Synthesis of Spinel LiNi_{0.5}Mn_{1.5}O_{4} by a Wet Chemical Method and Characterization for Lithium-Ion Secondary Batteries

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5 V cathode material LiNi_{0.5}Mn_{1.5}O_{4} was synthesized by a simple wet chemical reaction using acetates as precursor’s materials. Cathode active materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and Inductively Coupled Plasma (ICP). Electrochemical properties of active materials were evaluated through charge–discharge tests with operation voltage between 3.5 to 4.9 V at 0.3 C. The synthesized sample with high amount of Mn/Ni precursor (LMNO-I) shows a higher first discharge capacity but a faster degradation after 3 cycles. This behavior should be due to the lack of Mn substitute by Ni and therefore more significant Jahn–Teller effect as shown by Raman, ICP and XPS results.

Key-words : Lithium-ion secondary batteries, Spinel lithium nickel manganese oxide, Wet chemical method

1. Introduction

LiCoO_{2} has been commercialized as an attractive cathode material for a wide range of applications in electronic devices.\(^{1–3}\) The high cost and toxicity of LiCoO_{2} have promoted the search of new alternatives in cathode materials.\(^{11}\) Transition metal oxides like LiMn_{2}O_{4} are one of the most studied due to their several advantages as low cost, abundance, and nontoxicity.\(^{23–24}\) Spinel structure LiMn_{2}O_{4} has a three dimensional Li\(^{2+}\) diffusion pass way.\(^{25,26}\) It is expected to have better electrochemical properties than two-dimensional layered material. However, LiMn_{2}O_{4} shows a poor cycling performance. Therefore, many investigations have been focused on transition metal-substituted spinel compounds, such as LiM_{x}Mn_{2–x}O_{4} (M=Cr, Co, Fe, Ni, Cu).\(^{7–15}\) The role of the doped metal ions on the Li/LiM_{x}Mn_{2–x}O_{4} cell is to compensate for the capacity loss which originates from the oxidation state of Mn\(^{3+}\) to Mn\(^{4+}\) below 4.5 V by oxidizing Mn\(^{2+}\) to Mn\(^{4+}\) over 4.5 V.\(^{16,17}\)

Among those doped materials, the Ni substituted LiMn_{2}O_{4} spinel with the composition LiNi_{0.5}Mn_{1.5}O_{4} is special interest because high capacity of 130–140 mAh/g with a high operating voltage in the 5 V range\(^{15,17–28}\) and good electrochemical performance. In the charge–discharge process of the LiNi_{0.5}Mn_{1.5}O_{4} electrode, lithium ions are reversibly inserted into and extracted from the Li_{1}Ni_{0.5}Mn_{1.5}O_{4} spinel phase in two composition ranges of 0 \leq x \leq 1 and 1 \leq x \leq 2 over two potential plateaus located at around 4.7 and 2.7 V, respectively.\(^{29}\) LiNi_{0.5}Mn_{1.5}O_{4} has a rhombohedral layered structure with space group R3m, with lithium and transition metal ions in a close-packed oxygen array, leading to the formation of lithium and transition metal layers.\(^{30}\) About 8–10 at.% of nickel and lithium ions can interchange their sites in the layered structure, which is often referred to cation mixing.\(^{25}\)

The electrochemical performance is strongly dependent on the synthesis procedure. Various synthesis methods such as sol–gel method,\(^{17,29,30}\) solid-state method,\(^{31–34}\) molten salt method,\(^{25}\) co-precipitation,\(^{31,32,36,37}\) ultrasonic spray pyrolysis method,\(^{25}\) hydrothermal synthesis,\(^{38}\) etc., have been used to synthesize LiNi_{0.5}Mn_{1.5}O_{4}. In general, the LiNi_{0.5}Mn_{1.5}O_{4} materials prepared by the conventional solid-state method presents large particle grain size and heterogeneous particles, while through the wet chemical methods like sol–gel and co-precipitation can provide LiNi_{0.5}Mn_{1.5}O_{4} with narrow particle size distribution with highly homogenous composition and high discharge capacity. However, it is difficult to obtain higher active material LiNi_{0.5}Mn_{1.5}O_{4} due to the substantial Li/Ni disorder\(^{39}\) or structural impurity.\(^{17,40,41}\)

It is important to synthesize pure phase LiNi_{0.5}Mn_{1.5}O_{4} due to the presence of non-stoichiometric spinel which deteriorates its electrochemical performance. In this work, the structural and electrochemical properties of LiNi_{0.5}Mn_{1.5}O_{4} spinel by a simple wet chemical method was studied. A pure phase of LiNi_{0.5}Mn_{1.5}O_{4} spinel was obtained and the structure and electrochemical properties were compared with a commercial standard sample.

2. Experimental section

2.1 Synthesis

Two samples of LiNi_{0.5}Mn_{1.5}O_{4} spinel were synthesized from acetates precursors by wet chemical method. They were prepared at different chemical composition. The first one (LNMO-I) raw materials molar ratio is (Li/Mn = 0.66, Li/Ni = 2.38, Ni/Mn = 3.59) and another one (LNMO-2) raw materials molar ratio is (Li/Mn = 0.67, Li/Ni = 2.01, Ni/Mn = 3.00). The following compounds were used: Mn(CH_{3}COO)_{2}·4H_{2}O (Nacalai 99.0%), Ni(CH_{3}COO)_{2}·4H_{2}O (Nacalai, 98.0%), LiOH·H_{2}O (Nacalai, 99.0%). The LiNi_{0.5}Mn_{1.5}O_{4} commercial reagent (Aldrich, <0.5...
μm particle size by BET, >99% purity) was employed to compare the electrochemical behavior, dried in an evaporator between 40 to 10 hPa. First, the stoichiometric Ni(CH$_3$COO)$_2$·4H$_2$O (0.78 g) and Mn(CH$_3$COO)$_2$·4H$_2$O (2.73 g) were dissolved in 17 and 49.4 ml of distilled water, respectively. Then, both solutions were mixed into a flask under constant stirring. LiOH·(H$_2$O) (0.31 g) was added to the above solution. The mixture was refluxed at 100–110°C for 5 h and then it was dried in an evaporator between 40 to 10 hPa. The drying process was completed at 130°C. After, the obtained powder was pulverized by using an agate mortar. Pre-calcination of the sample was performed at 600°C for 2 h in air. The obtained powder was pulverized again by using an agate mortar, then calcination was performed at 800°C for 1 h. The same procedure was performed for the synthesis of LNMO-2 with the variation in the stoichiometric amount of raw materials: 2.66 g of Ni(CH$_3$COO)$_2$·4H$_2$O, 7.78 g of Mn(CH$_3$COO)$_2$·4H$_2$O and 0.893 g of LiOH·(H$_2$O). The sample LNMO-1 has higher amount of Mn but a high agglomeration.

### 2.2 Analysis Techniques

The crystal phases of the synthesized product were determined by X-ray Diffraction (XRD). XRD measurements was carried out on a Rigaku Multi-Purpose X-ray Diffractometer (Ultima IV) using Cu Kα radiation at 40 kV and 40 mA. The particle size and morphology of the synthesized powders were observed by using a Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS) JSM-6700F JED-2300, Japan Electronics Co. with an accelerating voltage of 5 kV for SEM and 15 kV for EDS analysis.

Bond vibrations analyses of the active materials were analyzed by Raman spectroscopy (X-Plora, Horiba, Ltd.) with green laser (532 nm) as source. The analysis of the chemical state of the elements were analyzed by X-ray Photoelectron Spectroscopy (XPS) ESCA 5800, Ulvac-Phi Inc., by using Al Kα 10 kV as X-rays source at 58.7 eV and vacuum at 2 × 10⁻⁹ Pa.

### 2.3 Electrochemical tests

The cathode pellets were prepared by mixing cathode materials with acetylene black as conducting agent and polyvinylidene fluoride (PVDF) as binder dissolved in the solvent of N-methylpyrrolidone, in a ratio of 85:10:5. The materials were pressed in an aluminum mesh and drying in an oven at 80°C for 8 h.

The charge and discharge measurements were conducted using stainless two electrode cell. The cells were assembled in an Ar-filled glove box using 1.0 M of LiPF$_6$ in ethylene carbonate (EC) and diethyl carbonate (DEC) with volume ratio of 1:1 as electrolyte and metallic lithium foil as counter electrode. The configuration of the cell is as follows: Li | 1M LiPF$_6$ in EC/DEC (v/v = 1/1) | LiNi$_{0.5}$Mn$_{1.5}$O$_4$.

The charge and discharge tests were performed between 3.5 and 4.9 V at 0.3 C.

### 3. Results and discussion

**Figure 1** shows the X-ray Diffraction (XRD) patterns of the synthesized cathode materials LNMO-1, LNMO-2 and the commercial one. The existence of a well-defined spinel phase with a Fd-3m space group was confirmed from the XRD patterns. The sample LNMO-2 shows a slightly additional peaks correspond to the by-products of Li$_{11-δ}$NiO and Ni$_6$MnO$_8$.

**Figure 2** shows the SEM images of the synthesized materials and the commercial one. It can be observed that LNMO-1 and LNMO-2 present small particles at the nanorange order and polyhedral morphologies with smooth surfaces. The sample LNMO-1 presents a particle size distribution between 100 to 300 nm and the sample LNMO-2 between 50 to 300 nm. It can be observed that LNMO-1 has higher homogeneity than the LNMO-2. The LNMO-commercial shows small particles around of 50 nm but a high agglomeration.

**Figure 3** shows Raman spectrum of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ synthesized materials. The signals observed around 619 cm⁻¹ are corresponding to the Mn-O stretching vibration of the MnO$_6$ octahedral. Mn-O stretching presents the following bands as reported in the literature: 625 (symmetric Mn-O stretching vibration of MnO$_6$ groups), 580, 483, 426, and 362 cm⁻¹, assigned to $A_{1g}$, $F_2(g)$, $F_2(g)$, $E_g$, and $F_2(g)$ modes, respectively, as predicted by group theory for a cubic compound. The signals around 476 cm⁻¹, and 378–382 cm⁻¹ are corresponding to the Ni$^{2+}$—O stretching vibration. Moreover the presence of those signals confirm the presence of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ in the Fd-3m spinel.

The symmetric Mn–O stretching vibration of MnO$_6$ octahedral shifts slightly to lower wavenumber for the synthesized samples specially LMNO-1, indicating that the Ni$^{2+}$ ions amount and
charge affects the MnO$_6$ symmetry. Probably it is caused by the increase of the average valence state of Mn ions.

The band around 564 cm$^{-1}$ is a shoulder band of the Mn–O (F$_2$g band) originates mainly from the vibration of the Mn$^{4+}$–O bond. The intensity of this band is enhanced upon nickel substitution.$^{43}$ The well split separation of these two bands (A$_1$g and F$_2$g) is attributed to the Ni$^{2+}$/Mn$^{4+}$ cation ordering in the material.$^{44}$ As shown in Fig. 3 this peak is clearly remarked and well splitted for the commercial sample but not for the synthetized one. This might be due to the change of the Mn$^{3+}$/Mn$^{4+}$ ratio vs Ni$^{2+}$ in the material, which indicates that the commercial sample has a higher amount of Ni$^{2+}$ than those synthetized one, also indicating an average Mn oxidation state close to +4 in the commercial one. In another way, it can be deduced that the cation ordering was partially depressed on the synthetized samples.

Figure 4 shows the X-ray Photoelectron Spectroscopy (XPS) spectra of Ni 2p and Mn 2p of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ powders. The Ni 2p spectrum shows signals of Ni 2p$^3$/2 with binding energies of 854.0 eV for all the samples, corresponding to the oxidation state of Ni$^{2+}$.$^{44,46}$ The Mn 2p spectrum shows two signals due to Mn 2p$^3$/2 at 641.7 eV and Mn 2p1/2 at 653.6 eV. The signals of Mn 2p$^3$/2 are used to determine the surface oxidation state of Mn. The signal of Mn 2p$^3$/2 with binding energy of 642.5 eV corresponds to Mn$^{4+}$ and the other one with 641.6 eV corresponds to Mn$^{3+}$.$^{44}$ The samples showed Mn 2p$^3$/2 at 641.6 eV indicating that the main oxidation state of surface Mn ions is +3 but a little contribution of +4 is obtained by peak separation of Mn 2p$^3$/2 peak. There is not a big difference in the oxidation states for the synthetized samples and the commercial one.

The atomic concentration obtained by XPS results is observed in the Table 1. It can be observed than at the surface level the two synthetized samples presents higher Mn/Ni ratio than the commercial one as in concordance with the Raman results. Table 2 shows the composition obtained by The Inductively Coupled Plasma (ICP). The synthetized LNMO-1 presents the least amount of nickel than LNMO-2 and the commercial one. Figure 5 shows the initial charge–discharge curves of the synthetized and commercial samples. The charge/discharge capacity values and the initial Coulombic efficiency (ICE) for the studied samples are given in Table 3. The discharge capacities of the LNMO-1 and LNMO-2 samples were 127 and 120 mAhg$^{-1}$, respectively. The two synthetized samples showed an increase of the discharge capacity and ICE compared with the commercial one.

**Table 1.** Atomic concentration obtained by XPS results

| Sample          | Atomic% | Atomic Ratio |       |       |       |       |
|-----------------|---------|--------------|-------|-------|-------|-------|
|                 | Li 1s   | C 1s | O 1s | Mn 2p | Ni 2p | Li/Ni | Mn/Ni |
| LNMO-Commercial | 3.59    | 9.08 | 51.25 | 27.61 | 8.47  | 0.42  | 3.26  |
| LNMO-1          | 6.7     | 10.15 | 53.21 | 24.77 | 5.16  | 1.29  | 4.80  |
| LNMO-2          | 7.66    | 7.82  | 53.00 | 25.69 | 5.84  | 1.31  | 4.40  |

**Table 2.** Composition of active material by Inductively Coupled Plasma (ICP)

| Sample          | Composition (wt%) | Molar Ratio |       |       |       |       |
|-----------------|-------------------|-------------|-------|-------|-------|-------|
|                 | Li    | Ni | Mn | Li/Mn | Li/Ni | Mn/Ni |
| LNMO-Commercial | 3.77  | 16.1 | 45.7 | 0.65 | 1.98 | 3.03 |
| LNMO-1          | 3.85  | 13.4 | 46.9 | 0.65 | 2.43 | 3.74 |
| LNMO-2          | 3.76  | 15.6 | 44.8 | 0.66 | 2.04 | 3.07 |
commercial samples exhibited voltage plateaus at around 4.7 V due Ni2+
and operation voltage between 3.5 to 4.9 V. These voltage plateaus and they are attributed to the LiNi0.5Mn1.5O4
the spinel with structure Fd-3m.19) The plateau behavior at 4.0 V

due to the lack of Mn substitute by Ni as shown by

due to the lack of stability of Mn substitution by Ni and therefore

degradation and cycle life of the cell.

As all the results showed, the sample synthesized with higher amount of Mn/Ni (LMNO-1) showed a high first discharge capacity and higher ICE but a shorter plateau at 4.6 V. This sample degrades faster than the synthesized with higher amount of Ni (LMNO-2), indicating that a lack of Ni substitution of Mn instead of Ni is presented at the spinel lattice and affecting the Ni2+/Ni4+ redox couple and therefore more significant Jahn–Teller effect.

4. Conclusions

Two cathode active materials of LiNi0.5Mn1.5O4 were synthesized by a simple wet chemical reaction using acetate precursors. The synthesized products have spinel structure with space group of Fd-3m, high crystallinity and uniform particle sizes and good electrochemical performance. The synthesized product showed obvious two discharge voltage plateau in comparison with the commercial one.

The sample synthesized with a higher Mn/Ni ratio shows a higher initial discharge capacity but a fast degradation behavior due to the lack of stability of Mn substitution by Ni and therefore more significant Jahn–Teller effect. The Ni redox reaction is affected as is shown by the difference of behavior of two voltage plateau.

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