Effect of Different Stoichiometry on the Electrochemical Behaviour of LiCo_{x}Ni_{1-x}O_{2} Cathode Materials

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Abstract. Pure, single phase, layered LiCo_{x}Ni_{1-x}O_{2} materials with good cation ordering are not easy to synthesize. Here, solid solutions of LiCo_{x}Ni_{1-x}O_{2} (x = 0.1, 0.2 and 0.3) were synthesized using a self-propagating combustion route and characterized. All the materials were observed to be phase pure and that cobalt has been successfully substituted in the crystal lattice. Their electrochemical properties were investigated by a series of charge-discharge cycling in the voltage range of 3.0 to 4.3 V. It was found that some of the stoichiometries exhibit specific capacities comparable or better than that of LiCoO_{2}.

1. Introduction
Many research groups have investigated various cathode materials with layered and spinel structure. Layered materials from lithium transition metal oxides possess high theoretical specific capacities compared to that of the spinels. LiCoO_{2} and LiNiO_{2} are two layered materials that have potential application as cathode materials for Li-ion batteries. LiCoO_{2} is a common commercial cathode material that has a high operating voltage and stable in structure but less environmentally benign and expensive production cost, that leads to the search for materials with less cobalt [1].

LiNiO_{2} has the advantage of being cheaper, but it is more difficult to synthesize due to ionic radius of Li^{+} (0.76 Å) is quite similar with Ni^{2+} (0.69 Å) [2]. Therefore, cation mixing between these two ions is more likely especially in the high content of nickel [3].

The weaknesses of LiCoO_{2} and LiNiO_{2} were overcome by incorporating LiCoO_{2} and LiNiO_{2} phases into LiCo_{x}Ni_{1-x}O_{2} compositions. This is because the presence of cobalt will be stabilizes the structure, thus favouring good reversibility of the intercalation and deintercalation reactions [4]. In this studies, three materials of LiCo_{x}Ni_{1-x}O_{2} (x = 0.1, 0.2 and 0.3) was prepared by a self-propagating combustion method.

2. Experimental
The LiCo_{x}Ni_{1-x}O_{2} (x = 0.1, 0.2 and 0.3) materials were synthesized using self-propagating combustion method. The annealed samples were then studied by X-Ray diffraction (Pan Analytical X’Pert Pro System) using Cu Kα radiation to identify the crystalline phases and purity of the materials. The
morphology and particle size of the samples were examined by Field Emission Scanning Electron Microscope (JEOL JSM-7600F).

The cathode was prepared using 80 wt% active material, 10 wt% binder and 10 wt% graphite. The electrolyte was 1.0 M LiPF₆ in 1:1 volume ratio of ethylene carbonate (EC) and dimethylcarbonate (DMC). Celgard 2400 microporous polyethylene film was used as the separator and the anode was lithium metal. The cells were assembled in an Ar-filled glove box (Unilab Mbraun).

The cells were cycled using a constant current of 1 mA at a voltage range between 3.0 and 4.3 V. The charge-discharge performance of the cell was characterized using a battery tester, the Wonatech (WBCS 3000) electrochemical testing equipment.

3. Results and discussions

The XRD patterns for LiCoₓNi₁₋ₓO₂ (x = 0.1 - 0.3) compounds are shown in Figure 1. Phase pure LiCoₓNi₁₋ₓO₂ (x = 0.1 - 0.3) were obtained with no impurity peaks detected in the XRD patterns. This means that the Ni⁺ ions have been successfully substituted in the LiCoO₂ structure. It can be clearly observed that all of the fingerprint peaks viz. (003), (101), (006), (012), (104), (018) and (110) are easily identifiable in all of the XRD patterns. All the diffraction peaks can be indexed with α –NaFeO₂ type structure based on the hexagonal crystal system (R-3m space group). They are isostructural with LiNiO₂ and LiCoO₂ phases as compared with the XRD patterns in the ICDD database. The XRD patterns clearly show that the materials were single phase and the sharp peaks in the spectra indicated a high degree of crystallinity of the materials.

![Figure 1. XRD patterns of (a) LiCo₀.₉Ni₀.₁O₂ (b) LiCo₀.₈Ni₀.₂O₂ (c) LiCo₀.₇Ni₀.₃O₂ cathode materials and enlargement of the XRD patterns at 30° and 50° for (d) LiCo₀.₉Ni₀.₁O₂ (e) LiCo₀.₈Ni₀.₂O₂ and (f) LiCo₀.₇Ni₀.₃O₂](image)

The SEM images of LiCoₓNi₁₋ₓO₂ (x = 0.1 - 0.3) are displayed in Figure 2. The images showed that all samples were well-formed polycrystalline materials. The LiCo₀.₉Ni₀.₁O₂ crystal size seemed larger than the LiCo₀.₈Ni₀.₂O₂ and LiCo₀.₇Ni₀.₃O₂ materials. It was also observed that as nickel content in the samples increased, the crystal size seemed to decrease. All the materials had mostly rounded
polyhedral type crystals. LiCo_{0.9}Ni_{0.1}O_{2} had crystallite size of about 50 – 300 nm which were bigger than those of LiCo_{0.8}Ni_{0.2}O_{2} and LiCo_{0.9}Ni_{0.1}O_{2} that had crystallite size of about 50 - 200 nm and 50 – 100 nm respectively. Some of the crystals seemed to aggregate slightly into larger particles.

Figure 2. SEM image of (a) LiCo_{0.9}Ni_{0.1}O_{2} (b) LiCo_{0.8}Ni_{0.2}O_{2} (c) LiCo_{0.7}Ni_{0.3}O_{2} cathode materials with magnification of 50000x

The 1st cycle charge-discharge curves of the materials are shown in Figure 3. Figure 4 shows the specific capacities of the cells up to 30 cycles.

Figure 3. Initial specific discharge capacities of (a) LiCo_{0.9}Ni_{0.1}O_{2} (b) LiCo_{0.8}Ni_{0.2}O_{2} (c) LiCo_{0.7}Ni_{0.3}O_{2} cathode materials
Figure 4. Cycling data of (a) LiCo$_{0.9}$Ni$_{0.1}$O$_2$ (b) LiCo$_{0.8}$Ni$_{0.2}$O$_2$ (c) LiCo$_{0.7}$Ni$_{0.3}$O$_2$ cathode materials

The electrochemical behavior of LiCo$_{x}$Ni$_{1-x}$O$_2$ ($x = 0.1 - 0.3$) was summarized in Table 1.

| Material          | 1st discharge capacity (mAh/g) | 30th discharge capacity (mAh/g) | Capacity loss after 30th cycles (%) |
|-------------------|---------------------------------|---------------------------------|-------------------------------------|
| LiCo$_{0.9}$Ni$_{0.1}$O$_2$ | 122                             | 48                              | 60.65                               |
| LiCo$_{0.8}$Ni$_{0.2}$O$_2$ | 140                             | 138                             | 1.43                                |
| LiCo$_{0.7}$Ni$_{0.3}$O$_2$ | 145                             | 141                             | 2.76                                |

The material LiCo$_{0.7}$Ni$_{0.3}$O$_2$ has the best specific capacity of 145 mAh/g in the first cycle. It shows the highest initial discharge capacity compared to LiCo$_{0.8}$Ni$_{0.2}$O$_2$ and LiCo$_{0.9}$Ni$_{0.1}$O$_2$ with the capacity of 140 mAh/g and 122 mAh/g respectively. It also noted that LiCo$_{0.8}$Ni$_{0.2}$O$_2$ and LiCo$_{0.7}$Ni$_{0.3}$O$_2$ materials shows very good performance over 30 cycles with a capacity fade of only 1.43% and 2.76% which can be explained that these materials have potential in application as a cathode material for lithium-ion batteries. The discharge capacities of all the materials seem to converge at about the same value at the 30th cycle even though LiCo$_{0.7}$Ni$_{0.3}$O$_2$ has better initial capacities. LiCo$_{0.7}$Ni$_{0.3}$O$_2$ shows better performance due to the smaller crystallite size. This is because small crystallite size provides high surface area to volume ratio resulting in produce good electrochemical performance [5].

4. Conclusion
Nickel substitution in LiCoO$_2$ synthesized using the self propagating combustion method has been successfully done in LiCo$_{x}$Ni$_{1-x}$O$_2$ ($x = 0.1, 0.2, \text{and} 0.3$). LiCo$_{0.7}$Ni$_{0.3}$O$_2$ material, annealed at 700 °C for 48 h, showed good promise for application in Li-ion batteries exhibiting an initial discharge capacity of 145 mAh/g. Different stoichiometry of the nickel substitution in LiCoO$_2$ effect the electrochemical behaviour of the cathode materials.

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