**Supporting information**

Electrochemical Properties and Crystal and Electronic Structures of Spinel

αMgCo2-xMnxO4-(1-α)Mg(Mg0.33V1.67-yNiy)O4 for Magnesium Secondary Batteries

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Table S1 Final results of Rietveld refinements for MgCo1.5Mn0.5O4-(1-α)Mg1.33V1.57Ni0.1O4 (α=0.3) after first discharge, after second charge and after 60th discharge obtained by one-phase analysis of *Fdm.*

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Sample |  | 1st discharge | 2nd  charge | 60th  discharge |
| *Fd-3m* |  |  |  |  |
| Lattice constant | *a*/nm | 0.8442(1) | 0.8445(1) | 0.8449(8) |
| 8*a* | Mg1(g) | 0.6850 | 0.5571 | 0.2800 |
| (0, 0, 0) | Co1(g) | 0.1525 | 0.1525 | 0.1525 |
|  | Mn1(g) | 0.0911 | 0.0911 | 0.0911 |
|  | Ni1(g) | 0.0713 | 0.0713 | 0.0713 |
|  | 102×*B* /nm2 | 1.482 | 1.482 | 1.482 |
| 16*d* | Mg2(g) | 0.3777 | 0.3777 | 0.3777 |
| (5/8, 5/8, 5/8) | Co2(g) | 0.2136 | 0.2136 | 0.2136 |
|  | Mn2(g) | 0.0424 | 0.0424 | 0.0424 |
|  | V2(g) | 0.3590 | 0.3590 | 0.3590 |
|  | Ni(g) | 0.0074 | 0.0074 | 0.0074 |
|  | 102×*B* /nm2 | 1.095 | 1.095 | 1.095 |
| 16*c* | Mg3(g) | 0.320(7) | 0.034(3) | 0.560(7) |
| (1/8, 1/8, 1/8) | 102×*B* /nm2 | 0.3 |  |  |
| 32*e* | *x* | 0.36940 | 0.36940 | 0.36940 |
| (*x*, *x*, *x*) | 102×*B* /nm2 | 0.186 | 0.186 | 0.186 |
| *R* -factors | *R*wp / % | 5.88 | 5.65 | 5.00 |
|  | *R*p / % | 4.44 | 4.13 | 3.62 |
|  | *R*e / % | 0.76 | 0.76 | 0.74 |



Fig. S1 Comparison of target composition and composition determined by ICP-AES.

Section S1

Battery characterization using 1 mol/L Mg[N(SO2CF3)2]2 / triglyme electrolytic solution

The results of charge-discharge testing performed on samples with α=0.3 and 0.5 are shown in Figures S2(a) and S2(b), and the discharge capacity, coulombic efficiency, and capacity retention are shown in Figures S2(c)-(e). 1.0M Mg(TFSA)2/triglyme was used for the electrolytic solution. The right-hand axis indicates the value converted as 0 V vs. Ag/Ag+ = 2.6 V vs. Mg/Mg2+ based on reported results for the deposition potential of Mg with respect to Ag/Ag+ by cyclic voltammetry (CV).19

As seen in Figure S2(a), for α=0.3, the initial discharge capacity was 70 mAh/g, and the discharge capacity after 11 cycles was 50 mAh/g. The discharge capacity exceeded the charge capacity in cycles 2 and 3. It is thought therefore thought that irreversible capacity developed because the Mg that had been intercalated during discharge was not completely desorbed. In addition, the discharge capacity was small compared to the results presented in Figure 3(b), and this is considered to result either from the initial charge largely not being carried out or from the charge capacity being small. Also, the voltage at the time of initial discharge went to 0 V(vs. Ag/Ag+) because the cord shorted during the measurement. This was repaired, and cycling was continued.

As seen in to Figure S2(b), the initial discharge capacity for α=0.5 had a high value of 150 mAh/g, but the cathode potential during the third discharge was chaotic. This is thought to be because a passivation layer formed on the negative electrode, and Mg migration was inhibited. In addition, there was a large overvoltage for both α=0.3 and 0.5, and initial charging was not effectively carried out.

Therefore, a 0.5M [Mg(G4)][TFSA]2/P13TFSA electrolytic solution was used to evaluate the oxidation resistance, as described in section 3.2.2.

 

(b)

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(a)

)

(e)



(d)

)

(c)

)



Fig. S2 Charge-discharge properties of αMgCo1.5Mn0.5O4-(1-α)Mg1.33V1.57Ni0.1O4/AZ31/Ag three-electrode cell using Mg(TFSA)2/triglyme 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): α=0.3 (b): α=0.5 (c): discharge capacity, (d): coulombic efficiency, (e): capacity retention rate for α=0.3, 0.5.

 

Fig. S3 Photographs of anode and cell interior for αMgCo1.5Mn0.5O4-(1α)Mg1.33V1.57Ni0.1O4 (α=0.3)after 60th discharge.



(a)

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(c)

)

(b)

)



Fig. S4 Rietveld refinement patterns for the αMgCo1.5Mn0.5O4-(1-α)Mg1.33V1.57Ni0.1O4 (α=0.3) (a) after first discharge, (b) after second charge, and (c) after 60th discharge by synchrotron X-ray powder diffraction analysis with one-phase analysis of *Fdm.*

**(1) (2)**

(a)

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(a)

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(b)

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(c)

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(b)

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(c)

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Fig. S5 EXAFS fitting curves for (1) Co K-edge, (2) V K-edge for pristine material and electrode for αMgCo1.5Mn0.5O4-(1-α)Mg1.33V1.57Ni0.1O4 (α= 0.3)prepared by reverse co-precipitation method.

(a): pristine (b): electrode after first discharge (c): electrode after second charge