Properties of LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2 as a high energy cathode material for lithium-ion batteries

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Abstract—Nickel-rich layered materials are prospective cathode materials for use in lithium-ion batteries due to their higher capacity and lower cost relative to LiCoO_2. In this work, spherical Ni_{x}Co_{y}Mn_{1−x−y}(OH)_2 precursors are successfully synthesized through a co-precipitation method. The synthetic conditions of the precursors - including the pH, stirring speed, molar ratio of NH_4OH to transition metals, and reaction temperature - are investigated in detail, and their variations have significant effects on the morphology, microstructure, and tap-density of the prepared Ni_{x}Co_{y}Mn_{1−x−y}(OH)_2 precursors. LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2 is then prepared from these precursors through a reaction with 5% excess LiOH·H_2O at various temperatures. The crystal structure, morphology, and electrochemical properties of the Ni_{x}Co_{y}Mn_{1−x−y}(OH)_2 precursors and LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2 were investigated. In the voltage range from 3.0 to 4.3 V, LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2 exhibits an initial discharge capacity of 193.0 mAh g$^{-1}$ at a 0.1 C-rate. The cathode delivers an initial capacity of 170.4 mAh g$^{-1}$ at a 1 C-rate, and it retains 90.4% of its capacity after 100 cycles.

Keywords: Lithium-ion Battery, Cathode Material, LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2, Co-precipitation, Electrochemical Properties

INTRODUCTION

Lithium-ion batteries are promising power supplies for use in electric vehicles due to their high energy density and long cycling life relative to other secondary batteries [1-5], and layered lithium transition metal oxides are by far the most extensively used cathode materials for lithium ion batteries [6-8]. However, these suffer from several shortcomings, including a poor structural stability, an inability to extract all lithium ions and the high cost and toxicity of cobalt [9-11]. Therefore it is important to develop alternative cathode materials in order to obtain a higher capacity, improved safety and lower cost. LiNiO_2 is one of the most attractive candidate materials that has been suggested so far to meet these requirements because it has been shown to attain a higher reversible capacity with its lower cost, reduced toxicity, improved thermal stability, and good cycling stability and safety [12]. However, LiNiO_2 suffers from an intrinsic poor thermal stability at a fully charged state with a poor cycling performance because a part of Mn does not change its valence state during charge and discharge cycles [14,16,17]. Various methods have been applied in the synthesis of Ni-rich layered cathode materials, including solid state [18], sol-gel [19-22], chloride co-precipitation [23], carbonate co-precipitation [19,24] and hydroxide co-precipitation [15,25-30] methods. A comparison of these synthesis methods shows that the co-precipitation method has many advantages in that it provides a homogeneous precursor with high tap-density, a uniform distribution for the Ni, Co, and Mn atoms, a controllable morphology, improved electrochemical properties and favorable process conditions for mass production. Ying et al. [31] prepared LiNi_{0.8}Co_{0.2}O_2 via co-precipitation and obtained a charge capacity of 217 mAh g$^{-1}$ followed by a discharge capacity of 172 mAh g$^{-1}$ and a 79.3% Coulombic efficiency during the initial cycle. Cheralathan et al. [32] also investigated the effect of the preparation conditions, such as the pH, NH_4OH concentration and co-precipitation time, to synthesize micro-spherical LiNi_{0.8}Co_{0.2}Mn_{0.08}O_2 materials. Spherical LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2 prepared under optimum conditions exhibited a hexagonally-ordered, layered structure and an initial charging capacity of 176 mAh g$^{-1}$ without cation mixing. More than 91% of the initial capacity was retained after 40 cycles at a 1 C-rate in a voltage range from 3.0 to 4.3 V.

In this work, we have successfully synthesized layered Ni-rich LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2 material. The synthesis conditions for spherical NiNi_{0.8}Co_{0.1}Mn_{0.1}(OH)_2 precursors, such as the pH, the ratio of the chelating agent (NH_4OH) to metal solution, the stirring speed, temperature and residence time have been studied in detail. These materials were synthesized through continuous co-precipitation by using a continuously stirred tank reactor (CSTR). The properties of the Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)_2 precursor and the electrochemical prop-
Table 1. Synthetic conditions of the precursors

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>NH$_4$OH : metal</th>
<th>Rotation speed/ rpm</th>
<th>Temperature/ °C</th>
<th>Residence time/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>P$_1$</td>
<td>11.2</td>
<td>1 : 1</td>
<td>600</td>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td>P$_2$</td>
<td>11.5</td>
<td>1 : 1</td>
<td>600</td>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td>P$_3$</td>
<td>11.8</td>
<td>1 : 1</td>
<td>600</td>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td>P$_4$</td>
<td>11.5</td>
<td>0.8 : 1</td>
<td>600</td>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td>P$_5$</td>
<td>11.5</td>
<td>1 : 2</td>
<td>600</td>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td>P$_6$</td>
<td>11.5</td>
<td>1 : 1</td>
<td>500</td>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td>P$_7$</td>
<td>11.5</td>
<td>1 : 1</td>
<td>800</td>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td>P$_8$</td>
<td>11.5</td>
<td>1 : 1</td>
<td>600</td>
<td>45</td>
<td>10</td>
</tr>
<tr>
<td>P$_9$</td>
<td>11.5</td>
<td>1 : 1</td>
<td>600</td>
<td>55</td>
<td>10</td>
</tr>
<tr>
<td>P$_{10}$</td>
<td>11.5</td>
<td>1 : 1</td>
<td>600</td>
<td>50</td>
<td>8</td>
</tr>
<tr>
<td>P$_{11}$</td>
<td>11.5</td>
<td>1 : 1</td>
<td>600</td>
<td>50</td>
<td>12</td>
</tr>
</tbody>
</table>

The optimum synthetic (co-precipitation) conditions were investigated because they affect the morphology, phase structure and electrochemical properties of the materials. Fig. 1 shows the SEM images of the Ni$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ powders (P$_1$, P$_2$, and P$_3$) that were prepared at different pH values. The morphology, phase structure and elemental composition of the powder were assessed using a scanning electron microscope (SEM, Hitachi S-4800) equipped with an energy dispersive spectroscopy (EDS).

EXPERIMENTAL

1. Materials Synthesis

The layered oxide LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ powders were prepared via co-precipitation [32]. At first, a stoichiometric amount of NiSO$_4$·6H$_2$O, CoSO$_4$·7H$_2$O, and MnSO$_4$·6H$_2$O with the corresponding molar composition of 0.8 : 0.1 : 0.1 were dissolved together in deionized water to obtain a transparent solution. The solution was then pumped into a continuously stirred tank reactor (CSTR, capacity 1.5 L) under an N$_2$ atmosphere. At the same time, the NaOH and NH$_4$OH solutions were separately pumped into the reactor. The optimum synthetic (co-precipitation) conditions were investigated in detail, and these conditions are summarized in Table 1. In general, the particle size and the morphology are the most important factors that determine the performance of the cathode material. We adjusted the corresponding parameters, including the pH, molar ratio of NH$_4$OH to the metal solution, reaction temperature, stirring speed, and residence time, because these have a great effect on the particle size and on the morphology of the materials. The co-precipitated spherical Ni$_{0.8}$Co$_{0.1}$Mn$_{0.1}$OH$_2$ powder was filtered, washed with de-ionized water and vacuum-dried at 110 °C for 24 h. Finally, the Ni$_{0.8}$Co$_{0.1}$Mn$_{0.1}$OH$_2$ precursors were mixed with LiOH·H$_2$O (with a molar ratio of Li/M=1.05), preheated to 480 °C for 5 h and then heated at 780, 800, and 820 °C for 16 h in air to obtain the LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ powder.

2. Material Characterization

The crystalline structure of the samples was characterized by X-ray diffraction (XRD) measurements using a Rigaku D Max/2000 PC with Cu Kα radiation in the 2θ angular range of 10 to 80° at a scanning rate of 4° min$^{-1}$. The particle morphology and the elemental composition of the powder were assessed using a scanning electron microscope (SEM, Hitachi S-4800) equipped with an energy dispersive spectroscopy (EDS).

3. Electrochemical Characterization

2016 coin-type cells were used to measure the electrochemical properties of the samples. The cells were cycled galvanostatically between 3.0 V and 4.3, 4.5 and 4.7 V. The cathodes that were used during the cell test were fabricated with a mixture of the active material (80 wt%), conductive agent (Super P, Timcal) (10 wt%), and polyvinylidene fluoride (PVDF, KF 1300, KUREHA) binder (10 wt%) by dispersion/dissolution in N-methyl-2-pyrrolidone (NMP).

RESULTS AND DISCUSSION

1. Characteristics of the Ni$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ Precursors

The synthesis conditions for the precursors are highly important because they affect the morphology, phase structure and electrochemical properties of the materials. Fig. 1 shows the SEM images of the Ni$_{0.8}$Co$_{0.1}$Mn$_{0.1}$OH$_2$ powders (P$_1$, P$_2$, and P$_3$) that were prepared at different pH values. The pH value also plays an important role in determining the purity of the manganese hydroxide precipitation because the formation of manganese oxides may be promoted by increasing the pH [33]. When the pH is 11.5, the particles are nearly uniform in shape [Fig. 1(b)] and the tap-density of the precursor is 1.91 g cm$^{-3}$. The particle shape of the precursor is spherical, and the average secondary particle diameter ($D_{50}$) is 16 µm with a primary particle that is smaller than 500 nm. When the pH increases, the particles become smaller and non-uniform, and a lot of fine particles can be observed [Fig. 1(c)]. The tap-density thus gradually decreases as the pH increases (1.26 g cm$^{-3}$ at pH=11.8). Therefore, the pH was fixed at 11.5 for the following experiments.

NH$_4$OH is a well-known chelating agent used in the co-precipitation method, and this material prevents phase separation and promotes the formation of homogeneous transition metal hydroxide [24,34]. The molar ratio of the transition metal to NH$_4$OH also influences the morphology and the microstructure, as can be clearly observed in Fig. 2. The primary crystalline grains become smaller when the molar ratio of NH$_4$OH to metal increases, and at a molar ratio of 1.0, the surface morphology of particles becomes sheet-like and the secondary particles are observed to be more uniform than the others. In addition, when the molar ratio of NH$_4$OH to transition metal increases, the concentration of the complex [Ni(NH$_3$)$_6$]$^{2+}$ in-
creases, which leads to an incomplete precipitation of Ni$^{2+}$ [33].

The stirring speed was adjusted to examine the effect of the stirring speed on the particle morphology. Highly agglomerated particles can be observed at a relatively low stirring speed (Fig. 3(a)). At a low stirring speed (500 rpm), the particles become larger than those that were obtained at a high stirring speed. The spherical particles of the 3 precursors that were obtained at stirring speeds of 500, 600 and 800 rpm have an average size of approximately 20, 16 and 13 µm, respectively. It is thus clear that the stirring speed greatly affects size of the particles of the precursor.

The effect of the reaction temperature is investigated by fixing the pH, the molar ratio of NH$_4$OH to metal and the stirring speed to the optimum values that have been previously determined. The morphology of the precursor particles is shown in Fig. 4. The highest purity and uniformity of the particle size and morphology were achieved at a 50°C co-precipitation temperature. The tap-density

Fig. 1. SEM images of Ni$_{0.8}$Co$_{0.1}$Mn$_{0.1}$(OH)$_2$ powders prepared at various pH. (a), (b) P1 11.2; (c), (d) P2 11.5; and (e), (f) P3 11.8 (magnification: I=1,500× and II=50,000×).
of the samples does not change significantly with variations in the reaction temperature. At 45°C, the precursor has a smaller primary particle size and a lower tap-density than those obtained at 50 and 55°C. Liang et al. reported that the purity of the particles becomes lower at higher temperatures than 50°C which may be a result of the presence of MnOOH or Mn$_3$O$_4$ impurities [28]. The stability of transition metal ions that are chelated by ammonium ions may also decrease as the co-precipitation temperature increases.

Finally, the effect of the residence time was investigated. The definition of the residence time is described in Eq. (1):

$$\tau = \frac{V}{q}$$  \hspace{1cm} (1)

where $\tau$ is the residence time, $V$ is the volume of the reactor, and $q$
is the flow rate of the reactants. In this study, the residence times were adjusted to 8 h, 10 h, and 12 h, and the SEM images of the particles that were obtained for each residence time are shown in Fig. 5. For a residence time of 8 h and 10 h, the particle size and the morphology are similar. However, as the residence time is further elongated (12 h), the particle size becomes smaller (9.18 µm) and non-uniform. The primary particles are also smaller and exhibit sheet-like nano-plates on the surface. Secondary particles are composed of aggregated primary particles, and the long residence time (low flow rate of the reactants) decreases the degree of supersaturation and hinders the aggregation process, which may be the reason for which smaller secondary particles are obtained at a long residence time.

Fig. 3. SEM images of Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)_{2} powders prepared at various stirring speed. (a) P₁ 500 rpm; (b) P₂ 600 rpm; and (c) P₃ 800 rpm (magnification: I=1,500× and II=50,000×).
2. Characteristics of the LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ Powder

The spherical Ni$_{0.8}$Mn$_{0.1}$Co$_{0.1}$(OH)$_2$ precursor (P$_2$ sample) is then used to investigate the relationship between the synthesis temperature and the physical/electrochemical properties of the LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ cathode materials that were lithiated via calcination at various temperatures from 780 to 820°C.

Fig. 6(a) shows the X-ray diffraction pattern of the Ni$_{0.8}$Mn$_{0.1}$Co$_{0.1}$(OH)$_2$ precursor (P$_2$ sample), which is similar to that of Ni(OH)$_2$ [31]. All of the diffraction lines are indexed to a hexagonal structure with a space group of P$\overline{3}$m1. The crystal lattice parameters of the layered Ni$_{0.8}$Mn$_{0.1}$Co$_{0.1}$(OH)$_2$ precursor are $a$=3.114 Å and $c$=4.617 Å. Fig. 6(b) displays the XRD patterns of the LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ samples that were prepared by calcining the precursor and LiOH-H$_2$O mixture at 780, 800, and 820°C for 16 h. The XRD patterns exhibit clear peak splits of 006/102 and 108/110 doublets, which indicate that the materials have a well-ordered crystalline struc-
All of the diffraction peaks are indexed to an $\alpha$-NaFeO$_2$ structure ($\bar{R}3m$), and no impurity peaks appear. The unit cell parameters are calculated and summarized in Table 2. The 'a' cell parameter is the measure of the intralayer metal-metal distance and the 'c' parameter is the sum of the MO$_6$ ($M=$transition metal) octahedra layer (slab) thickness (slab thickness S) and LiO$_6$ octahedra layer thickness (interslab thickness I) in the lamellar structure of LiMO$_2$ [35]. Therefore, the increase in the parameter reflects an increase in the effective ionic radius. From Table 2, the lattice parameters a and c increase from 2.8733 Å and 14.2123 Å to 2.8751 Å and 14.2217 Å, respectively, as the calcination temperature increases. The values of c/a for all samples are relatively high, which indicates the formation of a well-ordered layered structure [35,36]. In the material with a layer-structure, cation mixing is known to negatively impact the electrochemical performance. The intensity ratio of $I_{003}/I_{104}$ is an indicative parameter to determine the cation mixing in the lat-

Fig. 5. SEM images of Ni$_{0.8}$Co$_{0.1}$Mn$_{0.1}$(OH)$_2$ powders prepared at various residence time. (a) P$_1$, 8 h; (b) P$_2$, 10 h; and (c) P$_3$, 12 h (magnification: I=1,000× and II=50,000×).
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Table 2. Comparison of the lattice parameters of LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> samples at various calcination temperatures

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>c/a</th>
<th>R&lt;sub&gt;w&lt;/sub&gt;</th>
<th>R&lt;sub&gt;f&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNi&lt;sub&gt;0.8&lt;/sub&gt;Co&lt;sub&gt;0.1&lt;/sub&gt;Mn&lt;sub&gt;0.1&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt; - 780 °C</td>
<td>2.8733</td>
<td>14.2123</td>
<td>4.9463</td>
<td>1.4438</td>
<td>0.5068</td>
</tr>
<tr>
<td>LiNi&lt;sub&gt;0.8&lt;/sub&gt;Co&lt;sub&gt;0.1&lt;/sub&gt;Mn&lt;sub&gt;0.1&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt; - 800 °C</td>
<td>2.8753</td>
<td>14.2192</td>
<td>4.9419</td>
<td>1.3831</td>
<td>0.5068</td>
</tr>
<tr>
<td>LiNi&lt;sub&gt;0.8&lt;/sub&gt;Co&lt;sub&gt;0.1&lt;/sub&gt;Mn&lt;sub&gt;0.1&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt; - 820 °C</td>
<td>2.8751</td>
<td>14.2217</td>
<td>4.9464</td>
<td>1.3327</td>
<td>0.5366</td>
</tr>
</tbody>
</table>

3. Electrochemical Properties

The initial charge-discharge curves of the LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> samples that were calcined at various temperatures are shown in Fig. 9(a). The LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> electrodes were discharged at a 0.1 C-rate in the voltage range from 3.0 to 4.3 V at 25 °C and 60 °C. The discharge capacities increase as the calcination temperature increases from 780 to 800 °C. The initial discharge capacity for the samples calcined at 780, and 800 °C are 185.6 and 193.9 mAh g<sup>-1</sup>, respectively. However, the discharge capacity decreases to 186.2 mAh g<sup>-1</sup> when the calcination temperature increases to 820 °C. Although calcination at a higher temperature can increase the crystallinity, excessive lithium evaporation is unavoidable during heat treatment [40]. For the cell test at an elevated temperature (60 °C), the LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> calcined at 800 °C exhibits an initial discharge capacity of 211.1 mAh g<sup>-1</sup>. The cycling performance of the LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> calcined between 780 and 820 °C at a constant current density of 185 mA g<sup>-1</sup> (approximately 1 C) was also investigated, and the results are shown in Fig. 9(b). The cell delivers a capacity of 170.4 mAh g<sup>-1</sup> at the 1<sup>st</sup> cycle and 153.7 mAh g<sup>-1</sup> at the 100<sup>th</sup> cycle with a capacity retention of 90.41% while the samples calcined at 780 and 820 °C exhibited a capacity retention of 84.5 and 80.9%, respectively. In the high-temperature cycling test (60 °C), the cell delivers a capacity of 196.6 mAh g<sup>-1</sup> at the 1<sup>st</sup> cycle and 156.4 mAh g<sup>-1</sup> at the 100<sup>th</sup> cycle, with a capacity retention rate of 79.6%. The poor capacity retention for LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> is characteristic of Ni-rich cathode materials due to the structural transformation near the surface region. The spontaneous reduction of Ni<sup>3+</sup> to stable Ni<sup>2+</sup> and the evolution of oxygen species from the surface also contributes to the formation of LiOH and Li<sub>2</sub>CO<sub>3</sub> on the surface [18,41].

The cycling stability at a higher voltage was observed by increasing the upper cut-off voltage to 4.5 and 4.7 V vs. Li/Li for the LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> calcined at 800 °C. The cycling stability at a higher voltage was observed by increasing the upper cut-off voltage to 4.5 and 4.7 V vs. Li/Li for the LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> calcined at 800 °C.

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age is raised. In the voltage range from 3.0 to 4.3, 4.5 and 4.7 V, the initial discharge capacities of the LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ samples are 193.9, 210.4 and 217.7 mAh g$^{-1}$, respectively. The cycling stability of the LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ electrode is shown in Fig. 10(b). The discharge capacity gradually decreases from 170.4 mAh g$^{-1}$ at the 1$^{st}$ cycle (1 C-rate) to 153.7 mAh g$^{-1}$ at the 100$^{th}$ cycle with a capacity retention of 90.4% over 3.0 to 4.3 V. For cycling with 4.5 and 4.7 V of the upper cut-off voltage, only 43.8 and 47.8% of the initial capacity was retained at the 100$^{th}$ cycle. This severe capacity fading at a high cut-off voltage may be a result of the interfacial reaction between the electrolyte and the cathode material and a dissolution of the cobalt at a high operating potential (>4.3 V), which can lead to a significant degradation in the capacity retention [42,43].

The rate capability is well-known to be strongly affected by the surface area and the primary particle size of the cathode material. Fig. 11 shows the rate performance of the LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ calcined at 800$^\circ$C, as measured at various current densities in the voltage range from 3.0 to 4.3 V. The cells were cycled at 0.1 C (18.5 mA...
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...for 5 cycles, then at 0.2 C (37 mA g<sup>-1</sup>), 0.5 C (92.5 mA g<sup>-1</sup>), 1 C (185 mA g<sup>-1</sup>), 3 C (555 mA g<sup>-1</sup>), 5 C (925 mA g<sup>-1</sup>), 7 C (1,285 mA g<sup>-1</sup>) and finally returning to 0.1 C (18.5 mA g<sup>-1</sup>) each for 5 cycles. The LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> represents a good rate capability, as shown in the figure. Even at the 7 C-rate, the sample showed a capacity as high as 130.7 mAh g<sup>-1</sup> (68.8% of the capacity retention vs. 0.1 C), indicating that the LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> synthesized in optimum conditions has a superior rate capability that has not been attained in prior studies [19,25,26]. The above results indicate that the LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> synthesized via co-precipitation with optimum conditions (pH=11.5, 600 rpm, 50°C and 1.0 molar ratio of NH₄OH/metal solution) exhibit the highest initial capacity and a good rate capability. However, the cycling performance still needs to improve.

Cyclic voltammetry (CV) was carried out for the initial three cycles between 3.0 and 4.3 V at a scan rate of 0.1 mV·s<sup>-1</sup> in order to investigate the structural stability of the LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> materials against the electrochemical reaction, and the results are shown in Fig. 12. The CV profile of the first cycle can be seen to differ from those of the following cycles. The anodic peaks were observed at 3.94 and 4.24 V during the first delithiation; at 3.83, 4.02 and...
4.25 V during the second delithiation; at 3.83, 4.02 and 4.25 V during the third delithiation; and at 3.82, 4.02 and 4.25 V during the fourth delithiation. In the first anodic scan, there is a prominent anodic reaction at 3.94 V, but it is no longer observed during the subsequent cycles. This may be attributed to the activation of the electrode after which the potential of the delithiation reaction de-
creases [44]. Lu et al. [19] reported that the first oxidation peak corresponds to the transformation of the material from a pristine hexagonal phase (H1) to a new monoclinic phase (M), the second corresponds to the transformation between the monoclinic phase and the second hexagonal phase (H2), and the last corresponds to an H2 transformation to a third hexagonal phase (H3). Due to the complicated phase transformations during charge and discharge cycles, the material often shows an unstable cycle life performance. Furthermore, the high concentration of unstable Ni4+ in the delithiated state (H1 phase) can be easily reduced to a divalent and insulating NiO phase at the surface [39,45], which would also result in capacity fading during cycling, which helps to understand why the material often faces a rapid loss in capacity during cycling. There is no obvious difference in the redox peak (3.82 V of cathodic peak potential and 3.69 V of anodic peak potential), which indicates that the Li-ions are reversibly intercalated and de-intercalated in the LiNi0.8Co0.1Mn0.1O2 electrode with good stability.

CONCLUSIONS

1) Homogeneous, layered LiNi0.8Co0.1Mn0.1O2 cathode materials were successfully synthesized via co-precipitation at optimum conditions, and the samples that were obtained exhibited a spherical morphology, high tap-density and high capacity. Furthermore, we could control the morphology of the precursor particles by adjusting the conditions during synthesis.

2) The particle size of the precursors was dependent on the process variables during co-precipitation. An increase in pH from 11.2 to 11.8, stirring speed from 500 to 800 rpm and residence time from 8 to 12h resulted in a decrease in particle size while the increase in molar ratio of NH4OH to metal from 0.8 to 1.2 and temperature from 45 to 55°C did not have any consistent effect on the particle size. The optimum conditions for synthesis were thus determined according to these results.

3) All of the LiNi0.8Co0.1Mn0.1O2 samples obtained in this study exhibited clear XRD peak splits of 006/102 and 108/110 and a high c/a value, which indicates that the LiNi0.8Co0.1Mn0.1O2 materials have a well-ordered hexagonal structure.

4) The calcination temperature heavily influences the structure and the electrochemical performance of the samples. The results of the electrochemical experiments indicate that the layered LiNi0.8Co0.1Mn0.1O2 cathode materials that were calcined at 800°C for 16h possessed the highest initial discharge capacity of 193.7 mAh g⁻¹ at a current density of 18.5 mAh g⁻¹ in the voltage range from 3.0 to 4.3 V with a good rate capability.

5) The CV curves showed negligible differences in peak intensity and position in subsequent cycles after the 1st cycle, which indicates that the LiNi0.8Co0.1Mn0.1O2 samples have excellent stability during Li-ion intercalation and de-intercalation.

REFERENCES