Synthesis and characterization of sodium cobalt oxide nanostructures for sodium-ion batteries

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Abstract

The secondary lithium-ion battery has been widely used in various kinds of personal digital accessories, and is expected to be further spread into larger-sized applications such as power sources of hybrid automobiles. While cathode materials for secondary lithium-ion battery have been so far made mostly from lithium cobalt oxide, the development of substitute materials is essential because of the depletion and increasing prices of lithium and cobalt resources.

The sodium-ion secondary battery is an alternative for the lithium ion rechargeable battery that made utilizing mostly abundant sodium which has high electrochemical potential after the lithium. Therefore, in this study we have synthesized sodium cobalt oxide by the solid state reaction of cobalt carbonate and sodium carbonate at 700 °C. The product was characterized by an X-ray diffraction (XRD) technique.

The preliminary studies showed the cell has discharge capacity of $40 mAhg^{-1}$ discharging at current rate of 75mAhg (World Energy Issues Monitor, 2012). Further studies are needed to test for long cycle life and other battery performance requirements.

Keywords: *Rechargeable Batteries, Sodium Cobalt Oxide, Cathode Material.*

Introduction

Declining global energy resources have drawn the attention of the world to find new avenues of meeting the future energy demand. It is not only to cater to the current consumers of energy but also to the category of underprivileged to access their domestic needs of energy. It is found that 1.4 billion people live without access to electricity out of which 67% of them live in Asia[1]. The storage of energy is another dimension that should be looked into, parallel with its generation because energy from renewable sources such as hydropower, solar and wind are not sometimes available at the time of demand.

In order to develop new electrochemical power sources, world research efforts have been focused on rechargeable batteries. Research on lithium and sodium ion rechargeable batteries was started in the early years of the 1980s. Comparatively, the lithium ion rechargeable battery was chosen to be developed first because of its higher energy densities (Kim et al, 2006).

Because of the limitation imposed by the high cost of lithium metal, sodium has been promoted as a substitute for rechargeable batteries (Terasaki, 2003, Shin et al, 2002). The abundant sodium resource is easily accessible compared to lithium. Currently, a growing trend of sodium replacement in lithium ion rechargeable batteries has emerged and intense research work has already been initiated.

The present study involves the utilization of sodium cobalt oxide as the cathode material of sodium ion rechargeable batteries due to its remarkable physical and chemical properties. Na_xCoO_2 is synthesized, characterized and utilized in sodium ion rechargeable batteries to evaluate its performance.

Methodology

Polycrystalline samples of Na_xCoO_2 were prepared by a solid-state reaction where, starting materials, sodium carbonate (Na_2CO_3) and cobalt(II) oxide (CoO) were mixed in a molar at the ratio of Na to Co,x= 0.2, 0.3, 0.5, 0.7,1. Then the mixtures were sintered at 750 ^oC for 12 hours repeatedly, after grinding at the end of each sintering, until a blackish homogeneous powder was obtained.

X-ray diffraction (XRD) characterization was performed on the resulting powder with Brucker D8 Focus X-ray Diffractometer using Cu K_α radiation to analyze the structure of the sample. Crystallographic information was obtained with the aid of the ICDD database.

The developed Na_xCoO_2 were then used as the cathode material in sodium-ion batteries using the following fabrication process. A slurry was first made by grinding

1 World Energy Issues Monitor (2012). World Energy Council 2012 Report, p. 8.

Na_xCoO_2 85% with 5% acetylene black (AB) and 10% polyvinylidene fluoride (PVdF) dissolved in 1-methyl-2-pyrrolidinone (NMP) as the binder and casted on a stainless steel plate and then allowed for slow drying at 120 ^{0}C.

The half cell construction of the battery was performed in the Na_2 atmosphere with sodium foil as the anode Polyester membrane placed as the separator was soaked with the electrolyte where the electrolyte was a 1M solution of $NaClO_4$ in propylene carbonate. Charge discharge tests were performed to discover the charge retention of the rechargeable cell.

Results and Discussion

The samples corresponding to different molar ratios of Na_xCoO_2 where, x = 0.2, 0.3, 0.5, 0.7, 1.0 were scrutinized by charging/discharging tests. The charging and discharging of the Na/electrolyte/Na_xCoO_2 cell was carried out at a rate of 100 mA/g. The open circuit voltage of the cell was about 2.5 V and discharging of the cell was done until the cell voltage dropped down to 0.5 V.

Figure 01: Charge capacity on Sodium combinations to Cobolt synthesis-Na_xCoO2

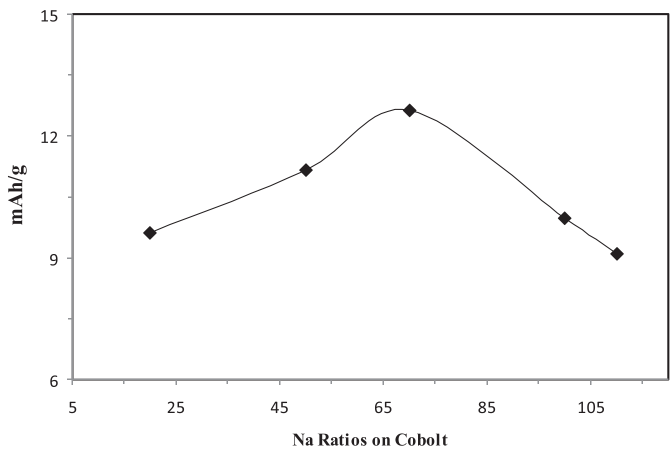


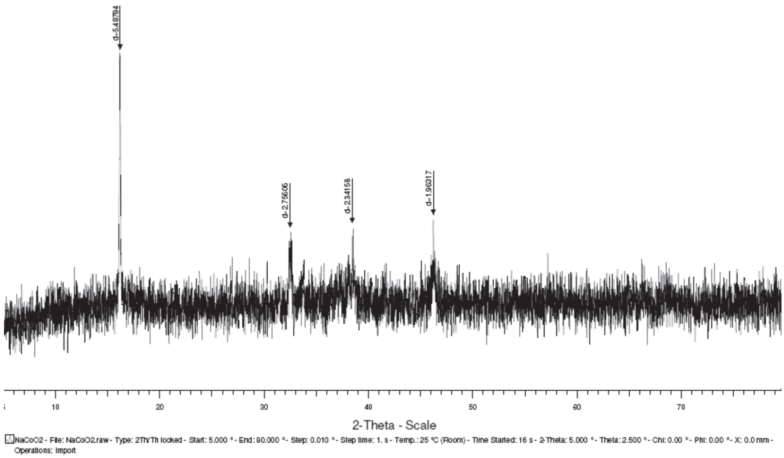
Figure 1 shows the dependence of the capacity of the cell on different Na and Co molar ratios. Initial introduction of sodium in the cobalt(II) oxide has made the capacity increase slightly, followed by a gradual decrease after reaching the maximum point as the cathode material occupy sodium higher than x= 0.7 mole fraction.

This study was aimed at selecting the maximum capacity retention sodium molar ratio for which further tests were conducted with the intention of studying the best composition of cathode material at the cell usage.

The XRD tests were performed for the cathode material to monitor the formation of the crystalline structure. XRD patterns of the Na_xCoO_2 sample for x =1.0 is shown in

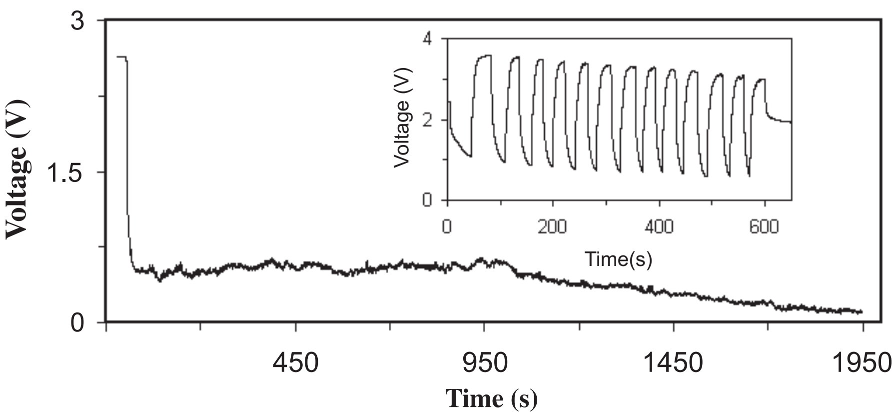
Figure 2. The amount of sodium affects the structure of the sodium cobalt oxide, as is observed in the final product when *x* =1. Comparison of the peaks of the XRD pattern of the samples with the standards, confirms that the synthesis root leads to the formation of $NaCoO_2$ at x = 0.1.

Figure 02: XRD pattern of Na_xCoO_2 for x = 1.0.



The apparent XRD peaks of the sample observed for 2θ values of XRD at 16, 33, 38 and 46 degrees matches 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 Scherrer's equation for the peak appearing at 16 degrees in the XRD.

Figure 03: First discharge in the cell made of Na_xCoO_2(x=0.7). Insertion is for ten charge discharge cycles of the same cell.



The charge / discharge is another cycling method to study the retention capacity of charges in a rechargeable battery. By this method the amount of charge which could be retained with time could be calculated.The cathode of the cell that was used is Na_xCoO_2(x=0.7), and this was discharged at a rate of 0.75mA until it reached a voltage of 0.1V. The retained capacity value was then calculated to be 40 mAh/g.

The inset in Figure 3 demonstrates more than ten charge / discharge cycles which continued until it reached faltering levels of 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 establish the stability of the cell developed in this study.

Conclusion

Highlighting the potential of the sodium ion battries comparable to the lithium ion battries, the suitability of a cathode material was tested with the introduction of sodium to cobalt(II) oxide with certain selected sodium ratios. The highest charge retention was obtained for cells of Na_xCoO_2 with the ratio $x = 0.7$. Further tests on the same cell were done and the XRD diffraction technique was used to conform the structure. By Scherrer's equation, the average particle size of materials was calculated to be the average size of ~ 42 nm. The number of charge / discharge cycles confirmed the potential stability of these cells.

References

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