Investigation of supersonic-wave treatment effect on $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$ as a cathode material of Li ion battery

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The electrochemical properties and crystal structure of $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$ treated by supersonic-waves in a Zn-containing solution were investigated by performing charge–discharge tests, X-ray diffraction (XRD), an inductively coupled plasma (ICP) analysis, scanning electron microscopy (SEM), transmission electron microscopy, energy dispersive X-ray spectroscopy (TEM-EDX) and synchrotron powder XRD. Furthermore, the supersonic-wave bath solution was characterized by pH measurements. The electrochemical properties and crystal structure of $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$ treated with supersonic-waves in a Zn-containing $\text{C}_2\text{H}_5\text{OH}$ solution did not change from pristine. On the other hand, Zn^{2+} was partially substituted in the $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$ treated with supersonic-waves in a Zn-containing aqueous solution. As a result of the ICP analysis of the supersonic-wave-treated samples and pH measurement of the supersonic-wave bath, the Li was dissolved in the supersonic-wave bath which contained H_2O from the $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$. This suggests that Li defects are the initial points of Zn substitution by the supersonic-wave treatment.

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1. Introduction

LiCoO_2 is widely used as a cathode material for Li ion batteries because of its low irreversible capacity loss, good cycling performance and simple synthesis.^{1)–5)} On the other hand, its high cost, environmental issues, toxicity problems and limited capacity has promoted research of alternative cathode materials. The compounds, $\text{Li}(\text{Ni},\text{Co},\text{Mn})\text{O}_2$, which have the α - NaFeO_2 layered structure, have been investigated and found to have properties that qualify them as possible candidates for the replacement of LiCoO_2 due to their good rate capability, lower cost and can operate at high voltage.^{4)–8)} Among them, $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ is a material having a high capacity and better thermal stability.^{9)–11)} However, this material is expected to improve the charge–discharge cycle performance.

In our previous studies, it was reported that the battery characteristics of LiMn_2O_4 and $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, which form a spinel structure, were improved by applying the supersonic-wave treatment in an aqueous solution containing Zn or Ni.^{12)–15)} The improvement in the battery characteristics of the LiMn_2O_4 and $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ upon supersonic-wave treatment was thought to be due to the partial substitution and/or surface coating. Therefore, we applied this method to the $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$, which has a composition near that of $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$, to improve its electrochemical property.

In this paper, we focus on the solution when using the supersonic-wave treatment. We investigated the electrochemical properties and the crystal structure of $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$ upon supersonic-wave treatment in an aqueous or nonaqueous Zn-containing solution. The $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$ powder that had been synthesized by a solution method was supersonic-wave

treated in an aqueous and/or nonaqueous Zn-containing solution. As for the samples with the supersonic-wave treatments, we investigated the crystal structures, compositions and cathode properties. Furthermore, the solution when using the supersonic-wave treatment was characterized by pH measurements. Based on these results, we discuss the relationship between the effect on the crystal structure of the obtained powder and the solution by the supersonic-wave treatment.

2. Experimental procedure

$(\text{Ni}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18})(\text{OH})_2$ was prepared by the co-precipitation method. The NaOH , and NH_4OH solution that contained stoichiometric amounts of nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), cobalt sulfate ($\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$), and manganese sulfate ($\text{MnSO}_4 \cdot 6\text{H}_2\text{O}$) was stirred for 3 h. The pH was then controlled between 11 and 12. The obtained $(\text{Ni}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18})(\text{OH})_2$ was mixed with Li_2CO_3 (molar ratio of Li:Metal = 1.07:1). The mixture was preheated at 680°C for 6 h and finally calcined at 900°C in air for 12 h.

Supersonic-wave treatment was applied for 10 min at a frequency of 28 kHz with a power of 300 W. It was applied to the obtained $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$ powder in the Zn-containing H_2O and $\text{C}_2\text{H}_5\text{OH}$ [$\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH}$ = 100:0, 50:50, 30:70, 0:100 (vol/vol)] solutions, which were prepared by dissolving zinc acetate (99.9%, Wako Pure Chemical Industries, Ltd.). The weight ratios of the Zn to solution were 0.05:99.95. The experimental conditions are summarized in **Table 1**. The obtained samples were examined by powder XRD (Philips, X'Pert Pro) and their metal compositions were determined by an inductively coupled plasma (ICP) analysis (Shimadzu Co., ICPE-9000). The powder morphologies were observed by scanning electron microscopy (SEM) (Hitachi Co., S-2600N) and the particle size was measured by a particle size analyzer (Nikkiso Co., Microtrac 3100). The powder cross sectional morphologies and Zn distribution were observed by transmission electron

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microscopy and energy dispersive X-ray spectroscopy [TEM-EDX] (JEOL Co., JEM-2100F, JED-2300T).

The electrochemical characterization was carried out using a conventional coin type cell (Hosen Co.). The working electrodes were prepared by mixing a 85:10:5 (w/w) ratio of the obtained sample, acetylene black and polyvinylidene difluoride (PVdF) binder, respectively. Li metal foils were utilized as the counter electrode. The electrolyte was a solution of 1.0 M LiPF_6 dissolved in a 1:2 (volume) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (Li-battery grade, Tomiyama Pure Chemical Industries, Ltd.). The charge and discharge performance was measured using a potentiogalvanostat (Hokuto Denko Co., HZ-3000).

Furthermore, the crystal structure of the obtained samples was determined by a Rietveld analysis (RIETAN-FP¹⁶) of the powder's synchrotron XRD data (wavelength: 0.050004 nm; BL19B2, SPring-8).

3. Results and discussion

3.1 Sample characterization

Figure 1 shows the XRD patterns of the $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$ samples in the scattering angle range between 10 and 70 degrees. The peaks were identified using a hexagonal structure with a $R\bar{3}m$ space group for both the pristine and supersonic-wave treated samples. In addition, the clear splitting of the

Table 1. Condition of supersonic-wave treatment

Sample	Frequency [kHz]	Zn concentration [wt %]	Treatment time [min]	Supersonic bath $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH}$ (vol.)
(A)	—	—	—	—
(B)	28	0.5	10	100:0
(C)	28	0.5	10	50:50
(D)	28	0.5	10	30:70
(E)	28	0.5	10	0:100

Fig. 1. X-ray diffraction patterns of $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$ and the sample after the supersonic-wave treatment.

(A) Untreated, (B) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 100:0$, (C) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 50:50$, (D) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 30:70$, (E) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 0:100$.

(006)-(102) and (108)-(110) doublet peaks suggested that it has a layered structure.¹⁷ **Table 2** lists the lattice constants calculated from the XRD patterns. The lattice constant became smaller due to the supersonic-wave treatment in the aqueous solution. It was assumed that partial substitutions of Li and Zn had occurred. **Table 3** shows their metal compositions obtained by ICP. The composition ratio was calculated by taking the total metal constituent composition as 2. From the analytical composition data, the composition of the obtained sample was almost the desired value. It was demonstrated that the samples after the supersonic-wave treatment in the Zn-containing solution ($\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 100:0, 50:50, 30:70$) contained Zn as a constituent element. On the other hand, the sample after supersonic-wave treatment in the Zn-containing $\text{C}_2\text{H}_5\text{OH}$ solution did not contain Zn as a constituent element. Furthermore, no Zn was found in sample (E) by TEM-EDX. These results suggested that the effect of the supersonic-wave treatment was changed by the supersonic-wave bath solution and the Li was dissolved from the $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$ in the supersonic-wave bath that contained H_2O .

In order to determine the particle size, SEM and particle size measurements were carried out. The SEM image of the samples is shown in **Fig. 2**. **Figure 3** shows the particle size distribution of the samples and **Table 4** lists the particle size which was measured by a particle size analyzer. These irregularly shaped particles had an average size of around $10\ \mu\text{m}$. By comparing these results of the samples before and after the applied supersonic-wave treatment, it was found that the particle size was not affected by the supersonic-wave treatment. It was assumed that the effect of the supersonic-wave treatment was not a physical improvement. However, the surface morphologies of the samples may have changed by the supersonic-wave treatment because Li dissolution was indicated by the ICP data of the samples treated by the supersonic-waves.

To study the distribution of Zn in the samples in more detail, TEM-EDX measurements of sample (B) were performed. The results are presented in **Fig. 4**. The experiments demonstrated that Zn was unevenly distributed not only on the surface, but also inside of the $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$ powder. Furthermore, the distribution of Zn was observed as inhomogeneous from elemental mapping of Zn. Such a result indicates an inhomogeneous substitution of Zn^{2+} in the bulk when the supersonic-wave treatment was applied for $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$ powder in a Zn-containing aqueous solution.

Table 2. Lattice constants of the samples with the supersonic-wave treatments. That of untreated $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$ is also listed as a reference

Sample	a [Å]	c [Å]
(A) Untreated	2.8657(7)	14.216(6)
(B) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 100:0$	2.8647(3)	14.204(2)
(C) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 50:50$	2.8666(3)	14.215(4)
(D) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 30:70$	2.8656(6)	14.212(5)
(E) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 0:100$	2.86616(4)	14.214(3)

Table 3. Compositions of samples with supersonic-wave treatments in Zn-containing solution. That of untreated $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$ is also listed as a reference

Sample	Li	Ni	Co	Mn	Zn
(A) Untreated	1.000(8)	0.6043(6)	0.2181(6)	0.1779(4)	0
(B) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 100:0$	0.979(5)	0.6142(2)	0.2221(1)	0.1779(7)	0.00638(1)
(C) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 50:50$	0.990(8)	0.6060(2)	0.2191(5)	0.1788(5)	0.00592(1)
(D) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 30:70$	0.997(6)	0.6023(9)	0.2180(3)	0.1761(3)	0.00592(1)
(E) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 0:100$	0.997(2)	0.606(1)	0.2183(3)	0.1786(3)	0

Fig. 2. SEM images of $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$ and the sample after the supersonic-wave treatment.

(A) Untreated, (B) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 100:0$, (C) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 50:50$, (D) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 30:70$, (E) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 0:100$.

The pH of solution when using the supersonic-wave treatment was measured by a pH meter (DKK-TOA Co., HM-25R). Table 5(a) shows the pH of the supersonic-wave bath with $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$ before and after the applied supersonic-wave treatment. Table 5(b) shows the pH of the supersonic-wave bath without $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$ before and after applied supersonic-wave treatment. The pHs of the supersonic-wave baths (B), (C), (D) with $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$ were around 9–11. On the other hand, the pHs of the supersonic-wave bath (E) with $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$ and the supersonic-wave baths (B), (C), (D) and (E) without $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$ were around 6–7. Based on this result, it was demonstrated that Li was dissolved in the supersonic-wave baths (B), (C), (D) which contained H_2O . These results are consistent with the ICP data listed in Table 3. Furthermore, the pH value of the supersonic-wave baths (B), (C), (D) decreased after the applied supersonic-waves. This indicated that the some kind of acid was produced in the supersonic-wave bath which contained H_2O when the supersonic-wave was applied.

3.2 Electrode property

The cathode behaviors of the $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$ after the supersonic-wave treatments are compared in Fig. 5, for a current of 33 mA g^{-1} within the potential window of 2.75–4.30 V vs. Li/Li^+ at room temperature. The charge and discharge capacities of the 1st cycle and the coulomb efficiency (%) of the samples are summarized Table 6. The initial potential of all the samples were around 3.80 V vs. Li/Li^+ , consistent with a previous report.⁹⁾ When the cell was cycled up to 4.30 V vs. Li/Li^+ , a reversible capacity of about 165 mAh/g was obtained. It can be seen that the initial charge and discharge behaviors for all the samples are similar.

Fig. 3. Particle size frequency and multiplication distribution of $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$ and the sample after the supersonic-wave treatment.

○: (A) Untreated, △: (B) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 100:0$, □: (C) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 50:50$, ◇: (D) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 30:70$, ●: (E) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 0:100$.

Table 4. Particle size of the samples with supersonic-wave treatments in Zn-containing solution. That of untreated $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$ is also listed as a reference

Sample	D10 [μm]	D50 [μm]	D90 [μm]
(A) Untreated	7.52	10.22	14.80
(B) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 100:0$	7.55	10.16	14.43
(C) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 50:50$	7.50	9.98	14.00
(D) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 30:70$	7.19	9.78	14.17
(E) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 0:100$	7.64	10.08	14.02

Fig. 4. (Color online) TEM-EDX images of samples after the supersonic-wave treatments in 0.05 wt% Zn aqueous solution ($\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 100:0$) [Sample (B)]. (a) Cross sectional morphologies, (b) Zn distribution.

Table 5. pH of the supersonic-wave bath

(a) Supersonic-wave bath with $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$		
Sample	Before applied supersonic-wave	After applied supersonic-wave
(B) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 100:0$	9.92	9.89
(C) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 50:50$	9.94	10.17
(D) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 30:70$	10.02	10.20
(E) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 0:100$	6.28	6.50
(b) Supersonic-wave bath without $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$		
Sample	Before applied supersonic-wave	After applied supersonic-wave
(B) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 100:0$	6.81	6.71
(C) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 50:50$	6.56	6.46
(D) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 30:70$	6.58	6.56
(E) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 0:100$	5.99	6.10

Fig. 5. Charge and discharge curves at the first cycle at room temperature.

○: (A) Untreated, △: (B) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 100:0$, □: (C) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 50:50$, ◇: (D) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 30:70$, ●: (E) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 0:100$.

Table 6. Charge and Discharge capacities at 1st cycle, and the coulomb efficiency (%) of the samples

Sample	Charge capacity [mAh/g]	Discharge capacity [mAh/g]	Coulomb efficiency [%]
(A) Untreated	195.2	164.6	84.3
(B) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 100:0$	200.7	168.6	84.0
(C) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 50:50$	189.7	161.3	85.0
(D) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 30:70$	192.1	163.9	85.3
(E) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 0:100$	205.8	169.4	82.3

Charge: 33 mA g^{-1} (0.2 C rate) to 4.3 V versus Li/Li^+ followed by a constant voltage of 4.30 V versus Li/Li^+ for a total of 10 h.

Discharge: 33 mA g^{-1} (0.2 C rate) to 2.75 V versus Li/Li^+ .

Figure 6 shows their cycle performances at room temperature. Table 7 lists the second and 50th discharge capacities and capacity retentions. Because the charge–discharge process during the 1st cycle is often affected by extra reactions, such as a solid electrolyte interphase (SEI) formation,^{18),19)} we evaluated the capacity retentions of the samples by the ratio of the capacities at the 50th cycle to the 2nd cycle. When charge–discharged over 2.75–4.30 V vs. Li/Li^+ for 50 cycles at room temperature, samples (B) and (C) showed a fast capacity fading. On the other hand, samples (A), (D) and (E) exhibited good electrochemical performance among the tested samples. These results indicated that the cycle performance declined as the H_2O ratio of the

Fig. 6. Cycle performances at room temperature for $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$ and the sample after the supersonic-wave treatment.

○: (A) Untreated, △: (B) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 100:0$, □: (C) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 50:50$, ◇: (D) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 30:70$, ●: (E) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 0:100$.

Table 7. Discharge capacities at 2nd and 50th cycles, and the capacity retentions (%) of untreated $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$ and the samples with the supersonic-wave treatments

Sample	Capacity at 2nd cycle [mAh/g]	Capacity at 50th cycle [mAh/g]	Capacity retention [%]
(A) Untreated	156.0	143.8	92.2
(B) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 100:0$	155.5	136.0	86.7
(C) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 50:50$	149.3	132.2	88.6
(D) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 30:70$	154.2	140.3	91.0
(E) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 0:100$	160.6	156.8	97.6

supersonic-wave bath increased. The reason why sample (E) showed the best capability is now being investigated.

3.3 Crystal structure analysis

In order to investigate the effect of the supersonic-wave treatment in more detail, powder synchrotron X-ray diffraction measurements were performed and the crystal structure was determined by a Rietveld analysis. The average crystal structure was assumed that in the space group $R\bar{3}m$, Li was in the 3a site (0,0,0), a transition metal was in the 3b site (0,0,1/2), and oxygen was the 6c site (0,0,z). For example, Fig. 7 illustrates the results of the Rietveld refinement patterns for sample (C) and Table 8 lists the refined structure parameters and the R values. Based on these results, a good agreement between the observed and calculated patterns was obtained. As a result of the Rietveld analysis, sample (A) and sample (E) are almost the same. On the other hand, the partial substitutions of Zn were indicated in samples (B), (C) and (D) which contained H_2O in the supersonic-wave bath. As for the transition-metal (3b) sites, partial substitutions of Li and Zn were indicated. These results concluded that the properties of the $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$ were not affected by the applied supersonic-wave in the $\text{C}_2\text{H}_5\text{OH}$ solution. Table 9 lists the Ni occupancy of the 3a site. For the supersonic-wave baths with the increased ratio of H_2O , the Ni occupancy of the 3a site, which is mainly occupied by Li, increased. This may be one reason why the cycle performance declined as the H_2O ratio increased in the supersonic-wave bath.

4. Conclusion

The $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$ was supersonic-wave treated. From the SEM and particle size analyses, it was indicated that the effect of supersonic-wave treatment was not a physical improvement.

Fig. 7. Rietveld refinement pattern of sample after the supersonic-wave treatments in 0.05 wt% Zn aqueous solution ($\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 50:50$) [Sample (C)]. Plus marks show observed intensities, and a solid line represents calculated intensities. Vertical marks below them indicate positions of allowed Bragg reflections. A curve at the bottom is a difference between the observed and calculated intensities in the same scale.

Table 8. Final results of Rietveld refinements for sample (A), (C) and (E) in space group $R\bar{3}m$ at room temperature

(a) Sample (A); $a = 2.86309(4) \text{ \AA}$, $c = 14.1913(1) \text{ \AA}$, $R_{wp} = 5.65\%$, $R_p = 3.97\%$, $R_{exp} = 2.18\%$.

Atom	Site	x	y	z	$10^2 \times B$ [nm^2]	Site occupancy [%]
Li1	3a	0	0	0	1.08(8)	0.9814
Ni1	3a	= Li1(x)	= Li1(y)	= Li1(z)	= Li1(B)	0.0186(9)
Ni2	3b	0	0	1/2	0.221(7)	0.5857
Li2	3b	= Ni2(x)	= Ni2(y)	= Ni2(z)	= Ni2(B)	0.0186
Co	3b	= Ni2(x)	= Ni2(y)	= Ni2(z)	= Ni2(B)	0.2181
Mn	3b	= Ni2(x)	= Ni2(y)	= Ni2(z)	= Ni2(B)	0.1779
O	6c	0	0	0.24116(6)	0.51(2)	1

(b) Sample (C); $a = 2.86386(3) \text{ \AA}$, $c = 14.1991(1) \text{ \AA}$, $R_{wp} = 4.52\%$, $R_p = 3.05\%$, $R_{exp} = 2.25\%$.

Atom	Site	x	y	z	$10^2 \times B$ [nm^2]	Site occupancy [%]
Li1	3a	0	0	0	1.08(7)	0.9810
Ni1	3a	= Li1(x)	= Li1(y)	= Li1(z)	= Li1(B)	0.0190(8)
Zn2	3b	= Ni2(x)	= Ni2(y)	= Ni2(z)	= Ni2(B)	0.0059
Ni2	3b	0	0	1/2	0.181(6)	0.5850
Li2	3b	= Ni2(x)	= Ni2(y)	= Ni2(z)	= Ni2(B)	0.0090
Co	3b	= Ni2(x)	= Ni2(y)	= Ni2(z)	= Ni2(B)	0.2191
Mn	3b	= Ni2(x)	= Ni2(y)	= Ni2(z)	= Ni2(B)	0.1788
O	6c	0	0	0.24121(6)	0.43(1)	1

(c) Sample (E); $a = 2.86366(3) \text{ \AA}$, $c = 14.2020(1) \text{ \AA}$, $R_{wp} = 4.45\%$, $R_p = 3.05\%$, $R_{exp} = 2.21\%$.

Atom	Site	x	y	z	$10^2 \times B$ [nm^2]	Site occupancy [%]
Li1	3a	0	0	0	1.03(1)	0.9826
Ni1	3a	= Li1(x)	= Li1(y)	= Li1(z)	= Li1(B)	0.0174(8)
Ni2	3b	0	0	1/2	0.171(6)	0.5886
Li2	3b	= Ni2(x)	= Ni2(y)	= Ni2(z)	= Ni2(B)	0.0144
Co	3b	= Ni2(x)	= Ni2(y)	= Ni2(z)	= Ni2(B)	0.2183
Mn	3b	= Ni2(x)	= Ni2(y)	= Ni2(z)	= Ni2(B)	0.1786
O	6c	0	0	0.24122(6)	0.45(2)	1

Table 9. Ni occupancy in the 3a site of untreated $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$ and the samples with the supersonic-wave treatments

Sample	Ni occupancy in the 3a site [%]
(A) Untreated	0.0186(9)
(B) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 100:0$	0.0211(8)
(C) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 50:50$	0.0190(8)
(D) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 30:70$	0.0164(8)
(E) $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 0:100$	0.0174(8)

The result of the supersonic-wave treatment showed differences based on the type of solution used. There is little significant difference in the electrochemical properties and crystal structure between the untreated sample and the sample treated with supersonic-waves in a Zn-containing $\text{C}_2\text{H}_5\text{OH}$ solution. On the other hand, the partial substitutions of Zn occurred by the supersonic-wave treatment when treated in the aqueous solution. In the supersonic-wave bath which contained H_2O , the Li dissolution from $\text{LiNi}_{0.60}\text{Co}_{0.22}\text{Mn}_{0.18}\text{O}_2$ was indicated by the pH measurement of the supersonic-wave bath. These results suggest that the Li defect is the initial point of Zn substitution by the supersonic-wave treatment. It is indicated that the effect of the supersonic-wave treatment is a chemical improvement.

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