characteristics and performance.

## METHODOLOGY

Polycrystalline samples of  $\text{NaCoO}_2$  were prepared by solid-state reaction where, starting materials, sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and cobalt(II) oxide ( $\text{CoO}$ ) were mixed in appropriate molar ratio (De Silva and Perera, 2013). Thermal Gravimetric (TG) analysis was carried out to find the exact range of temperature that the solid-state reaction takes place.

The mixtures were further sintered at 700 °C for 12 hours. X-ray diffraction (XRD) characterization was performed on the resulting powder with Bruker D8 Focus X-ray Diffractometer using  $\text{Cu K}_\alpha$  radiation and scanning electron micrographs (SEM) were taken to analyze the structure of the sample.

The synthesized  $\text{NaCoO}_2$  powder was then used as the cathode material in sodium-ion batteries and devices were fabricated as follows. A slurry was first made by grinding  $\text{NaCoO}_2$  85% with 5% acetylene black (AB) and 10% polyvinylidene fluoride (PVDF) as the binder dissolved in 1-methyl-2-pyrrolidinone (NMP) and cast on a stainless steel plate. Then it was allowed to slow dry at 120 °C on a hot plate. The half cell of the battery was constructed in  $\text{N}_2$  atmosphere with sodium foil as the anode. A polyester membrane was placed in between the cathode and anode as the separator that soaked with the electrolyte,

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<sup>1</sup> Correspondences should be addressed to R.C.L. De Silva, Department of Physics, The Open University of Sri Lanka (email: [chinthakades@yahoo.com](mailto:chinthakades@yahoo.com))

where the electrolyte is 1M solution of NaClO<sub>4</sub> in propylene carbonate. In charge discharge tests the cell was discharged at a rate of 0.75 mA/mg until it reached a voltage of 0.1V.

## RESULTS AND DISCUSSION

Figure 1 shows the variations of weight of the reactants, Na<sub>2</sub>CO<sub>3</sub> and CoO<sub>2</sub> with temperature in the synthesis of NaCoO<sub>2</sub>. The observation shows a dramatic loss of weight of the NaCoO<sub>2</sub> sample in-between 350 °C to 455 °C and average stability after 455 °C as the temperature increases. A slight drop of weight can also be observed at the very beginning due to removal of moisture from the reactants. The cause of the intense weight loss in between the regions of 250 °C to 450 °C reported due to dissociation of Na<sub>2</sub>CO<sub>3</sub> evolving CO<sub>2</sub>. Therefore effective formation of NaCoO<sub>2</sub> polycrystalline begins at the temperature range in-between 350 °C to 455 °C. However, the initial reaction rate seems to be low as evident from the gradient of the curve just after 350 °C which becomes steeper after 400 °C.

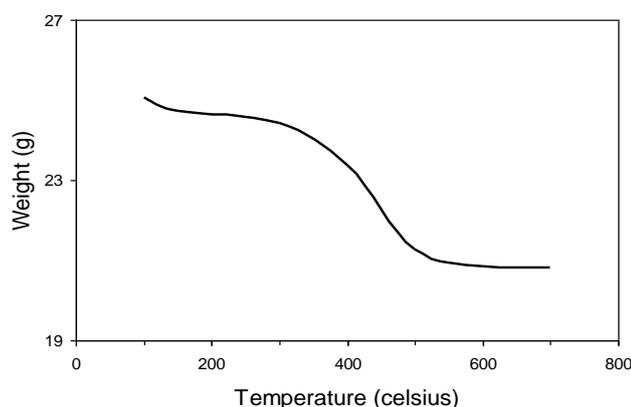


Figure 1 : Variations of weight of the reactants, Na<sub>2</sub>CO<sub>3</sub> and CoO<sub>2</sub> with temperature in the synthesis of NaCoO<sub>2</sub>

The XRD characterization assured the correct formation of the crystalline structure of the cathode material. XRD patterns of the NaCoO<sub>2</sub> sample is shown in figure 2. The amount of sodium affects the structure of the sodium cobalt oxide as observed in the final product. Comparison of the peaks of the XRD pattern of the samples with the standards, confirmed that the synthesis route leads to formation of the NaCoO<sub>2</sub> as the active material.

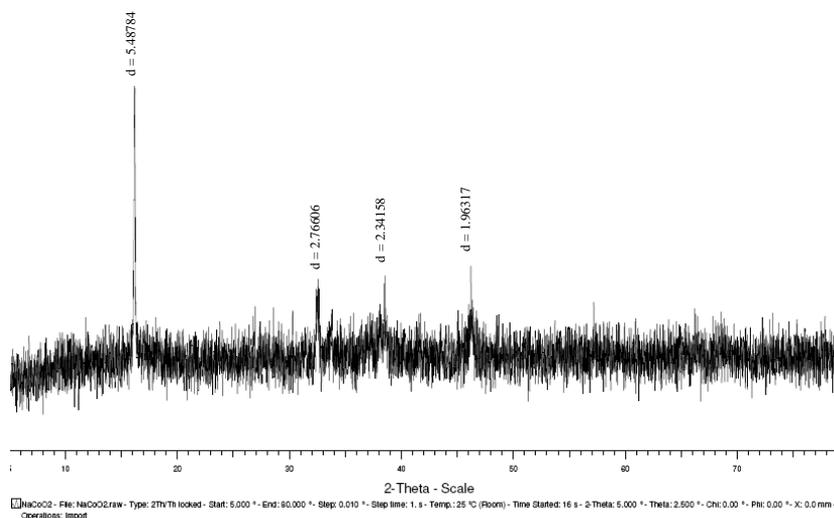


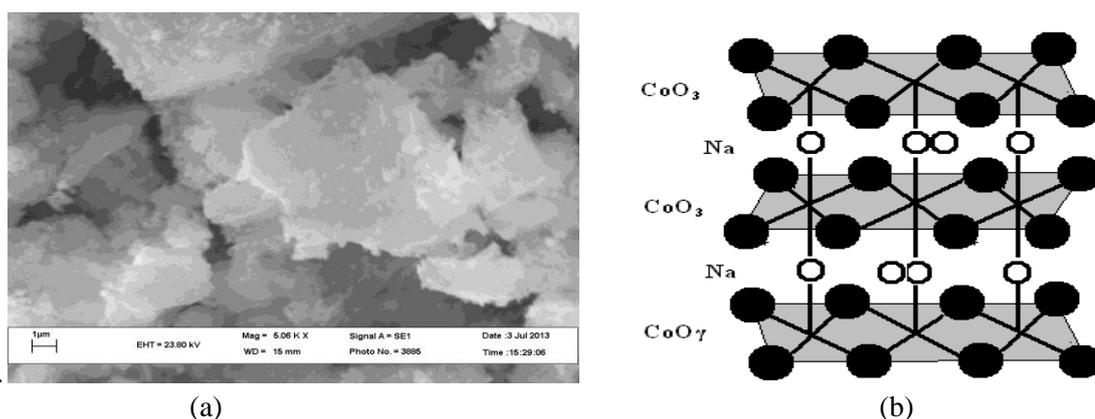
Figure 2 : XRD pattern of NaCoO<sub>2</sub>

The apparent XRD peaks of the sample observed for  $2\theta$  values at 16, 33, 38 and 46 degrees where  $h, k, l$  values obtained at the range of  $-7 < h, k < 7, -40 < l < 40$  by Yasuhiko, 2002, *et al.* matched with the standard confirming the proper synthesis of sodium cobalt oxide which is the active cathode material of the secondary sodium-ion battery. The crystal size of the sodium cobalt oxide was about 42 nm calculated using the Scherrer's equation for the peak appeared at 16 degrees in the XRD.

The lattice structure of  $\text{NaCoO}_2$  consists of two separated  $\text{CoO}_2$  layers per unit cell and sodium layer located in between them as shown in figure 3.b (Takada *et al.*, 2003). This structure strongly depends on the sodium content and is not well defined. Each cobalt oxide layer forms an edge-sharing  $\text{CoO}_6$  octahedral network.

This crystalline structure is similar to that of high- $T_c$  cuprate superconductors, except that in each layer Co atoms form a triangular (hexagonal) lattice rather than a square lattice. In a crystal having sodium content of  $x = 0.7$  the lattice constants (distances between ions) are equal to  $a = 2.75 \text{ \AA}$  and  $c = 10.85 \text{ \AA}$  (Takada *et al.*, 2003).

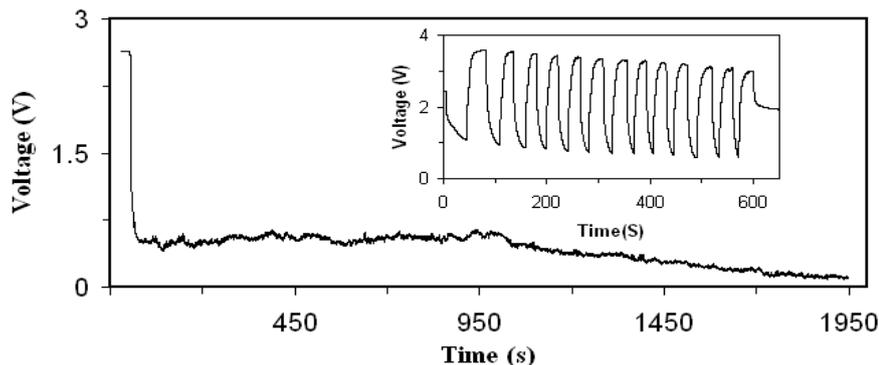
Physical properties of the substance in the context of particle size, crystal arrangement and shape could further be seen by a scanning electron micrograph of the sample (figure 3a). The result thus clearly indicates the difficulty of obtaining  $\text{NaCoO}_2$  in nanometer scale with desired morphologies under the traditional high temperature solid-state process (Kumar Rai, et al., 2013). The porous structure of the film enables the insertion of sodium ions in charge discharge process.



**Figure 3** (a) Scanning electron microscopic (SEM) image of  $\text{NaCoO}_2$  sample (b) Schematic view of  $\text{NaCoO}_2$  structure.

The charge/discharge is another cyclic method to study the capacity of a rechargeable battery. By this method the amount of charge which could be retained with time could be calculated. The cell was discharged at a rate of 0.75 mA/mg until it was reached to a voltage of 0.1V. The retained capacity value was then calculated to be 40 mAh/g.

The insert in figure 4 demonstrated more than ten charge/discharge cycles which kept until it reach the fluttering level at each cycle and the stability was monitored. The cell reported a voltage of 2.6 V initially and at no-load level again it reached a value just more than 2.3 V after undergoing eleven charge discharge cycles. These patterns confirmed the stability of the cells developed in this study.



**Figure 4:** First discharge in the cell made of NaCoO<sub>2</sub>. Insertion is for ten charge discharge cycles of the same cell.

## CONCLUSION

Revealing the best charge retention of NaCoO<sub>2</sub> cathode material from our earlier studies, the effective range of temperature for solid state reaction was observed in between 350 °C to 455°C. The Hexagonal structure of porous crystalline was justified by characterization with XRD and SEM. The capacity of the cell tested with charge-discharge cycles found to be 40 mAh/g. Considering all these facts it can be recommended that NaCoO<sub>2</sub> is a potential cathode material for the secondary sodium-ion battery.

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