Synthesis, Electrochemical Properties and Changes of Crystal and Electronic Structures in Charge/Discharge Process of Spinel Type Cathode-Materials Mg(Mg2.5V4.5x-1Ni1x)O4 (x = 0, 0.1, 0.2, 0.3) for Magnesium Secondary Batteries

Yasushi IDEMOTO,* Natsumi KAWAKAMI, Naoya ISHIDA, and Naoto KITAMURA

Faculty of Science & Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan
* Corresponding author: idemoto@rs.noda.tus.ac.jp

1. Introduction

In recent years, research has been conducted into high-performance next-generation batteries due to problems with stability and limits on capacity. The applications of rechargeable batteries can be categorized into three main directions: automotive and transport equipment (large and mobile), the smart grid (large and stationary), and mobile equipment (small and mobile). The functions and performance required for each of these is different, and the design considerations are important.

Although research into multivalent cation batteries has been conducted on rechargeable batteries with calcium and aluminum as the mobile ions, discharge capacity and battery characteristics matching those of lithium have not been obtained, and the devices have not reached practical application. Among these, currently the most widely researched is rechargeable batteries that use divalent Mg2+ as the mobile ion. The road to magnesium rechargeable batteries started in 2000 with research by Aurbach et al.1 They demonstrated that high Coulomb efficiency was possible through reductive precipitation and oxidative dissolution of metallic magnesium by using a solution of tetrahydrofuran (THF) with Grignard reagent and aluminum salt dissolved into it, and they also showed that Chevrel compounds can be used as a cathode active material that can be discharged and recharged repeatedly. The redox potential of Mg is +0.7 V higher than that of Li, meaning that it is worse in terms of cell potential. However, it has been reported that Mg does not form dendrites, and this could be used to increase the capacity of batteries that use a metal anode. Because of this, it is expected that around double the electrical capacity per unit volume could be obtained. In terms of stability, although both Mg and Li react violently with water, Mg actually forms a passive film on the surface and does not react with water. Since this film forms a barrier to the motion of Mg ions, controlling the passive film is required in order for reversible precipitation and dissolution of Mg. Previously reported cathode materials include MnO2,2 V2O5,3 and Chevrel compounds,4 but these suffer from problems in terms of cycle characteristics and battery voltage. It is also reported that a delithiated iron silicate, FeSiO4, could deliver discharge capacity about 300 mAh/g.2 From such background, we have focused on chemically delithiated Li0.13Mn0.54Ni0.13Co0.13O2 as a cathode material of Mg rechargeable battery, and then found that a high capacity of 273 mAh/g was obtained as the first discharge capacity,5 but problems also remained for this such as reduced capacity retention rate and degraded Coulomb efficiency in the second and subsequent cycles. There is therefore a need to search for a cathode material to improve the cycle characteristics.

The existence of a spinel compound MgMn2O4 (M: transition metal) has been reported. The battery characteristics when Mg2Co2O4 and Mg2Ni3O4 are used as the cathode material have been widely reported,6,7,11 and research is also progressing into substitution for the samples.12 The synthesis and crystal structure of MgV2O413 has been reported, and research is being conducted into the battery characteristics of substitution into Mg(Mg0.5V1.5)O414 made with an excess of Mg. V is thought to have high reversibility due to its broad mixed valence. Ni-substituted Mg(V1.5−xNi1x)O4 based on Mg(Mg0.5V1.5)O4 with the aims of increasing the discharge capacity and improving the battery characteristics, and investigated the crystal and electron structure, and the charge and discharge characteristics depending on the amount of substitution and the structural changes accompanying charging and discharging.

2. Experimental

2.1 Sample synthesis

The raw ingredients used for synthesis were MgO (99.0%, Wako Pure Chemical Industries Ltd.) crushed in advance using a planetary ball mill under conditions of 300 rpm for 3 h (15 min × 12), V2O5 (95%, Wako Pure Chemical Industries Ltd.), and NiO (99.9%, Wako Pure Chemical Industries Ltd.). The raw ingredients were weighted...
and dry mixed for 2 h at molar ratios of Mg:V:Ni = 1.5:1.5:0, 1.5:1.4:0.1, 1.5:1.3:0.2, and 1.5:1.2:0.3. After this, the target samples were obtained by sintering the samples under conditions of 1000°C and 10−4 Pa for 24 h in a vacuum furnace (MEMS, FDB14-16).14

2.2 Sample characterization

Phases in the obtained samples were identified by powder X-ray diffraction measurement (PAAnalytical X’Pert Pro, Cu-Kα, 45 kV, 40 mA). The metal compositions of the samples were found by ICP emission spectroscopy (ICPE-9000, Shimadzu Corporation). The particle morphology of the samples was observed by transmission electron microscopy (JEOL, JEM-2100F, 200 kV, JED-2300F), and particle shape, electron beam diffraction, and element analysis were performed.

Crystal structure analysis was performed using synchrotron X-ray diffraction measurement (SPRing-8, BL19B2) and Rietveld analysis (RIETAN-FP15), and the electron density distribution was evaluated by applying the maximum-entropy method (MEM) (Dysnomia16). Furthermore, XAFS measurement (SPRing-8, BL14B2) was performed, and the valences of the transition metals were determined by powder X-ray absorption (SPring-8, BL14B2) and Rietveld analysis (SPring-8, BL19B2) was performed, and the valences of the transition metals were investigated by analysis of the XANES area. Athena17 was used for XAFS analysis.

2.3 Electrochemical measurements

Electrochemical measurements were performed using a three-electrode cell (Hohnsen Ltd.). The synthesized samples were crushed using a ball mill (300 rpm, 15 min × 12) and a complex was formed with an electrical conductor (SuperC65). The synthesized sample, an electrical conductor containing the complex, and a binding agent (PTFE) were mixed at a mass ratio of 5:5:1, and pressed onto an Al electrical conductor containing the complex, and a binding agent to use as the cathode for the 90°C measurement. Mg alloy AZ31 (Mg:Al:Zn = 96:3:1 mass ratio) was used as the anode. A solution of 1 mol/L Mg[N(SO2CF3)2]2/triglyme (Kishida Chemical Co., Ltd.) was used as the electrolyte solution, and a glass fiber filter (Tokyo Roshi Kaisya, Ltd.) was used as the separator.

Charging and discharging were performed at a current density of 5 mA/g over the range of the maximum end-of-charge voltage of 0.345 V vs. Ag/Ag+ to the maximum end-of-discharge voltage of −1.155 V vs. Ag/Ag+ (2.845 to 1.345 V vs. Mg/Mg2+) using the three-electrode cell. A 5-minute rest interval was used between charging and discharging. Cell assembly was performed inside a glove box in an argon atmosphere. Charge and discharge experiments were performed using a charger and discharger system (H-SD8, Hokuto Denko). Battery operation was performed in a thermostatic chamber at 90°C.

3. Results and Discussion

3.1 Sample characterization

Figure 1 shows the powder X-ray diffraction patterns of the synthesized samples Mg(Mg0.5V1.5−x,Nix)O4 (x = 0.0, 0.1, 0.2, 0.3). All of the peaks of the Ni-substituted samples were attributed to the cubic spinel type Fd3m space group. On the other hand, a small peak due to an impurity phase could be observed in Mg(Mg0.5V1.5−x,Nix)O4. It is quite difficult to determine the impurity phase only from the single peak, but the peak may be attributable to a tiny amount of VO2. Table 1 shows the changes in the lattice parameters and the results of metal composition analysis by ICP. The lattice parameters exhibited an increasing trend up to x = 0.2. This is thought to arise from the fact that the ionic radius of Ni2+ (6 coordinate, 0.069 nm19) is larger than that of V3+ (6 coordinate, 0.064 nm20). The cause of the decrease at x = 0.3 is thought to be due to deviation from the target composition due to an increase in subphases. From the results of ICP emission spectroscopy, this was controlled to values near the mixing composition. Since the position of the peak of the starting material MgO overlaps the spinel type peaks, it is not possible to accurately judge whether an unreacted MgO peak remains simply from XRD. Thus, element mapping was performed on the powder by STEM-EDS and the crystal structure and proportions of subphases were investigated in detail by the electron beam diffraction and Rietveld analysis of synchrotron X-ray diffraction data. Figure 2 shows the results of element mapping by STEM-EDS, the results of observation of the lattice image, and the results of electron beam diffraction. The mapping results in Fig. 2(a) show that for some particles, all of the elements Mg, V, and Ni are uniformly distributed. Figure 2(b) shows a comparison of the EDS analysis results with the results of composition analysis by ICP. In the EDS analysis results, Particle 1 had a composition of MgV:Ni = 1.25:1.68:0.07, which differs from the results of analysis by ICP. Furthermore, variations in the composition were observed in other particles, and particles with small V and high Mg composition were also observed suggesting the possibility that MgO remains. The lattice spacing obtained from the TEM lattice image shown in Fig. 2(c) was 0.47 nm. This lattice spacing corresponds to the (111) plane, which produces relatively high intensities in XRD. The results of the electron beam diffraction shown in Fig. 2(d) show a spot from incidence from the [311] direction of the spinel type, suggesting that a spinel type compound was successfully synthesized.

3.2 Crystal structure analysis

Rietveld analysis was performed for the powder samples using the results of the synchrotron X-ray diffraction measurement. Figure 3 shows the results of analysis for (a) the Fd3m structure at x = 0 and (b) the F43m structure. Tables 2 and S1 show the structure parameters, respectively. Since a good fit was obtained for the structure in (a), the subsequent analysis was performed using the Fd3m structure. Table 2 shows the structure parameters when each sample was analyzed as Fd3m. Based on the R-factors shown in Table 2, good fits were obtained for each sample. However, since
the peaks of the rock salt type MgO starting ingredient differ from the peaks of the main phase, the proportion of MgO remaining was evaluated by performing two-phase analysis using this. Figure 3(c) shows the two-phase analysis pattern for the \( x = 0 \) sample taking the second phase as MgO, and Table S2 shows the structure parameters. A better fit was obtained than for the one-phase analysis. The lattice constant from the analysis of the second phase was around 0.42 nm, which is thought to be a valid value as a lattice constant for MgO. At this time, the result that around 25 mol\% of MgO remained was obtained for the \( x = 0 \) sample. Table 3 shows the parameters for each sample after analysis. From this result, the value for MgO increased as the amount of Ni substitution increased, and at \( x = 0.2 \) the proportion of subphases became larger than the main phase. Because of this, it is thought that a deviation from the composition of the target substance occurred, and Mg, V, and Ni did not follow the mixing composition. Table 4 shows the distortion parameters \( \lambda \) and \( \sigma^2 \) and the bond valence sums (BVS) for the octahedral MO_6 computed for the analyzed spinel phase. As the value of \( x \) increased, the values of \( \lambda \) and \( \sigma^2 \) decreased. From this result, it is thought that the crystal structure is stabilized by Ni substitution. The BVS decreased as \( x \) increased, which is thought to be the effect of substitution with low-valence Ni. Furthermore, the fact that the BVS is lower than 3 is thought to be because of synthesis in a vacuum furnace.

From the results of the two-phase analysis in the Rietveld analysis, the electron density distribution was found by applying the MEM to the spinel phase. Figure 4 shows the electron density line profiles between the 8a and 32e sites and between the 16d and 32e sites. When the two profiles are compared, the electron density decreases more between the 8a and 32e sites, and the ion binding becomes stronger between the 8a and 32e sites, and it is thought that it is easy for Mg to desorb from the 8a site. Furthermore, the electron density decreases the most in the \( x = 0.1 \) sample, and the Mg-O ion binding is stronger, and it is thought that desorption of Mg is promoted. Furthermore, when the electron densities between the 16d and 32e sites are compared, the electron density is higher in the \( x = 0 \) and \( x = 0.1 \) samples, and since this means that the covalent binding strength is higher, the structure is thought to be stable. Because of this, it is thought that stable cycles were realized in the \( x = 0.1 \) sample.

3.3 Electrode properties

Figure 5 shows the results of charge and discharge experiments for different amounts of Ni substitution. As can be seen in this figure, the first charge capacities were very low in all the samples, indicating the small desorption amount of Mg^{2+}. On the other hand, Mg^{2+} insertion amounts at the first discharging process exceed the desorption amounts because Mg^{2+} could be inserted into the vacant space of the spinel structure. At subsequent cycles, reversible charging and discharging was repeated in each sample. If we assume that V and Ni are oxidized up to pentavalent and tetravalent, respectively. The theoretical charge capacities of the samples are
3.4 Study of the valence of the transition metal elements

In order to study the valences of V and Ni in each sample, XAFS measurements were performed, and a comparison of the resulting XANES was performed. Figure 7 shows a comparison of the XANES spectra for V and Ni in the powder samples. Note that V2O3, VO2, V2O5 and NiO, LiNiO2 were used as the reference materials.

Consider the valence of V in the $x = 0$ sample from the perspective of charge compensation. If we consider that the composition of Mg2 is 1.5, and the composition of O2$^-$ is 4, then the valence of V can be estimated to be V$^{3.33}$. Furthermore, if Ni$^{2+}$ is substituted for V, then in order to maintain electrical neutrality, the valence of V can be estimated to be V$^{3.43}$. Figure 7(b) shows an enlargement of the area inside the red frame in Fig. 7(a). The dotted line shows the reference material. Since each sample is between the trivalent and tetravalent standard materials, this suggests that the

![Graph showing Rietveld refinement patterns for Mg(Mg0.5V1.5)O4 obtained using synchrotron X-ray powder diffraction. Plus marks correspond to observed synchrotron X-ray diffraction patterns [BL19B2] and the solid line represents calculated intensities. The vertical marks indicate positions of allowed Bragg reflections. The curve at the bottom is the difference between the observed and calculated intensities on the same scale. (a) Structure of Fd3m, (b) structure of Fd3m, (c) and two-phase analysis of Mg(Mg0.5V1.5)$-\times$O4 with Fd3m and MgO with Fd3m.](image)

Table 2. Final results of Rietveld refinements for the Mg(Mg0.5V1.5-Ni)xO4 structure of Fd3m by synchrotron X-ray powder diffraction.

<table>
<thead>
<tr>
<th>Lattice constant</th>
<th>$x = 0$</th>
<th>$x = 0.1$</th>
<th>$x = 0.2$</th>
<th>$x = 0.3$</th>
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</thead>
<tbody>
<tr>
<td>$a$/nm</td>
<td>0.840331(8)</td>
<td>0.84074(1)</td>
<td>0.84117(1)</td>
<td>0.846019(5)</td>
</tr>
<tr>
<td>8$\alpha$ Mg1(g)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(0, 0, 0)</td>
<td>0.77(2)</td>
<td>1.08(3)</td>
<td>1.34(4)</td>
<td>1.35(5)</td>
</tr>
<tr>
<td>16d Mg2(g)</td>
<td>0.257</td>
<td>0.263</td>
<td>0.271</td>
<td>0.244</td>
</tr>
<tr>
<td>(5/8, 5/8, 5/8)</td>
<td>0.744</td>
<td>0.689</td>
<td>0.639</td>
<td>0.624</td>
</tr>
<tr>
<td>V(g)</td>
<td>0.049</td>
<td>0.0839</td>
<td>0.136</td>
<td></td>
</tr>
<tr>
<td>Ni(g)</td>
<td>0.145(9)</td>
<td>0.10(1)</td>
<td>0.191</td>
<td>0.10(1)</td>
</tr>
<tr>
<td>$x$</td>
<td>0.3851(1)</td>
<td>0.3840(1)</td>
<td>0.3832(1)</td>
<td>0.3826(1)</td>
</tr>
<tr>
<td>$x$, $x$, $x$</td>
<td>0.49(2)</td>
<td>0.136(3)</td>
<td>0.32(4)</td>
<td>0.18(4)</td>
</tr>
<tr>
<td>$R_{wp}$/%</td>
<td>8.75</td>
<td>11.6</td>
<td>14.0</td>
<td>15.9</td>
</tr>
<tr>
<td>$R_p$/%</td>
<td>5.73</td>
<td>8.38</td>
<td>9.64</td>
<td>10.4</td>
</tr>
<tr>
<td>$R_f$/%</td>
<td>3.68</td>
<td>3.16</td>
<td>3.79</td>
<td>4.19</td>
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Table 3. Final results of Rietveld refinements for Mg(Mg$_{0.5}$V$_{1.5-x}$Ni$_x$)$_2$O$_4$ and MgO by synchrotron X-ray diffraction.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice constant</th>
<th>a/Å</th>
<th>R$_{wp}$/%</th>
<th>R$_{B}$/%</th>
<th>R$_{fact}$/%</th>
<th>BVS</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0</td>
<td>(Mg, V)-O$_6$</td>
<td>1.007</td>
<td>26.82</td>
<td>2.75</td>
<td>6.37</td>
<td>0.77(2)</td>
</tr>
<tr>
<td>x = 0.1</td>
<td>(Mg, V, Ni)-O$_6$</td>
<td>1.006</td>
<td>21.07</td>
<td>2.68</td>
<td>4.33</td>
<td>1.14(3)</td>
</tr>
<tr>
<td>x = 0.2</td>
<td>(Mg, V, Ni)-O$_6$</td>
<td>1.005</td>
<td>17.62</td>
<td>2.58</td>
<td>3.67</td>
<td>1.20(2)</td>
</tr>
<tr>
<td>x = 0.3</td>
<td>(Mg, V, Ni)-O$_6$</td>
<td>1.004</td>
<td>14.78</td>
<td>2.53</td>
<td>3.57</td>
<td>0.53(3)</td>
</tr>
</tbody>
</table>

valence of V is between V$^{3+}$ and V$^{4+}$. When the peak shift near 5477 eV is compared between $x = 0$, $x = 0.1$, and $x = 0.2$, it is found that spectra for $x = 0.1$ and $x = 0.2$, which are expected to have a higher valence for V, are on the lower energy side than the spectra for $x = 0$. This is thought to be because unreacted material remained, which caused a deviation in the composition and reduced the valence of V. We now discuss the results of element mapping for $x = 0.2$ in Fig. 2. Since the composition rate of some particle is Mg:V:Ni = 1.25:1.68:0.07, it was determined stoichiometrically to be Mg$_{1.25}$V$_{1.68}$Ni$_{0.07}$O$_4$. The valence of V at this time was calculated to be V$^{3+}$. The positional relationship of the spectrum is thought to have exhibited a shift to the low energy side, as shown in Fig. 7(b), because of this. Furthermore, when the V spectra of $x = 0.1$ and $x = 0.2$ were compared, it was found that the peak near 5477 eV is slightly on the higher energy side for $x = 0.2$. This is thought to be because a slight difference in the amount of Ni substitution in the main phase was observed in samples with a large Ni mixing composition, increasing the valence of V. Figure 7(c) shows the XANES spectra for Ni, and an enlargement of the area in the red frame is shown in Fig. 7(d). When the peak shift near 8340 eV is compared, since the $x = 0.1$ and $x = 0.2$ samples have the same position as the valence 2 reference materials, Ni$^{2+}$ is thought to exist.
In order to investigate the valences of the transition metals depending on charging and discharging, XAFS measurement of the electrodes was performed after charging and after discharging, and the XANES were compared. Figure 8 shows the sample after the initial charge compared to the powder state for \( x = 0.1 \). Figure 8(a) shows the XANES spectra for V after the initial charge for \( x = 0.1 \), and Fig. 8(b) shows an enlargement of Fig. 8(a). When the sample after initial charge was compared to the powder state peak, the peak position near 8344 eV was found to be shifted slightly to the higher energy side. This is thought to arise from desorption of Mg\(^{2+}\), which suggests that V is oxidized during charging. Furthermore, Fig. 8(c) shows the XANES spectra of Ni and Fig. 8(d) shows an enlargement of Fig. 8(c). When the peak shift near 8340 eV is compared, since the valence of Ni does not change and remains virtually divalent even after charging, it is thought that oxidation of Ni does not contribute to the initial charging. Figure S1 shows a comparison of the XANES spectra of the powder state and after four discharge cycles for \( x = 0.2 \). Figure S1(a) shows the XANES spectra for V, (b) shows an enlargement of (a), (c) shows the XANES spectra for Ni, and (d) shows an enlargement of (c). Compared to the powder state, both the V and Ni spectra are found to be shifted to the low energy side. This is thought to arise from the intercalation of Mg\(^{2+}\), which suggests that reduction of V and Ni contributes to discharging as the cycles increase.

4. Conclusions

Ni substitution was performed into a spinel type compound containing V, and characterization and evaluation of the battery characteristics were performed. Rietveld analysis on synchrotron X-ray diffraction data suggested that MgO, which is a starting material, remains in the samples. The proportion is around 25\% in Mg(Mg\(_{0.5}\)V\(_{1.5}\)Ni\(_{0.1}\))O\(_4\), and the proportion of MgO increased with the amount of Ni substitution. In terms of battery characteristics, charging and discharging was able to be performed repeatedly on all of the samples, and it was confirmed that reversible charging and discharging could be performed on Ni substituted samples. Furthermore, in the Mg(Mg\(_{0.5}\)V\(_{1.5}\)Ni\(_{0.1}\))O\(_4\)
sample, Mg desorbs easily from the 8a site, which may stabilize the structure of the 16d-32e site, and this sample exhibited the best cycle characteristics and 19 cycles of charging and discharging were performed. The Coulomb efficiency was roughly 1, and the capacity retention rate increased with the number of cycles. At this time the discharge capacity of the 19th cycle was 66 mAh/g, and the energy density was 142 Wh/kg. Since the XANES spectra of the powder samples and electrodes after discharge showed that redox of V occurred with charging, this showed that oxidation of V contributed to desorption of Mg in the first charging. The above indicates that the Mg(Mg0.5V1.4Ni0.1)O4 fabricated in this work is a candidate for a magnesium rechargeable battery cathode material that has good battery characteristics.

Figure 7. XANES spectra observed at (a) V K-edge, (b) the magnified patterns of (a), (c) Ni K-edge, and (d) the magnified patterns of (c) for Mg(Mg0.5V1.5−xNi0.1)O4 (x = 0, 0.1, 0.2, 0.3). − x = 0, − − − x = 0.1, − − − − x = 0.2.

Figure 8. XANES spectra observed at (a) V K-edge, (b) the magnified patterns of (a), (c) Ni K-edge, and (d) the magnified patterns of (c) for Mg(Mg0.5V1.5−xNi0.1)O4 and 1st charge. − Mg(Mg0.5V1.4Ni0.1)O4, 1st charge.
Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.19-00031.

Acknowledgments

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References