Characterization of LiMn$_{0.3}$Co$_{0.3}$Ni$_{0.3}$Cr$_{0.1}$O$_2$ and LiMn$_{0.333}$Co$_{0.333}$Ni$_{0.333}$O$_2$ synthesized via Sol-gel Method: XRD, SEM and XPS Studies.

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Abstract. One of the aspects most intensively researched in the continuing improvisation of lithium battery is the search for high capacity, high energy density and high performance cathode materials. Substitution of the electroactive elements with heteroatoms is one of the promising methods. In this study, a potential cathode material with a layered structure was successfully synthesized via a sol-gel method. As a comparison, the well-known LiMn$_{1/3}$Co$_{1/3}$Ni$_{1/3}$O$_2$ (LiMn$_{0.333}$Co$_{0.333}$Ni$_{0.333}$O$_2$) was also synthesized using exactly the same method and conditions. Both materials were characterized using simultaneous thermogravimetric analysis (STA), X-ray powder diffraction (XRD), field-emission scanning electron microscopy (FESEM) and X-ray photoelectron spectroscopy (XPS). The stoichiometries of the compounds were also confirmed through energy-dispersive X-ray spectroscopy (EDX) measurement. XRD results show that both compounds are single phase and impurity-free with well-ordered hexagonal layered structure characteristics of R-3m space group. Both compounds also show similar morphologies with well-formed crystals and clean surfaces as depicted by the SEM images. XPS measurement reveals that the introduction of chromium into LiMn$_{1/3}$Co$_{1/3}$Ni$_{1/3}$O$_2$ results in a considerable change in the chemical environment as observed by significant changes in the binding energies (BE) of manganese, cobalt and nickel respectively.

Introduction

Since the great achievement by Sony Corporation in 1990 in solving the safety problem in lithium secondary battery, the development of electrode materials has progressed rapidly due to high demands for high power and high density rechargeable batteries. As a result, cathode materials has been investigated extensively and significant improvement in some aspects of the batteries has been achieved such as better capacity and cycling performance, reduced toxicity and lower production cost. One of the factors that lead to these improvement are the discoveries of novel preparation methods such as sol-gel which not only reduce the preparation cost due to lower annealing temperature, but also produce material with submicron grain size which is believed to be good for battery applications [1].

Substitutions of other cations for Co in the LiCoO$_2$ in order to reduce toxicity and improve cyclability have been tried with a variety of results. Ohzuku and Makimura [2] have reported that LiMn$_{1/3}$Co$_{1/3}$Ni$_{1/3}$O$_2$ prepared via hydroxides precipitation method showed excellent characteristics as cathode material with discharge capacity of 170 mAhg$^{-1}$ within the voltage range of 2.5 – 4.4 V with good cyclability even at the high rate of 5C. In the present study, LiMn$_{0.333}$Co$_{0.333}$Ni$_{0.333}$O$_2$ and the isostructural LiMn$_{0.3}$Co$_{0.3}$Ni$_{0.3}$Cr$_{0.1}$O$_2$ were synthesized using a simple sol-gel method. Both compounds which have been subjected to the same heat treatment were characterized using XRD, SEM and XPS in order to make a structural comparisons and determine their structural differences.
Experimental Description

The layered $\text{LiMn}_{0.333}\text{Co}_{0.333}\text{Ni}_{0.333}\text{O}_2$ and $\text{LiMn}_{0.3}\text{Co}_{0.3}\text{Ni}_{0.3}\text{Cr}_{0.1}\text{O}_2$ systems will henceforth, for convenience, be referred to as 333 and 333Cr respectively. The compounds were prepared using a simple sol-gel method as described in [3] with slight modification. Lithium acetate dihydrate, manganese (II) acetate tetra-hydrate, cobalt (II) acetate hexahydrate, nickel (II) acetate hexahydrate, and for the preparation of 333Cr, chromium nitrate nonahydrate were used as starting materials. Stoichiometric amounts of the starting materials were dissolved in deionised water and stirred continuously at 80 °C for 4 hours. The homogeneous sol obtained was then heated at 100 °C with continuous stirring until a viscous gel was produced. The gel was then heated at 120 °C for about 48 hours to remove water from the mixture and obtain the precursor. The dry precursor was first precalcined at 500 °C for 5 hours and subsequently calcined at 900 °C for 24 hours. The black powder was then cooled to room temperature and finely ground before the subsequent calcinations for another 24 hours.

The thermal properties of the precursor were characterized using STA with Setaram Setsys Evolution. The heat treatment is from 30 °C to 1200 °C at the rate of 10 °C/min. The XRD patterns were obtained with PanAnalytical X’pert Pro MPD with Cu $K_\alpha$ radiation ($\lambda = 1.5406$) in the 20 range from 15° to 80°. Surface morphology of the powder was observed using FESEM JEOL JSM-7600F. To determine the difference in chemical environment, the binding energies (BE) of the 2p$^{3/2}$ electrons for both compounds were measured using XPS JEOL JPS9900 spectrometer.

Result and Discussions

The compositions of both 333 and 333Cr compounds are confirmed by the energy dispersive X-ray (EDX) measurements using JEOL HRTEM JEM 2100F.

The XRD spectra for both compounds annealed at 900 °C for 48 hours are shown in Fig.1. Both patterns are similar to the pattern of the 333 systems reported by Ohzuku and Makimura [2] as well as the one synthesized by Yabuuchi and Ohzuku [4]. The sharp peaks observed in the spectra for both compounds indicate a high degree of crystallinity and the well-defined pattern, confirm the
formation of pure and single phase layered structure for the materials. The X-ray peaks are indexed by assuming a hexagonal lattice structure with R3-m space group using twelve well-resolved reflection peaks.

The intensity ratio of $I(003)/I(104)$ and $[I(006)+I(102)]/I(101)$ also known as RIR and R-factor respectively have been acknowledged as indicative of an ordered distribution of lithium and transition metal ions in the hexagonal structure with the value of $I(003)/I(104)$ larger than unity indicates reduced cation mixing [5]. Therefore, from the values of RIR for 333 and 333Cr which is 1.27 and 1.20 respectively, coupled with the clear splitting of the (006)/(012) as well as (018)/(110) Bragg lines indicate a well-ordered hexagonal structure with minimal cation mixing [6]. This is in agreement with the low R-factors values of 0.503 and 0.431 for the 333 and 333Cr respectively [7]. Thus, it seems that the hexagonal layered structure is preserved after the addition of Cr$^{3+}$ ions into the 333 lattice. However, it is worthy to remark that after the introduction of the Cr$^{3+}$ ions, the value of RIR decreases, but it is still nevertheless, well above unity.

![FESEM images of the 333 and 333Cr as prepared samples](image)

Fig. 2 SEM micrographs for (a) 333 and (b) 333Cr compounds prepared via sol-gel method.

FESEM images of the 333 and 333Cr as prepared samples show clean and well-crystallized single phases with both materials exhibiting similar morphologies as depicted by Fig. 2. The micron-sized particles are almost uniform in shape and size.

Table 1 The changes of BE for each element after introduction of Cr$^{3+}$ ions.

<table>
<thead>
<tr>
<th>Element</th>
<th>333</th>
<th>333Cr</th>
<th>ABE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>55.1</td>
<td>51.6</td>
<td>3.5</td>
</tr>
<tr>
<td>Mn</td>
<td>643.1</td>
<td>643.9</td>
<td>0.8</td>
</tr>
<tr>
<td>Co</td>
<td>780.6</td>
<td>781.5</td>
<td>0.9</td>
</tr>
<tr>
<td>Ni</td>
<td>855.0</td>
<td>855.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Cr</td>
<td>-</td>
<td>577.9</td>
<td>-</td>
</tr>
<tr>
<td>O</td>
<td>532.4</td>
<td>531.4</td>
<td>1.0</td>
</tr>
</tbody>
</table>

X-Ray photoelectron spectroscopy is one of the most powerful and established tools for investigation of chemical and electronic structure of materials. Fig. 3 shows the binding energy curves for each element for the 333 as well as 333Cr compounds obtained by XPS measurements and the corresponding changes of their BE after the introduction of Cr$^{3+}$ ions are tabulated in Table 1. It can be observed from Table 1 that the BEs of transition metals are increased whilst those of Li and O are decreased by the introduction of the Cr$^{3+}$ ions. The changes in the chemical environment of the material after the addition of Cr$^{3+}$ ions confirm the insertion of Cr$^{3+}$ ions into the 3b layers of the hexagonal structure. These changes are attributed to the increase in the positive character in the 3b layers which pulls the electrons from the Li and O atoms and hence reduces their BE [8].
Fig. 3 The XPS spectra for each element comprise the 333 and 333Cr materials.

Conclusion

The present study shows that pure and single phase LiMn$_{0.3}$Co$_{0.3}$Ni$_{0.3}$Cr$_{0.1}$O$_2$ and the isostructural LiMn$_{0.333}$Co$_{0.333}$Ni$_{0.333}$O$_2$ can be prepared via the simple sol-gel method without using any chelating agent. Both synthesized materials exhibit hexagonal layered structure with uniform particle size and shape. The introduction of Cr$^{3+}$ ions into the 333 system increases the positive character in the transition metal layer of the compound.
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References

Characterization of
LiMn$_{0.3}$Co$_{0.3}$Ni$_{0.3}$Cr$_{0.1}$O$_2$
and
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Synthesized via Sol-Gel Method: XRD, SEM and XPS Studies

DOI References


