Electronic Supplementary Information(ESI) for :

Anti-site Mixing Governs Electrochemical Performances of Olivine-type MgMnSiO₄ Cathode for Rechargeable Magnesium Battery

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Experiment of the reported condition of the charge-discharge of the MgMnSiO₄

We try to measure the electrochemical properties of MgMnSiO₄ synthesized by the flux method at 1000 $^{\circ}C^{1}$ on a Cu foil in 0.25 M Mg(AlCl₂EtBu)₂/THF electrolyte. The observed results are shown in **Figure S1**.



Figure S1. Charge–discharge curves of MgMnSiO₄ on a Cu foil current collector in 0.25 M $Mg(AlCl_2EtBu)_2/THF$ electrolyte at 25 °C, 14 μ A cm⁻².

The charge–discharge behavior of MgMnSiO₄ resembles the reported one.¹ However, the redox potential of MgMnSiO₄ are lower than the theoretical values.² We measured the Mn *K*-edge X-Ray absorption spectroscopy (XAS) for both charged and discharged electrodes. The Mn *K*-edge X-Ray absorption near edge structure (XANES) spectra are shown in **Figure S2**.



Figure S2. Mn *K*-edge XANES spectra of Mg_xMnSiO_4 (x = 1.0, 0.75, 0.5, 0.25, 0.0) for (a) charging and (b) discharging.

If the Mn atoms take part in the reduction/oxidation along with magnesium insertion/deinsertion, the Mn *K*-edge XANES spectra would be shifted to lower/higher energies after discharging/charging. However, Mn *K*-edge XANES spectra do not shift with charging/discharging. This behavior indicates that the Mn atoms in MgMnSiO₄ do not contribute to the redox reaction.

For the reported measurements, it is expected that the capacity of MgMnSiO₄ includes subreactions from the components of the composite electrodes. We tested the electrochemical window of the only Cu current collector in the 0.25 M Mg(AlCl₂EtBu)₂/THF solution. **Figure S3** shows the charge–discharge curves of the Cu foil in 0.25 M Mg(AlCl₂EtBu)₂/THF solution.



Figure S3. Charge–discharge behavior of the Cu current collector in 0.25 M $Mg(AlCl_2EtBu)_2/THF$ solution at 25°C, 14 μ A cm⁻².

The results show that the charge–discharge of the Cu current collector resembles the behavior of **Figure S1**. The Cu current collector is not stable in this electrolyte.³

We also confirmed the activity of the MgMnSiO₄ during the potential range of 0.5V - 1.8V vs. Mg²⁺/Mg by using stable current collector in the 0.25 M Mg(AlCl₂EtBu)₂/THF electrolyte. Charge-discharge curves of MgMnSiO₄ synthesized by 450°C onto the stainless steel foil were shown in Figure S4.



Figure S4. Charge–discharge curves of MgMnSiO₄ on a Stainless Steel current collector in 0.25 M Mg(AlCl₂EtBu)₂/THF electrolyte at 25 °C, 14 μ A cm⁻² during the voltage range of 0.5-1.8V vs. Mg²⁺/Mg.

Little capacity which should be caused by capacitance from conductive carbon was observed. These results clearly shows the MgMnSiO₄ was inactive in the voltage range of 0.5 - $1.8 \text{ V vs. Mg}^{2+}/\text{Mg}$.

Determination of the condition for the charge-discharge experiment

Based on theoretical calculation, it is estimated that the potential of MgMnSiO₄ will exceed the electrochemical window of the conventional electrolyte such as a Grignard reagent.² To measure the charge–discharge experiment of MgMnSiO₄, we need a highly stable electrolyte. We selected Mg(TFSA)₂/acetonitrile (AN) as the electrolyte, and measures the electrochemical window of various current collectors. **Figure S5** shows the electrochemical window of the aluminum, stainless steel (SUS), and platinum current collectors. Our results show that platinum is the most stable current collector.



Figure S5. Cyclic voltammograms of various metal electrodes in 0.5 M Mg(TFSA)₂/AN solution at 25 mV s⁻¹; (a) results of aluminum, SUS, and platinum plate ranging from -1.0 to 1.5 V vs. Ag⁺/Ag, and (b) results of SUS, and platinum plate ranging from -1.0 to 2.5 V vs. Ag⁺/Ag.

Finally, we investigated the electrochemical window of the composite electrode without any active material, i.e., the electrode comprising acetylene black, a PTFE binder, and a Pt mesh current collector. **Figure S6** shows the charge–discharge curves of the composite electrode without any active material. The electrochemical window is observed at -1.2 to 1.5 V vs. Ag⁺/Ag (which translates to about 1.3–4.0 V vs. magnesium⁴) without active materials. Hence, we were able to determine the performance of the MgMnSiO₄ cathode.



Figure S6. Charge–discharge curves of the composite electrode without active materials in 0.5 M Mg(TFSA)₂/AN solutions at 55°C. The current density is 20 μ A cm⁻².

SEM observations



Figure S7. SEM images of the MgMnSiO₄ synthesized at various temperatures.



Figure S8. Particle size distributions of the MgMnSiO₄ synthesized at various temperatures.



Figure S9. Average particle size estimated from SEM measurements as a function of the synthesis temperature.

Rietveld refinement



Figure S10. Rietveld refinement of synchrotron X-ray diffraction data for MgMnSiO₄ synthesised at 450°C. Inset shows the refined crystal structure of MgMnSiO₄. Blue and purple polyhedral indicate the SiO₄ tetrahedra and FeO₆ octahedra, respectively. Magnesium atoms are indicated in green.

Table S1. Atomic coordinates, occupancies, and atomic displacement parameters obtained by Rietveld refinement of synchrotron X-ray diffraction data for MgMnSiO₄ synthesised at 450 °C.

Atom	Wickoff site	g	x	у	Z	В
Sil	4c	1.00	0.0920	0.25	0.4244	0.36
O1	4c	1.00	0.0900	0.25	0.7548	0.50
O2	4c	1.00	0.4469	0.25	0.2274	0.48
O3	8d	1.00	0.1629	0.0412	0.2815	0.50
Mg1	4a	0.81	0	0	0	0.42
Mn1	4c	0.81	0.2787	0.25	0.9857	0.42
Mn2	4a	0.19	0	0	0	0.42
Mg2	4c	0.19	0.2787	0.25	0.9857	0.42

 $R_{wp} = 3.04\%$ $R_p = 2.39\%$ $R_e = 1.75\%$ GOF = 1.74



Figure S11. Rietveld refinement of synchrotron X-ray diffraction data for MgMnSiO₄ synthesised at 500 °C.

Atom	Wickoff site	g	x	У	Z	В
 Si1	4c	1.00	0.0917	0.25	0.4248	0.36
01	4c	1.00	0.0914	0.25	0.7500	0.50
O2	4c	1.00	0.4485	0.25	0.226	0.48
O3	8d	1.00	0.1622	0.0422	0.2839	0.50
Mg1	4a	0.78	0	0	0	0.42
Mn1	4c	0.78	0.2792	0.25	0.9854	0.42
Mn2	4a	0.22	0	0	0	0.42
Mg2	4c	0.22	0.2792	0.25	0.9854	0.42

Table S2. Atomic coordinates, occupancies, and atomic displacement parameters obtained by Rietveld refinement of synchrotron X-ray diffraction data for MgMnSiO₄ synthesised at 500 °C.

 $R_{wp} = 2.83\%$ $R_p = 2.19\%$ $R_e = 1.77\%$ GOF = 1.59



synthesised at 700 °C.

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Atom	Wickoff site	g	x	У	Z	В
Si1	4c	1.00	0.0924	0.25	0.4266	0.36
01	4c	1.00	0.0908	0.25	0.7509	0.50
O2	4c	1.00	0.4487	0.25	0.2225	0.48
O3	8d	1.00	0.1628	0.0420	0.2850	0.50

0

0.2798

0

0.2798

0

0.25

0

0.25

0

0.9856

0

0.9856

0.42

0.42

0.42

0.42

Table S3. Atomic coordinates, occupancies, and atomic displacement parameters obtained by Rietveld refinement of synchrotron X-ray diffraction data for MgMnSiO₄ synthesised at 700

 $R_{wp} = 3.02\%$ $R_p = 2.36\%$ $R_p = 2.04\%$ GOF = 1.48

4a

4c

4a

4c

0.70

0.70

0.30

0.30

Mg1

Mn1

Mn2

Mg2



Figure S13. Rietveld refinement of synchrotron X-ray diffraction data for MgMnSiO₄ synthesised at 900 °C.

Table S4. Atomic coordinates, occupancies, and atomic displacement parameters obtained by Rietveld refinement of synchrotron X-ray diffraction data for MgMnSiO₄ synthesised at 900 $^{\circ}$ C.

Atom	Wickoff site	g	x	У	Z	В
Sil	4c	1.00	0.0935	0.25	0.4257	0.36
O1	4c	1.00	0.0895	0.25	0.7561	0.50
O2	4c	1.00	0.4513	0.25	0.2223	0.48
O3	8d	1.00	0.1607	0.0425	0.2837	0.50
Mg1	4a	0.68	0	0	0	0.42
Mn1	4c	0.68	0.2792	0.25	0.9871	0.42
Mn2	4a	0.32	0	0	0	0.42
Mg2	4c	0.32	0.2792	0.25	0.9871	0.42
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 $R_{wp} = 2.68\%$ $R_p = 2.07\%$ $R_e = 1.71\%$ GOF = 1.57



Figure S14. Rietveld refinement of synchrotron X-ray diffraction data for MgMnSiO₄ synthesised at $1000 \,^{\circ}$ C.

Table S5. Atomic coordinates, occupancies, and atomic displacement parameters obtained by Rietveld refinement of synchrotron X-ray diffraction data for MgMnSiO₄ synthesised at 1000 $^{\circ}$ C.

Atom	Wickoff site	g	x	У	Z	В
Sil	4c	1.00	0.0933	0.25	0.4254	0.36
O1	4c	1.00	0.0904	0.25	0.7585	0.50
O2	4c	1.00	0.4527	0.25	0.2227	0.48
O3	8d	1.00	0.1606	0.0404	0.2823	0.50
Mg1	4a	0.67	0	0	0	0.42
Mn1	4c	0.67	0.2794	0.25	0.9876	0.42
Mn2	4a	0.33	0	0	0	0.42
Mg2	4c	0.33	0.2794	0.25	0.9876	0.42

 $R_{wp} = 2.93\%$ $R_p = 2.25\%$ $R_e = 1.49\%$ GOF = 1.96

Annealing Temperature (°C)	Space group	a (Å)	b (Å)	c (Å)	α =β = γ (°)	V (Å ³)
450	Pnma	10.4643(1)	6.1131(1)	4.7971(1)	90	308.87(0)
500	Pnma	10.4527(0)	6.1136(1)	4.7961(1)	90	306.49(0)
700	Pnma	10.4352(2)	6.1158(1)	4.8059(1)	90	306.71(0)
900	Pnma	10.4821(2)	6.1505(2)	4.8273(1)	90	311.22(0)
1000	Pnma	10.4888(3)	6.1536(2)	4.8293(2)	90	311.72(0)

Table S6. Structural parameters obtained from Rietveld refinement of MgMnSiO₄ synthesised at various temperatures

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ex situ XRD

Table S7. Structural parameters	obtained from Levail profile	fitting of Mg_xMnSiO_4 (x = 1.0,
0.9, 0.8, 0.7).		

composition	Space group	a (Å)	b (Å)	c (Å)	<i>α</i> =β =γ (°)	V (Å ³)
MgMnSiO ₄	Pnma	10.4623(4)	6.1159(2)	4.7977(2)	90	306.77(3)
Mg _{0.9} MnSiO ₄	Pnma	10.4514(6)	6.1064(4)	4.7933(3)	90	305.91(4)
Mg _{0.8} MnSiO ₄	Pnma	10.4505(6)	6.1050(3)	4.7930(2)	90	305.79(4)
Mg _{0.7} MnSiO ₄	Pnma	10.4380(3)	6.1030(3)	4.7880(1)	90	305.00(3)
Mg _{0.8} MnSiO ₄	Pnma	10.4642(5)	6.1077(3)	4.7976(2)	90	306.63(4)
Mg _{0.9} MnSiO ₄	Pnma	10.4709(8)	6.1089(5)	4.7983(4)	90	306.92(6)
MgMnSiO ₄	Pnma	10.4782(6)	6.1104(4)	4.8031(3)	90	307.52(4)

ex situ EXAFS : Local structural change of the MgMnSiO₄ during charging process

Local structural changes around the Mn ion during Mg^{2+} extraction were also probed by extended x-ray absorption fine structure (EXAFS) analysis. Fourier transform (FT) magnitudes of k^3 -weighted EXAFS oscillations during charge–discharge processes are shown in **Figure S15**.



Figure S15. Mn-K edge EXAFS spectra of Mg_xMnSiO_4 (x = 1.0, 0.9, 0.8, 0.7) during charging.

The peak position of the FT magnitude spectrum represents the distance between the absorbance atoms and the neighboring scattering atoms, in which the phase shift results in the deviation from the actual bond length. The peak intensity reflects the number of the coordination ions as well as the degree of local distortion. The first main peak at 1.5 Å corresponds to the contribution of the Mn-O shell. During the charging process, the peak intensity decreases, suggesting an increase in the local structural distortion of Mn-O bonds. During charging, the increase in the valency state of the Mn cation imparts distortion to MnO₆ owing to the Jahn-Teller effect of oxidized Mn³⁺ ions. Therefore, changes in the observed local structure imply changes in the oxidation state of Mn cations induced by the extraction of Mg²⁺ in MgMnSiO₄.

References

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