Electrochemical Properties and Crystal and Electronic Structures of Spinel 
$\alpha$MgCo$_{2-x}$Mn$_x$O$_4$-(1 − $\alpha$)Mg(Mg$_{0.33}$V$_{1.67-y}$Ni$_y$)$_4$O$_4$ for Magnesium Secondary Batteries

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Electrochemical Properties and Crystal and Electronic Structures of Spinel 
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Abstract

In the present study, $\alpha\text{MgCo}_{1.5}\text{Mn}_{0.5}\text{O}_4-(1-\alpha)\text{Mg}_{1.33}\text{V}_{1.57}\text{Ni}_{0.1}\text{O}_4$ was synthesized by a reverse co-precipitation method. The products were assigned to a spinel structure with a space group Fd-3m based on powder X-ray diffraction analysis. Inductively coupled plasma atomic emission spectroscopy revealed that the composition was not close to the target composition; the Mg content was higher and the V content was lower than expected. Charge/discharge cyclic tests showed that the discharge capacity exceeded 180 mAh g$^{-1}$ and that the cyclability was reversible up to 60 cycles at 90 °C with a cut-off voltage of 0.945 to -1.055 V vs. Ag/Ag$^+$ (3.545 V - 1.545 V vs. Mg/Mg$^{2+}$) for $\alpha=0.3$. The electronic structure was analyzed using the maximum-entropy method based on a Rietveld analysis, and it was found that Mg insertion was easier for $\alpha=0.3, 0.5, 0.9$ than for $\text{MgCo}_{1.5}\text{Mn}_{0.5}\text{O}_4$ and $\text{Mg}_{1.33}\text{V}_{1.57}\text{Ni}_{0.1}\text{O}_4$. The strain in MO$_6$ octahedra for $\alpha=0.1, 0.3, 0.5, 0.7$ was smaller than that for $\text{MgCo}_{1.5}\text{Mn}_{0.5}\text{O}_4$ and $\text{Mg}_{1.33}\text{V}_{1.57}\text{Ni}_{0.1}\text{O}_4$, which suggests that the host structure was stabilized by forming a solid solution. A Rietveld analysis after the first discharge and second charge confirmed a partly reversible phase transition from the spinel phase to a rock-salt phase. The valence of the transition metals was examined by X-ray absorption fine structure (XAFS) measurements, and the Co and Mn K-edge spectra revealed that Co and Mn were present as Co$^{2.67+}$ to Co$^{2+}$ and Mn$^{4+}$ to Mn$^{3+}$ species for $\alpha=0.3$. Both Co and Mn redox processes are considered to contribute to Mg intercalation. Extended XAFS (EXAFS) Co K-edge and Mn K-edge spectra for the powder specimens and after the first discharge and second charge showed that bonds between Co, V atoms and nearest-neighbor O atoms were distorted after the first discharge, and that this distortion was relaxed after the second charge.

Keywords: Magnesium Secondary Battery; Cathode; Crystal Structure; Electrochemical Properties;
1. Introduction

In recent years, the demand for high-energy-density and highly safe secondary batteries has risen not only for small devices such as smart phones and laptops, but also for large equipment such as electric automobiles, and consequently, high-performance next-generation secondary batteries are being developed.

Secondary batteries that use magnesium as a carrier have been a particular area of focus. The advantages of using magnesium are that it has a high capacity (2205 mAh g\(^{-1}\), 3832 mAh cm\(^{-3}\)) and a negative electrode potential (-2.356V vs. SHE), that as the 8th most abundant metal in the Earth it has cost advantages, and that unlike Li, Mg does not form dendrites, and therefore, Mg metal can be used as an anode. In addition, from a safety perspective, Mg forms a nonconductive film on its surface, and consequently does not react with water. However, because this film is a barrier to Mg ion mobility, it hinders reversible dissolution and deposition.\(^1\) According to research by Aurbach et al.,\(^2\) ether-based electrolytes such as Grignard reagent and aluminum salt dissolved in tetrahydrofuran (THF), in combination with an Mo\(_6\)S\(_8\) Chevrel phase can dissolve and deposit magnesium and exhibit high coulombic efficiency. Chevrel compounds\(^3\) such as V\(_2\)O\(_5\),\(^4\) MnO\(_2\),\(^5\) have been reported thus far; however, there are issues regarding cycling characteristics and battery voltage.

One potential candidate for practical applications is spinel MgM\(_2\)O\(_4\), where Mg occupies the 8\(a\) sites, and M occupies the 16\(d\) sites. The 3\(d\) transition metals mainly used as redox species include Mn,\(^6\) Co,\(^6\) and V.\(^7\) A synthesis method for MgV\(_2\)O\(_4\) and Mg-superabundant Mg\(_{1.5}\)V\(_{1.5}\)O\(_4\), and their battery characteristics have been reported.\(^7\) It was found that there was a high probability that unreacted MgO was present in the Mg\(_{1.5}\)V\(_{1.5}\)O\(_4\), and a reappraisal of the Mg/V ratio was needed. The authors synthesized Mg\(_{1.27}\)V\(_{1.67}\)Ni\(_y\)O\(_4\)(y=0, 0.1, 0.2, 0.33)\(^8\) in which the Mg/V ratio in Mg(Mg\(_{0.5}\)V\(_{1.5-x}\)Ni\(_x\))O\(_4\)(x = 0, 0.1, 0.2, 0.3)\(^9\) was changed, and Ni substitution was carried out. While it was reported that 14 cycles of stable charging and discharging could be performed, the weight energy density at the time of initial discharge was 212 Wh/kg, and a high energy density exceeding that of lithium-ion battery cathode materials was not obtained. MgCo\(_2\)O\(_4\) has been a point of focus for Mg/Co spinels,\(^10\)-\(^12\) and because Co is a redox species, high-potential and high-capacity electrochemical properties have been reported.\(^12\) Synthesis of MgCo\(_2\)O\(_4\) by reverse co-precipitation, and the resulting battery characteristics have been reported, but since there is a problem with Mg and Co cation mixing, highly reversible battery characteristics have not been obtained.\(^11\) To reduce cation mixing, we previously reported that by synthesizing MgCo\(_{2-x}\)Mn\(_x\)O\(_4\), in which a controlled amount of Mn was substituted into MgCo\(_2\)O\(_4\), an initial discharge capacity of 140 mAh/g was exhibited for samples with x=0.4.\(^13,14\) We also synthesized Mg\(_{1.4}\)Co\(_{2-x}\)Mn\(_x\)O\(_4\) with an excess Mg content and found that the most favorable battery characteristics were
exhibited for samples with x=0.5, with an initial discharge capacity of 220 mAh/g (weight energy density: 515 Wh/kg).\textsuperscript{15} With increasing Mg content, the Mg occupancy along the diffusion path containing 8a sites increased, and the amount of Co cation mixing decreased. However, there was a problem in that the discharge capacity decreased beginning at the second cycle. Therefore, there is a need to investigate novel secondary battery cathode materials in which Mg ions can be reversibly intercalated and desorbed, and which have a high energy density.

In order to utilize the advantages of both MgCo\textsubscript{2-x}Mn\textsubscript{x}O\textsubscript{4} and Mg\textsubscript{1.33}V\textsubscript{1.67-\textit{y}}Ni\textsubscript{\textit{y}}O\textsubscript{4}, and to investigate systems that have high capacity and high cycling characteristics, spinel type solid solutions of \(\alpha\text{MgCo}_{1.33}\text{Mn}_{0.5}\text{O}_{4}-\left(1-\alpha\right)\text{Mg}\left(\text{Mg}_{0.33}\text{V}_{1.57}\text{Ni}_{0.1}\right)\text{O}_{4}\) (\(\alpha = 0.1, 0.3, 0.5, 0.7, 0.9\)) were synthesized as novel cathode materials, and their battery characteristics were evaluated. In addition, average structure analyses using synchrotron X-ray diffraction and XAFS analyses were performed on pristine electrodes and electrodes before and after charge/discharge testing. The relationship between the battery characteristics and the crystal and electronic structure is reported in this paper.
2. Experimental

2.1 Synthesis of samples

Synthesis was performed using the reverse co-precipitation method based on previous reports.\textsuperscript{15} A total of 28 g of sodium carbonate Na\textsubscript{2}CO\textsubscript{3} (99.8\%, Wako Pure Chemical Industries) was dissolved in ion-exchanged water and heated to 70°C. A 1.0 mol/L aqueous solution of magnesium nitrate Mg(NO\textsubscript{3})\textsubscript{2} (Wako Pure Chemical Industries), a 1.0 mol/L aqueous solution of cobalt nitrate Co(NO\textsubscript{3})\textsubscript{2} (Wako Pure Chemical Industries), a 1.0 mol/L aqueous solution of manganese nitrate (Mn(NO\textsubscript{3})\textsubscript{2}) (Wako Pure Chemical Industries), a 1.0 mol/L aqueous solution of vanadium oxide sulfate VO\textsubscript{2}O\textsubscript{4} (Wako Pure Chemical Industries), and a 1.0 mol/L aqueous solution of nickel nitrate Ni(NO\textsubscript{3})\textsubscript{2} (Wako Pure Chemical Industries) were mixed in accordance with the nominal composition ratio and diluted to make 200 mL of solution. This was heated to 70°C and added dropwise to the above sodium carbonate solution while stirring, and then allowed to stand for 30 minutes. After this, the precipitate formed was vacuum filtered, washed with 3 L of 70°C hot water, and dried in a dryer (100°C) for 24 hours to obtain the precursor. The precursor was ground and mixed in a ball mill for 12 hours and fired at 500°C in air for 24 hours to obtain the desired sample.

2.2 Characterization of samples

Phase identification of the synthesized samples was carried out using powder X-ray diffraction (PANalytical Empyrean Cu-K\textalpha, 45 kV, 40 mA). The metal content of the sample was determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Shimadzu ICPE-9000). Particle shape observations, electron diffraction, and elemental mapping were carried out using transmission electron microscopy (JEOL, JEM-2100F, 200 kV, JED-2300T). Crystal structure analysis was carried out by Rietveld refinement (RIETAN-FP)\textsuperscript{16} using the results from synchrotron X-ray diffraction measurements (SPRING-8, BL19B2). In addition, the maximum entropy method (MEM; Dysnomia)\textsuperscript{17} was used to determine the electron density distribution. X-ray absorption fine structure (XAFS) measurements (SPRING-8, BL14B2) were performed, and from analysis of the X-ray absorption near edge structure (XANES), the valence of the transition metals was determined. By examining the X-ray absorption fine structure (EXAFS), the local structural distortion associated with charging and discharging was investigated. Bond lengths were estimated by performing EXAFS fitting. Athena and Artemis\textsuperscript{18} were used for XAFS analysis.

2.3 Electrochemical measurements

Electrochemical measurements were performed using a 3-electrode cell (Toyo System Co.,
To produce the cathode, the synthesized sample, an electroconductive material (SuperC65), and a binding agent (PTFE) were mixed in a 5:5:1 weight ratio. The mixture was pressure bonded to an aluminum mesh at approximately 20 MPa and vacuum-dried overnight at 100°C. For the anode, Mg alloy AZ31 (Mg:Al:Zn = 96:3:1 weight ratio, Fujiisougyou Co., Ltd.) was used. The electrolyte solutions used were 1 mol/L Mg[N(SO$_2$CF$_3$)$_2$]$_2$/triglyme (Kishida Chemical Co., Ltd.) and 0.5 M [Mg(G4)][TFSA]$_2$/P13TFSA. A glass fiber filter (Tokyo Roshi Kaisha, Ltd.) was used for the separator.

Using 1 mol/L Mg[N(SO$_2$CF$_3$)$_2$]$_2$/triglyme (Kishida Chemical Co., Ltd.), the cut-off potential was set taking the end-of-charge voltage to be 0.345 V vs. Ag/Ag$^+$ and the end-of-discharge voltage to be -1.155 V vs. Ag/Ag$^+$ (converting with 0 V vs. Ag/Ag$^+$ = 2.6 V vs. Mg/Mg$^{2+}$, $^{19,20}$ 2.945 V to 1.545 V vs. Mg/Mg$^{2+}$).

Using 0.5M [Mg(G4)][TFSA]$_2$/P13TFSA, the end-of-charge voltage and end-of-discharge voltage were set as follows.

(1) $\alpha$=0.5: -1.155 to 0.845 V vs. Ag/Ag$^+$ (1.445 to 3.445 V vs. Mg/Mg$^{2+}$)

(2) $\alpha$=0.1, 0.3, 0.7, 0.9: -1.055 to 0.945 V vs. Ag/Ag$^+$ (1.545 to 3.545 V vs. Mg/Mg$^{2+}$)

The current density was 5 mA/g, and the C rate corresponded to 0.018 C when $\alpha$ = 0.5. The control times for discharging and charging were each set to 55 hours, and a 5-minute open-circuit time was set between each step. Cell fabrication was carried out inside a glove box under an argon atmosphere. Charge-discharge cycle testing was performed using a charge-discharge device (HJ-SD8, Hokuto Denko) at a constant temperature of 90°C.

3. Results and discussion

3.1 Characterization of samples

Figure 1 shows XRD patterns for samples of $\alpha$MgCo$_{1.5}$Mn$_{0.5}$O$_4$·(1-$\alpha$)Mg$_{1.33}$V$_{1.57}$Ni$_{0.1}$O$_4$ ($\alpha$ = 0.1, 0.3, 0.5, 0.7, 0.9) synthesized by the reverse co-precipitation method. For samples fired at a temperature of 500°C, the peaks were ascribed to the spinel-type space group $Fd\bar{3}m$ in a cubic crystal. The spectral intensity was low and the peaks were broad. The particles synthesized by the reverse co-precipitation method are thought to be very small. It is also found that the relative peak intensities depend on the $\alpha$ value. Since the change is caused by a difference of the site occupancies of the metals at the tetrahedral and octahedral sites, we measured synchrotron X-ray diffraction patterns and performed the Rietveld refinements in the section of 3.3. The lattice constants are described in section 3.3. Table 1 presents the metal content determined by ICP-AES, and Figure S1 shows the target composition and the measured composition. The result of calculations taking the total metallic component content to be 3 was that for $\alpha$= 0.1, 0.3, and 0.5, the Mg content was superabundant and the V content was smaller than intended. Studies were
performed involving increasing the agitation rate, providing an excess concentration of NaCO$_3$ solution as a precipitant, and adding an excess of VOSO$_4$ solution, but the target composition was not obtained. The reason is thought to be that the precipitated V salt dissolved during washing, or that precipitation of V did not occur in accordance with the nominal preparation quantity because the pH at which each metal ion precipitated was different. Next, to evaluate the particles obtained, a quantitative analysis was performed by energy-dispersive X-ray spectroscopy (EDS) on samples with $\alpha=0.5$. The results are presented in Figure 2(a), where the numbers 1 to 5 on the horizontal axis indicate the particle analyzed. Particle 1, particles 2 and 3, and particles 4 and 5 had different compositions. For particle 1, the Mg and V content was smaller than that determined by ICP-AES, whereas the Co and Mn content was higher. Particles 2 and 3 had compositions that were closer to those determined by ICP-AES. In particles 4 and 5, the Co and Mn content was smaller than those determined by ICP-AES, while the Mg and V content was higher. From these results, it is possible that precipitates form selectively as (1) Mg, Co, Mn, and Ni, (2) Mg, Co, Mn, V, and Ni, and (3) Mg, V, and Ni. The reason why the V content was less than the target value is thought to be that particles like those in (3) do not preferentially precipitate.

The particle observation and elemental mapping results are shown in Figure 2(b). In addition, electron diffraction results are shown in Figure 2(c). According to the elemental mapping, Mn is not as uniformly distributed at other elements. In addition, areas where V is more scantily distributed than Co are observed. This is consistent with the results of the quantitative analysis. Also, in the electron diffraction pattern, spots associated with (111) planes in the spinel structure were observed. The presence of Debye-Scherrer rings implies that the sample is polycrystalline. Thus, the co-precipitation method succeeded in synthesizing a single-phase spinel-type oxide.

3.2 Evaluation of battery characteristics

3.2.1 1 mol/L Mg[N(SO$_2$CF$_3$)$_2$]$_2$/triglyme electrolytic solution

The results of charge-discharge testing of samples with $\alpha=0.3$ and 0.5 are presented in section S1, Figure S2.

3.2.2 0.5M [Mg(G4)][TFSA]$_2$/P13TFSA electrolytic solution

The results of charge-discharge testing of samples with $\alpha=0.1$, 0.3, 0.5, 0.7, and 0.9 using 0.5 M [Mg(G4)][TFSA]$_2$/P13TFSA for the electrolytic solution are presented in Figures 3(a) to 3(e). Also, the discharge capacity, coulombic efficiency, and capacity retention for each sample are presented in Figures 3(f) to 3(h).

For all the samples, we tried to desorbed Mg$^{2+}$ from the cathodes and thus started the measurements by a charging process. As discussed in the sections of 3.3 and 3.4, however, it can
be concluded that Mg$^{2+}$ was not desorbed in the first charge process, since the crystal structures were partially converted from the spinel to the rock-salt structures and transition-metal valences were reduced in comparison with the pristine state even after the charging process. Therefore, the capacities at the first discharge may be due to a side reaction. As seen in Fig. 3(a), for $\alpha=0.1$, the initial discharge capacity was 117 mAh/g, and the capacity after 15 cycles decreased to 95 mAh/g. Although the discharge capacity in cycles 2 to 5 was 170 mAh/g to 189 mAh/g, this exceeds the charge capacity, and it is thought that the intercalation of Mg quantity exceeds the amount desorbed. In addition, because the cathode potential became unstable at -1 V (vs. Ag/Ag$^+$) in cycle 5, and at the same time the anode-cathode potential also became unstable, it is possible that side reaction products were formed on the cathode because of excess intercalation of Mg. Subsequently, as shown in Fig. 3(f), the capacity decreased until cycle 15, and it can be seen from Fig. 3(g) that the coulombic efficiency was close to 100%, and that the Mg desorption and intercalation rates became similar.

As seen in Fig. 3(b), for $\alpha=0.3$, the initial discharge capacity was 185 mAh/g, the discharge capacity in cycle 60 was 168 mAh/g, and the capacity retention was 90%. Compared to Figure S1(b), the cycling characteristics greatly improved, and this is thought to be because more Mg can desorb with increasing charging time by expanding in the positive direction to the cut-off potential. Although the discharge capacity in cycles 14 to 16 was large at 252 mAh/g to 191 mAh/g, the discharge capacity exceeded the charge capacity, and the intercalated quantity of Mg exceeded the desorbed quantity, similar to the case for $\alpha=0.1$. In addition, because the cathode potential became unstable with respect to the reference electrode near -1 V (vs. Ag/Ag$^+$) in cycle 14, it is possible that side reaction products were formed on the cathode because of excess intercalation of Mg, similar to the case for $\alpha=0.1$. Subsequently, the capacity decreased compared to the initial discharge capacity; however, the capacity retention stabilized in the 80 to 90% range at cycles 20 to 50, and charging-discharging was repeated. In Fig. 3(g), the coulombic efficiency has a value of 95 to 100% even between cycles 23 to 33, and it is thought that reversible Mg migration was occurring. Subsequently, the coulombic efficiency decreased toward 60 cycles and was 87% at cycle 60. As described in section 3.3, it is possible that a structural change occurred because cycling continued in which the Mg desorption quantity was greater than the intercalation quantity.

As seen in Fig. 3(c), for $\alpha=0.5$ the initial discharge capacity was 110 mAh/g, and the discharge capacity was 120 mAh/g after 24 cycles. Compared to the material presented in section S1, the characteristics improved greatly. This is thought to be because more Mg could desorb with increasing charging time because the cut-off potential became more positive. Although the discharge capacity in cycle 12 exhibited a high value of 154 mAh/g, the discharge capacity exceeded the charge capacity, and it is thought that the intercalated quantity of Mg exceeded the
desorbed quantity, similar to the case for $\alpha=0.1$ and $\alpha=0.3$. In addition, because the cathode potential was unstable with respect to the reference electrode near -1.1 V (vs. Ag/Ag$^+$) in cycle 14, it is possible that side reaction products were formed on the cathode because of excess intercalation of Mg, similar to the case for $\alpha=0.1$ and 0.3. Subsequently, the capacity decreased toward cycle 19.

As seen in Fig. 3(d), for $\alpha=0.7$, the initial discharge capacity was 160 mAh/g, and the discharge capacity after 4 cycles was 124 mAh/g. Although the charge capacity at cycles 2 to 4 exceeded the discharge capacity, the Mg desorption quantity was larger than the intercalation quantity.

In addition, as seen in Fig. 3(e), for $\alpha=0.9$, the initial discharge capacity was 125 mAh/g, and the cathode potential in cycles 2 and 3 became unstable with respect to the reference electrode near -1.1 V (vs. Ag/Ag$^+$). However, the discharge capacity decreased from cycle 2 onward, similar to the end component MgCo$_{2.3}$Mn$_x$O$_4$. Looking at the distortion parameter and electron density distribution presented in section 3.3, both had values that were close to those for the end component, and it is thought that similar charge-discharge behavior was exhibited because the crystal and electronic structures were close to those of the end component.

In Figs. 3(f) and 3(h), for $\alpha=0.1$, 0.3 and 0.5, the capacity retention was similarly 140 to 160%. That is, after producing a discharge capacity that was 1.4 to 1.6 times the initial value, the discharge capacity decreased sharply. The capacity after decreasing when expressed as capacity retention fell to 80% to 100%. In subsequent cycling, behavior similar to that for $\alpha=0.1, 0.3$ was observed, and the coulombic efficiency in Fig. 3(g) came close to 100%. When the discharge capacity suddenly increased as shown in Figure S3, it is possible that side reaction products formed within the cell. It is thought that the discharge capacity decreases, and the charge-discharge behavior changes because the concentration of redox species Co, Mn, and Ni decreases, and an irreversible phase forms.

From the above, the sample with $\alpha=0.3$ exhibited the most favorable battery characteristics, and it became possible to perform 60 cycles of charging and discharging, which exceeds cycle performances at 90 °C exhibited by the end components of MgCo$_{1.5}$Mn$_{0.5}$O$_4$ and the 14 cycles exhibited by the end component Mg(Mg$_{0.33}$V$_{1.57}$Ni$_{0.1}$)O$_4$. The initial discharge capacity was 180 mAh/g, and the energy density was 372 Wh/kg, which greatly exceeds the value of 212 Wh/kg exhibited by Mg(Mg$_{0.33}$V$_{1.57}$Ni$_{0.1}$)O$_4$.

3.3 Crystal structure analysis

To elucidate the primary factors behind the cathode characteristics, Rietveld refinement was carried out using the results of synchrotron X-ray diffraction measurements of powdered samples with $\alpha=0.1, 0.3, 0.5, 0.7$, and $0.9$. Using the spinel structure ($Fd\bar{3}m$) for the structure model, the occupancy rate for each sample was determined by the metal content found from metallic
composition analysis. As linear constraints, the occupancy rate for site 8a was determined such that the total content of Mg, Co, Mn, and Ni was 1, and the occupancy rate for 16d sites was determined such that the total content of Mg, Co, Mn, V, and Ni was 1. The fitting patterns for synchrotron X-ray diffraction measurements for each sample are presented in Figures 4(a) to 4(e). The crystal structure parameters refined from the synchrotron X-ray diffraction patterns are presented in Table 2. A good fit was obtained for each sample from the R-factor values, and cation mixing of Mg, Mn, Co, and Ni was confirmed at 8a sites. The lattice constant decreased with increasing solid solution ratio α. From the results of XANES presented in section 3.4, Co had a valence of 2.67, Mn had a valence of 4, V had a valence of 5, and Ni had a valence of 2. The ionic radius of tetracoordinate Mn with valence 4 was particularly small.\textsuperscript{21} The Mn composition ratio increased as α went from 0.1 to 0.9, and the lattice constant decreased accordingly. From this it became clear that a solid solution was forming when α changed from 0.1 to 0.9.

A high proportion of Mg occupied 8a sites in samples where α=0.1 and 0.3. This is thought to be because there was excess Mg, and it is possible that Mg migrating from 8a sites strongly enhanced the cathode characteristics.

The M (16d)-O\textsubscript{6} octahedral distortion parameters\textsuperscript{22} \( \lambda \) and \( \sigma^2 \) determined by Rietveld refinement and the initial discharge capacity and capacity retention for each sample are shown in Table 3. The distortion parameters \( \lambda \) and \( \sigma^2 \) between 16d-32e when α=0.1 to 0.7 were smaller compared to other samples. Based on this, it is thought the distortion of the host structure in which Mg intercalation and desorption occur is small and stable, and allows high-capacity retention. The electron density distribution was determined by MEM based on the average structure model obtained from Rietveld refinement. Figure 5 shows electron density line profiles between the 8a and 32e sites and between the 16d and 32e sites, and Table 4 presents values for the saddle point of the electron densities for each site. The electron density between the 16d and 32e sites was higher than between the 8a and 32e sites for α=0.3, 0.5 and 0.9, and it can be seen that there was a high degree of covalency. This suggests that the 16d site structure, which is the host structure, is stabilized, and site 8a Mg ions easily diffuse, which is believed to be connected to favorable battery characteristics. Indeed, the samples with α=0.3 and 0.5 showed higher cycle performance than the other samples. Concerning the sample with α=0.9, the high structure distortion (Table 3) may deteriorate the cathode properties. On the other hand, the sample with α=0.1 has high covalency between the 8a and 32e sites, and such a change in the electron density is one of the reasons why the cycle performance of the samples was inferior to the others. From the above results, it is thought that the superiority of samples with α=0.3 and 0.5 resulted from the fact that the M (16d)-O\textsubscript{6} octahedral distortion was small when the samples were made into a powder, and that the electron density structure was beneficial to intercalation and desorption of Mg.
Next, Rietveld refinement was carried out to investigate changes in the electrode crystal structure with $\alpha=0.3$ after the initial discharge, after the cycle 2 discharge and after the cycle 60 discharge. Figures 6(a) to 6(c) show the results of a 2-phase analysis carried out on the spinel phase and the rock-salt phase, and Table 5 presents the crystal structure parameters. In addition, Figure S4 shows the results of a Rietveld refinement, which suggest that Mg intercalates at 16$c$ sites in the spinel phase, and Table S1 presents the crystal structure parameters. A good fit was obtained for each sample from the $R$-factor values. Here, the results of the 2-phase analysis are described. The molar ratio for the rock-salt phase after the initial charge and discharge was 89%, and it can be seen that a phase transition occurred from the spinel phase to the rock-salt phase in the initial discharge. In addition, the lattice constant for the remaining spinel phase increased to 0.839(1) nm compared to the pristine lattice constant of 0.83371(7) nm. This is thought to be because when Mg was intercalated into 16$c$ sites, the transition metal was reduced, and the ionic radius increased.\textsuperscript{21} After the second cycle charge, the spinel phase:rock-salt phase molar ratio was 64%:36%, and the rock-salt phase that increased after discharge again returned to the spinel phase. It is clear from these results that a reversible phase transition occurs in association with charging and discharging. After the 60th cycle discharge, the spinel phase:rock-salt phase molar ratio was 78%:22%, and the fraction of the spinel phase after discharge was larger. As shown in Figs. 3(b) and 3(g), in cycle 33 to 60, cycling continued in which the Mg desorption rate was larger than the intercalation rate, and thereby, Mg at 16$c$ and 8$a$ sites was desorbed. During discharges, Mg was intercalated at 8$a$ and 16$c$ sites, and as a result, it is thought that the majority retained the spinel phase. It is clear from the above that in the $\alpha=0.3$ sample that had the best cycling characteristics, a reversible phase transition occurred in association with charging and discharging.

3.4 Investigation of the valence and local structure of transition metal elements by XAFS

XAFS measurements were carried out to investigate the valence of Co, Mn, V and Ni for electrodes fabricated from powdered samples with $\alpha=0.3$ after the initial discharge and after 2 cycles of charging, and then comparisons were made of the XANES region. Figures 7(a) to 7(d) show a comparison of XANES spectra for the Co K-edge, Mn K-edge, V K-edge, and Ni K-edge regions. The valences of each transition metal for pristine material were Co: 2.67-3, Mn: 4, V: 5, Ni: 2. After the initial discharge, the Co and Mn spectra underwent an energy shift toward a lower valence, and Co and Mn were both reduced to near valence 2. After the second charge cycle, the Co and Mn spectra underwent an energy shift toward higher valence. Co was oxidized to near valence 2.67-3, and Mn was oxidized to near valence 3. The pre-edge peaks for V after the initial discharge and after the second charge cycle were smaller than those for the pristine case. This indicates that V was reduced to a lower valence state during the initial discharge, and no change in valence occurred after the second charge cycle. From the above, it is thought that oxidation and
reduction of Co and Mn contribute to the intercalation and desorption of Mg after the initial discharge.

Next, comparisons were made of the EXAFS region to investigate local structural changes of Co, Mn, V, and Ni. Figures 8(a), 8(b), and 8(c) show a comparison of EXAFS spectra in the Co K-edge, Mn K-edge, and V K-edge regions. Ni was excluded because its content was small and because there was a large amount of noise. A Fourier transform of an EXAFS spectrum represents the radial distribution of electron density as a function of distance from the subject atom. The values on the vertical axis reflect bond distortion, and the larger the value, the more the distortion is relaxed.

Focusing on changes in the distortion of Co-O, Mn-O, and V-O bonds, which are first proximity for each transition metal, it is clear that the Co-O distortion relaxed and the Mn-O and V-O distortions increased after the initial discharge, and that these distortions came close to returning to the powder state after the 2\textsuperscript{nd} charge cycle.

From the above, the reason that the $\alpha=0.3$ sample exhibits high cycling characteristics is thought to be that even in going through the charge-discharge cycle, the sample still had a local structure close to the powder state.

Fitting was performed on the Co K-edge and V K-edge EXAFS spectra, and the Co-O and the V-O bond distances and Debye–Waller factors $\sigma^2$ were estimated. The fitting patterns for the powder samples for each synthesis method and the electrodes after charge-discharge testing are shown in Figure S5, and the bond lengths $r$ estimated from the analysis, the bond lengths $r$ determined by the calculation below, and the Debye–Waller factors $\sigma^2$ are presented in Table 6. To calculate the bond lengths, the valence of the transition metals was estimated from the XANES spectra. Co was taken to be a mixture of valence 2 and valence 3, and V was taken to be valence 5. The bond length for Co was determined by calculating the bond length for valence 2 and the bond length for valence 3 and then combining them so as to achieve a valence of 2.67. The coordination numbers for each metal were taken to be 4 for 8\textit{a} sites and 6 for 16\textit{d} sites, and were determined based on the occupancy rates presented in Table 2. The bond length was calculated by taking the sum of the ionic radii of the transition metal and oxygen.\textsuperscript{21}

The Co-O bond length increased after the initial discharge and decreased after the second charge cycle. This supports the results of the XANES analysis in that when Mg is desorbed and intercalated, Co is oxidized and reduced, respectively, and as a result, the ionic radii correspondingly increase and decrease. In addition, there is general agreement between the $r$ values estimated for Co-O from the analysis and the calculated values, which suggests that the occupancy rates obtained as a result of Rietveld refinement are valid. The V-O bond length increased after the initial discharge, and almost no change was observed after the 2\textsuperscript{nd} charge cycle. This is thought to be because V was reduced during the initial discharge, and its ionic radius
increased. The fact that the XANES pre-edge peak became smaller during the initial discharge suggests that V was reduced to a lower valence, and this is supported by the EXAFS results.

4. Conclusion

The synthesis by reverse co-precipitation of a novel cathode material of the solid solution \( \alpha \text{MgCo}_{1.5}\text{Mn}_{0.5}\text{O}_4 \cdot (1-\alpha)\text{Mg}_{1.33}\text{V}_{1.57}\text{Ni}_{0.1}\text{O}_4 \) \((\alpha=0.1, 0.3, 0.5, 0.7, 0.9)\) was investigated, and the synthesized material was characterized. Electrolyte solutions were investigated by charge-discharge testing using a 3-electrode cell, and battery characteristics were evaluated. In addition, Rietveld refinement was carried out using synchrotron X-ray diffraction measurements, the relationship between the average structure and the battery characteristics was investigated, and the phases present in the cathode were explored after charge and discharge by 2-phase analysis. XAFS measurements were performed to investigate the valence and local structure of transition metals.

The results revealed that each sample had a spinel structure, and ICP-AES indicated that except for V, the samples had mainly the nominal composition ratio. Charge-discharge testing indicated that repeated charging and discharging could be performed for \( \alpha=0.1, 0.3, \) and 0.5, which confirmed that reversible charging and discharging could be achieved. The sample with \( \alpha=0.3 \) exhibited the most favorable battery characteristics, and 60 cycles of charging and discharging could be performed, which exceeds the 14 cycles exhibited by the end component \( \text{Mg(Mg}_{0.33}\text{V}_{1.57}\text{Ni}_{0.1}\text{O}_4 \). The initial discharge capacity was 180 mAh/g, and the energy density was 372 Wh/kg, which greatly exceeds the value of 212 Wh/kg for \( \text{Mg(Mg}_{0.33}\text{V}_{1.57}\text{Ni}_{0.1}\text{O}_4 \). This is thought to stem from the fact that the distortion parameters for the 16\text{d}-32\text{e} host structure were small, and the structure was stable. Additionally, the electron density distribution was such that the covalence of the 8\text{a}-32\text{e} sites on the diffusion path was low, and Mg easily diffused. In addition, from the results of the 2-phase analysis, it was clear that the rock-salt phase increased after the initial discharge, the spinel phase increased after the second charge cycle, and that a reversible phase transition occurred in association with charging and discharging. From the XANES spectra, it was revealed that after the initial discharge, Co and Mn were reduced to near valence 2, that after the second charge cycle, Co was reduced to valence 2.67-3, Mn was reduced to near valence 3, and that the oxidation and reduction of Co and Mn contribute to the intercalation and desorption of Mg. From the EXAFS spectra, it became clear that the Co-O distortion relaxed and the Mn-O and V-O distortions increased after the initial discharge, and that these distortions came close to returning to those for the pristine state after the second charge cycle. It is thought that the reason that the \( \alpha=0.3 \) sample exhibited high cycling characteristics is that even in going through the charge-discharge cycle, the material still had a local structure close to pristine.
From the above, the spinel-type cathode material $\alpha\text{MgCo}_{1.5}\text{Mn}_{0.5}\text{O}_4-(1-\alpha)\text{Mg}_{1.33}\text{V}_{1.57}\text{Ni}_{0.1}\text{O}_4$ had electrochemical characteristics that surpassed those of existing magnesium secondary battery spinel-type cathode materials, and samples with a solid solution ratio of $\alpha=0.3$ had high cycling characteristics with a high initial discharge capacity of 180 mAh/g, and could be reversible charged and discharged for 60 cycles. In addition, the formation of a spinel phase and a rock-salt phase in the charge-discharge process and changes to the local structure were made clear, and new possibilities were found for the practical application of a magnesium secondary battery spinel-type cathode material.

Supporting Information: The Supporting Information is available on the website at DOI: xxxxxxxxxxxxxxx.

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Table caption

Table 1 Metal content of $\alpha$MgCo$_{1.5}$Mn$_{0.5}$O$_4$-(1-$\alpha$)Mg$_{1.33}$V$_{1.57}$Ni$_{0.1}$O$_4$ ($\alpha$=0.1, 0.3, 0.5, 0.7, 0.9) The total metal content is 3.

Table 2 Results of Rietveld refinements for $\alpha$MgCo$_{1.5}$Mn$_{0.5}$O$_4$-(1-$\alpha$)Mg$_{1.33}$V$_{1.57}$Ni$_{0.1}$O$_4$ ($\alpha$=0.1, 0.3, 0.5, 0.7, 0.9) structure of $Fd\bar{3}m$ by synchrotron X-ray powder diffraction.

Table 3 Distortion parameters ($\lambda$, $\sigma^2$) of M(16d)-O$_6$ octahedra and battery properties for $\alpha$MgCo$_{1.5}$Mn$_{0.5}$O$_4$-(1-$\alpha$)Mg$_{1.33}$V$_{1.57}$Ni$_{0.1}$O$_4$ ($\alpha$=0.1, 0.3, 0.5, 0.7, 0.9), MgCo$_{1.5}$Mn$_{0.5}$O$_4$ and Mg$_{1.33}$V$_{1.57}$Ni$_{0.1}$O$_4$.

Table 4 Electron density between 8$a$ and 32$e$ and between 16$d$ and 32$e$ for MgCo$_{1.5}$Mn$_{0.5}$O$_4$-(1-$\alpha$)Mg$_{1.33}$V$_{1.57}$Ni$_{0.1}$O$_4$ ($\alpha$=0.1, 0.3, 0.5, 0.7, 0.9), MgCo$_{1.5}$Mn$_{0.5}$O$_4$ and Mg$_{1.33}$V$_{1.57}$Ni$_{0.1}$O$_4$.

Table 5 Results of Rietveld refinements for MgCo$_{1.5}$Mn$_{0.5}$O$_4$-(1-$\alpha$)Mg$_{1.33}$V$_{1.57}$Ni$_{0.1}$O$_4$ ($\alpha$=0.3) after first discharge, after second charge and after 60th discharge with two phase analysis of $Fd\bar{3}m$ and $Fm\bar{3}m$.

Table 6 EXAFS fitting parameter $\sigma^2$, estimated $r$, expected $r$ for $\alpha$MgCo$_{1.5}$Mn$_{0.5}$O$_4$-(1-$\alpha$)Mg$_{1.33}$V$_{1.57}$Ni$_{0.1}$O$_4$ ($\alpha$=0.3) prepared by reverse co-precipitation method.
Table 1: Metal content of $\alpha\text{MgCo}_{1.3}\text{Mn}_{0.3}\text{O}_{4-(1-\alpha)}\text{Mg}_{1.33}\text{V}_{1.57}\text{Ni}_{0.1}\text{O}_{4}$ ($\alpha=0.1, 0.3, 0.5, 0.7, 0.9$).
The total metal content is 3.

| Sample | Mg     | Co     | Mn     | V     | Ni     |
|--------|--------|--------|--------|-------|--------|
| $\alpha=0.1$ | 1.793(3) | 0.2454 | 0.0455(1) | 0.771(1) | 0.1440(2) |
| Nominal | 1.297 | 0.15 | 0.05 | 1.413 | 0.09 |
| $\alpha=0.3$ | 1.440(1) | 0.5798(6) | 0.1758(2) | 0.7180(2) | 0.08606 |
| Nominal | 1.231 | 0.45 | 0.15 | 1.099 | 0.07 |
| $\alpha=0.5$ | 1.255(3) | 0.7510(9) | 0.289(0) | 0.651(1) | 0.05313(6) |
| Nominal | 1.165 | 0.75 | 0.25 | 0.785 | 0.05 |
| $\alpha=0.7$ | 1.085(0) | 1.152(3) | 0.3604(3) | 0.3698(4) | 0.03217(4) |
| Nominal | 1.099 | 1.05 | 0.35 | 0.471 | 0.03 |
| $\alpha=0.9$ | 0.972(2) | 1.431(2) | 0.446(0) | 0.1405(1) | 0.01052(3) |
| Nominal | 1.033 | 1.35 | 0.45 | 0.157 | 0.01 |
Table 2 Results of Rietveld refinements for $\alpha$MgCo$_{1.33}$Mn$_{0.5}$O$_4$($1-\alpha$)Mg$_{1.33}$V$_{1.57}$Ni$_{0.1}$O$_4$ ($\alpha$=0.1, 0.3, 0.5, 0.7, 0.9) structure of $Fd\bar{3}m$ by synchrotron X-ray powder diffraction.

| Sample | $a$/nm | $a=0.1$ | $a=0.3$ | $a=0.5$ | $a=0.7$ | $a=0.9$ |
|--------|--------|---------|---------|---------|---------|---------|
| Lattice constant | $a$/nm | 0.83371(7) | 0.83185(6) | 0.82380(7) | 0.81980(5) | 0.81668(2) |
| $8a$ | $a$/nm | Mg1(g) | 0.8520 | 0.685 | 0.5535 | 0.4992 | 0.4838 |
| (0, 0, 0) | $a$/nm | Co1(g) | 0.018(2) | 0.1525(1) | 0.201(1) | 0.297(1) | 0.2879(9) |
| Mn1(g) | 0.031(3) | 0.0912(1) | 0.216(2) | 0.183(1) | 0.225(1) |
| Ni1(g) | 0.099(2) | 0.0713(2) | 0.030(1) | 0.021(1) | 0.0025 |
| $10^2 \times B$/nm$^2$ | 2.283 | 1.00(3) | 0.42(2) | 0.44(1) | 0.56(1) |
| $16d$ | $a$/nm | Mg2(g) | 0.4703 | 0.3777 | 0.3512 | 0.2925 | 0.2746 |
| (5/8, 5/8, 5/8) | $a$/nm | Co2(g) | 0.1134 | 0.2136 | 0.2751 | 0.4277 | 0.5310 |
| Mn2(g) | 0.0075 | 0.0423 | 0.0363 | 0.0886 | 0.1121 |
| V2(g) | 0.3855 | 0.359 | 0.3255 | 0.1849 | 0.0785 |
| Ni2(g) | 0.0225 | 0.0074 | 0.0118 | 0.0056 | 0.0037 |
| $10^2 \times B$/nm$^2$ | 1.07(5) | 0.21(4) | 0.20(2) | 0.17(1) | 0.091(7) |
| $32e$ | $a$/nm | x | 0.3710(2) | 0.3702(2) | 0.3778(1) | 0.3792(1) | 0.38501(8) |
| ($x$, $x$, $x$) | $a$/nm | $10^2 \times B$/nm$^2$ | 0.186 | 0.2403(2) | 0.47(3) | 0.22(2) | 0.85(1) |
| $R$-factors | $R_{wp}$/% | 3.92 | 4.46 | 5.51 | 3.74 | 2.98 |
| $R_{p}$/% | 2.98 | 3.38 | 4.41 | 2.95 | 2.39 |
| $R_{c}$/% | 1.05 | 0.78 | 0.68 | 0.80 | 0.95 |
Table 3 Distortion parameters ($\lambda$, $\sigma^2$) of M(16d)-O$_6$ octahedra and battery properties for $\alpha$MgCo$_{1.5}$Mn$_{0.5}$O$_4$-(1-$\alpha$)Mg$_{1.33}$V$_{1.57}$Ni$_{0.1}$O$_4$ ($\alpha$=0.1, 0.3, 0.5, 0.7, 0.9), MgCo$_{1.5}$Mn$_{0.5}$O$_4$ and Mg$_{1.33}$V$_{1.57}$Ni$_{0.1}$O$_4$.

| Sample                        | $\lambda$ | $\sigma^2$/deg$^2$ | Initial discharge capacity (mAh/g) | Capacity retention rate / Number of cycle |
|-------------------------------|-----------|--------------------|-----------------------------------|----------------------------------------|
| Mg(Mg$_{0.33}$V$_{1.57}$Ni$_{0.1}$)O$_4^8$ | 1.008     | 30.35              | 120                               | 131% / 14                             |
| $\alpha$=0.1                  | 1.001     | 3.43               | 70                                | 130% / 17                             |
| $\alpha$=0.3                  | 1.001     | 5.49               | 180                               | 90% / 60                              |
| $\alpha$=0.5                  | 1.002     | 1.90               | 110                               | 106% / 25                             |
| $\alpha$=0.7                  | 1.001     | 4.36               | 160                               | 77% / 5                               |
| $\alpha$=0.9                  | 1.007     | 25.87              | 125                               | 100% / 3                              |
| MgCo$_{1.5}$Mn$_{0.5}$O$_4^{15}$ | 1.007     | 35.37              | 220m                              | 29% / 3                               |
Table 4 Electron density between 8a and 32e and between 16d and 32e for MgCo$_{1.5}$Mn$_{0.5}$O$_4$-(1-$\alpha$)Mg$_{1.33}$V$_{1.57}$Ni$_{0.1}$O$_4$ ($\alpha$=0.1, 0.3, 0.5, 0.7, 0.9), MgCo$_{1.5}$Mn$_{0.5}$O$_4$ and Mg$_{1.33}$V$_{1.57}$Ni$_{0.1}$O$_4$.

| Sample | Saddle point of electron Density / e $\cdot$ Å$^{-3}$ | Between 8a and 32e sites | Between 16d and 32e sites |
|--------|----------------------------------------------------|--------------------------|--------------------------|
| Mg(Mg$_{0.33}$V$_{1.57}$Ni$_{0.1}$)O$_4$ | 0.89 | 1.06 |
| $\alpha$=0.1 | 0.98 | 0.70 |
| $\alpha$=0.3 | 0.48 | 0.78 |
| $\alpha$=0.5 | 0.43 | 0.55 |
| $\alpha$=0.7 | 1.30 | 0.84 |
| $\alpha$=0.9 | 0.46 | 0.88 |
| MgCo$_{1.5}$Mn$_{0.5}$O$_4$ | 0.50 | 0.82 |
Table 5 Results of Rietveld refinements for MgCo$_{1.33}$Mn$_{0.5}$O$_4$-(1-α)Mg$_{1.37}$V$_{1.57}$Ni$_{0.1}$O$_4$ (α=0.3) after first discharge, after second charge, and after 60th discharge with 2-phase analysis of Fd$_3$m and Fm$_3$m.

| Sample       | 1st discharge | 2nd charge | 60th discharge |
|--------------|---------------|------------|----------------|
| $a$/nm       | 0.839(1)      | 0.8398(8)  | 0.848(2)       |
| Mg$_1$(g)    | 0.6850        | 0.6850     | 0.6850         |
| Co$_1$(g)    | 0.1525        | 0.1525     | 0.1525         |
| Mn$_1$(g)    | 0.0911        | 0.0911     | 0.0911         |
| Ni$_1$(g)    | 0.0713        | 0.0713     | 0.0713         |
| $10^2\times B$/nm$^2$ | 1.482 | 1.482 | 1.482 |
| Mg$_2$(g)    | 0.3777        | 0.3777     | 0.3777         |
| Co$_2$(g)    | 0.2136        | 0.2136     | 0.2136         |
| Mn$_2$(g)    | 0.0424        | 0.0424     | 0.0424         |
| V$_2$(g)     | 0.3590        | 0.3590     | 0.3590         |
| Ni(g)        | 0.0074        | 0.0074     | 0.0074         |
| $10^2\times B$/nm$^2$ | 1.095 | 1.095 | 1.095 |
| Mg$_3$(g)    | 0.6100        | 0.6100     | 0.6100         |
| Co$_3$(g)    | 0.1450        | 0.1450     | 0.1450         |
| Mn$_3$(g)    | 0.0439        | 0.0439     | 0.0439         |
| V$_3$(g)     | 0.1795        | 0.1795     | 0.1795         |
| Ni$_3$(g)    | 0.0215        | 0.0215     | 0.0215         |
| $10^2\times B$/nm$^2$ | 0.186 | 0.186 | 0.186 |

Fd$_3$m : Fm$_3$m molar ratio | 0.11:0.89 | 0.64:0.36 | 0.78:0.22
Table 6 EXAFS fitting parameter $\sigma^2$, estimated $r$, expected $r$ for $\alpha$MgCo$_{1.5}$Mn$_{0.5}$O$_{4}$-
(1-\(\alpha\))Mg$_{1.33}$V$_{1.57}$Ni$_{0.1}$O$_{4}$ ($\alpha = 0.3$) prepared by reverse co-precipitation method.

| Metal-O | Sample      | $\sigma^2$(Å$^2$) | estimated $r$(Å) | expected $r$ (Å) |
|---------|-------------|-------------------|------------------|------------------|
| Co-O    | Pristine    | -0.00386          | 1.9168           | 1.95             |
|         | 1st Discharge| -0.00572          | 2.0540           | 2.03             |
|         | 2nd Charge  | -0.98673          | 2.0169           | 2.01             |
| V-O     | Pristine    | 0.00455           | 2.0898           | 1.94             |
|         | 1st Discharge| 0.00446           | 2.1587           | 1.94             |
|         | 2nd Charge  | 0.00331           | 2.1554           | 1.94             |
Figure caption

Fig. 1 Powder X-ray diffraction pattern for $\alpha$MgCo$_{1.5}$Mn$_{0.5}$O$_4$-(1-$\alpha$)Mg$_{1.33}$V$_{1.57}$Ni$_{0.1}$O$_4$ prepared by reverse co-precipitation method. (a): $\alpha$=0.1 (b): $\alpha$=0.3 (c): $\alpha$=0.5 (d): $\alpha$=0.7 (e): $\alpha$=0.9

Fig. 2 (a): Metal composition ratio of $\alpha$MgCo$_{1.5}$Mn$_{0.5}$O$_4$-(1-$\alpha$)Mg$_{1.33}$V$_{1.57}$Ni$_{0.1}$O$_4$($\alpha$=0.5) from EDS and ICP-AES analysis. (b): TEM image and STEM-EDS map. (c): SAED for $\alpha$=0.5 sample.

Fig. 3 Charge-discharge properties of $\alpha$MgCo$_{1.5}$Mn$_{0.5}$O$_4$-(1-$\alpha$)Mg$_{1.33}$V$_{1.57}$Ni$_{0.1}$O$_4$/AZ31/Ag three-electrode cell using 0.3M Mg[Mg(G4)][TFSA]$_2$/P13TFSA electrolyte at 90°C. The working potential is plotted versus the reference electrode potential (Ag/Ag$^+$). The measurements were carried out at a current density of 5 mA/g. (a): $\alpha$=0.1 (b): $\alpha$=0.3 (c): $\alpha$=0.5 (d): $\alpha$=0.7 (e): $\alpha$=0.9 (f) discharge capacity (g) coulombic efficiency (h) capacity retention rate for $\alpha$=0.1, 0.3, 0.5, 0.7, 0.9 samples.

Fig. 4 Rietveld refinement patterns for the $\alpha$MgCo$_{1.5}$Mn$_{0.5}$O$_4$-(1-$\alpha$)Mg$_{1.33}$V$_{1.57}$Ni$_{0.1}$O$_4$ by synchrotron X-ray powder diffraction. Plus marks show observed synchrotron X-ray diffraction patterns [BL19B2] and the solid line represents the 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): $\alpha$=0.1 (b): $\alpha$=0.3 (c): $\alpha$=0.5 (d): $\alpha$=0.7 (e): $\alpha$=0.9

Fig. 5 Line profiles of electron densities between (a) 8$d$-32$e$, (b) 16$d$-32$e$ for $\alpha$MgCo$_{1.5}$Mn$_{0.5}$O$_4$-(1-$\alpha$)Mg$_{1.33}$V$_{1.57}$Ni$_{0.1}$O$_4$($\alpha$=0.1, 0.3, 0.5, 0.7, 0.9).

Fig. 6 Rietveld refinement patterns for $\alpha$MgCo$_{1.5}$Mn$_{0.5}$O$_4$-(1-$\alpha$)Mg$_{1.33}$V$_{1.57}$Ni$_{0.1}$O$_4$($\alpha$=0.3) (a) after first discharge, (b) after second charge, and (c) after 60th discharge by synchrotron X-ray powder diffraction.

Fig. 7 XANES spectra observed at (a) Co K-edge, (b) Mn K-edge, (c) V K-edge and (d) Ni K-edge for pristine material and electrode for $\alpha$MgCo$_{1.5}$Mn$_{0.5}$O$_4$-(1-$\alpha$)Mg$_{1.33}$V$_{1.57}$Ni$_{0.1}$O$_4$($\alpha$=0.3).

Fig. 8 Fourier transforms of EXAFS spectra at (a) Co K-edge, (b) Mn K-edge, (c) V K-edge and (d) Ni K-edge for pristine material and electrode for $\alpha$MgCo$_{1.5}$Mn$_{0.5}$O$_4$-(1-$\alpha$)Mg$_{1.33}$V$_{1.57}$Ni$_{0.1}$O$_4$($\alpha$=0.3).
Fig. 1

Intensity / arb. unit

2θ / degree

111 202 311 400 333 404

(a) (b) (c) (d) (e)
Fig. 2

(a) Metal composition ratio (total: 3)

(b) Mg, Co, Mn, V, Ni ICP analysis

(c) [111] Miller index for crystal plane
Fig. 3

(a) Potential / V vs. Ag/Ag
-0.4 0.0 0.4 0.8 1.2
Capacity / mAh g
0 50 100 150 200 250

(b) Potential / V vs. Mg/Mg^2
-0.4 0.0 0.4 0.8 1.2 1.6 2.0 2.4 2.8 3.2 3.6 4.0
Capacity / mAh g
0 50 100 150 200 250

(c) Potential / V vs. Ag/Ag
-0.4 0.0 0.4 0.8 1.2
Capacity / mAh g
0 50 100 150 200 250

(d) Potential / V vs. Mg/Mg^2
-0.4 0.0 0.4 0.8 1.2 1.6 2.0 2.4 2.8 3.2 3.6 4.0
Capacity / mAh g
0 50 100 150 200 250

(e) Potential / V vs. Ag/Ag
-0.4 0.0 0.4 0.8 1.2
Capacity / mAh g
0 50 100 150 200 250

Legend:
- 1st
- 2nd
- 3rd
- 5th
- 10th
- 15th
- 20th
- 24th
- 30th
- 40th
- 50th
- 60th

(e) c) d)
Fig. 5

Electron Density / e•Å⁻³

Solid line: 8a-32e
Dotted line 16d-32e

α=0.1
α=0.3
α=0.5
α=0.7
α=0.9

Distance from 8a to 32e / Å
Fig. 6

(a) Observed intensities
Calculated intensities
Positions of allowed Bragg reflections of spinel phase
Positions of allowed Bragg reflections of rock salt phase
Difference between the calculated and the observed intensities

(b) Observed intensities
Calculated intensities
Positions of allowed Bragg reflections of spinel phase
Positions of allowed Bragg reflections of rock salt phase
Difference between the calculated and the observed intensities

(c) Observed intensities
Calculated intensities
Positions of allowed Bragg reflections of spinel phase
Positions of allowed Bragg reflections of rock salt phase
Difference between the calculated and the observed intensities
Fig. 7
Fig. 8

Fourier Transform / arb.unit

(a)

(b)

(c)