Electronic Supplementary Information

# Mechanism of Mg Extraction from $MgMn_2O_4$ during Acid Digestion

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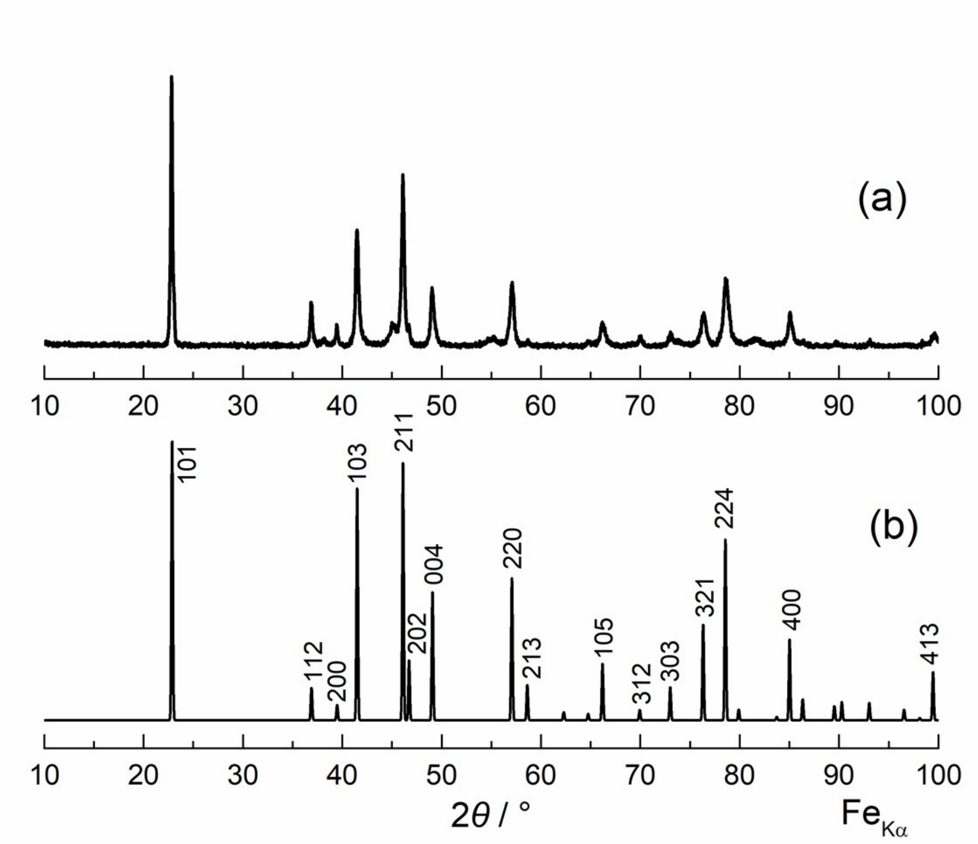


Figure S1. Powder X-ray diffraction patterns of $MgMn_2O_4$: (a) as-prepared and (b) simulated.

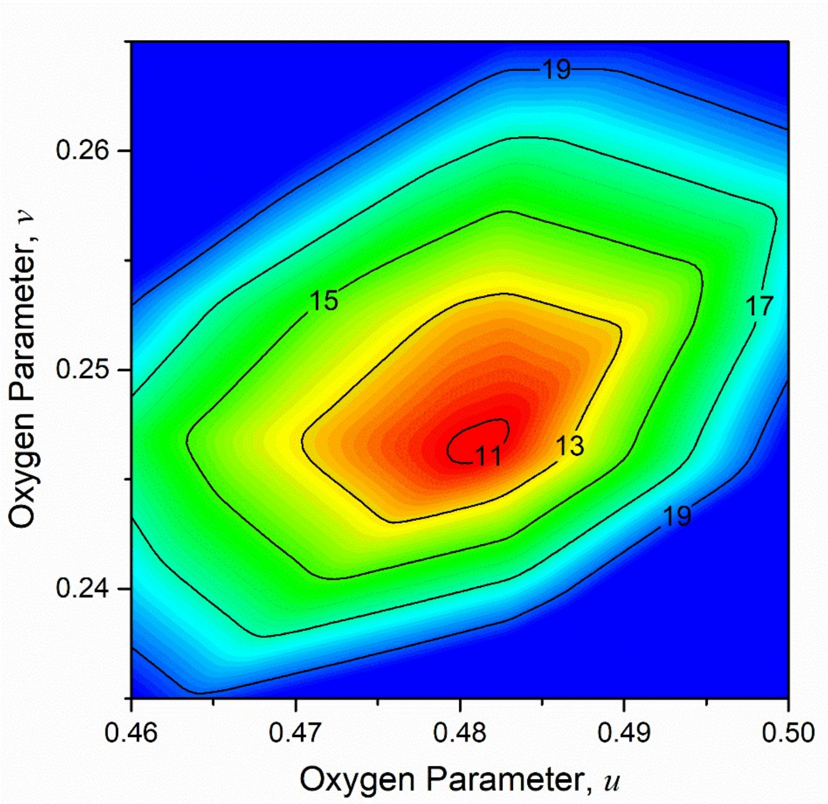


Figure S2. Results of classical Rietveld refinement of $MgMn_2O_4$ assuming a space group of $I4_1/amd$. Reliability factor defined by $\Sigma|I_{obs} - I_{calc}|/\Sigma I_{obs}$, where $I_{obs}$ and $I_{calc}$ are the observed and calculated integrated intensities, respectively, are plotted against two oxygen positional parameters.

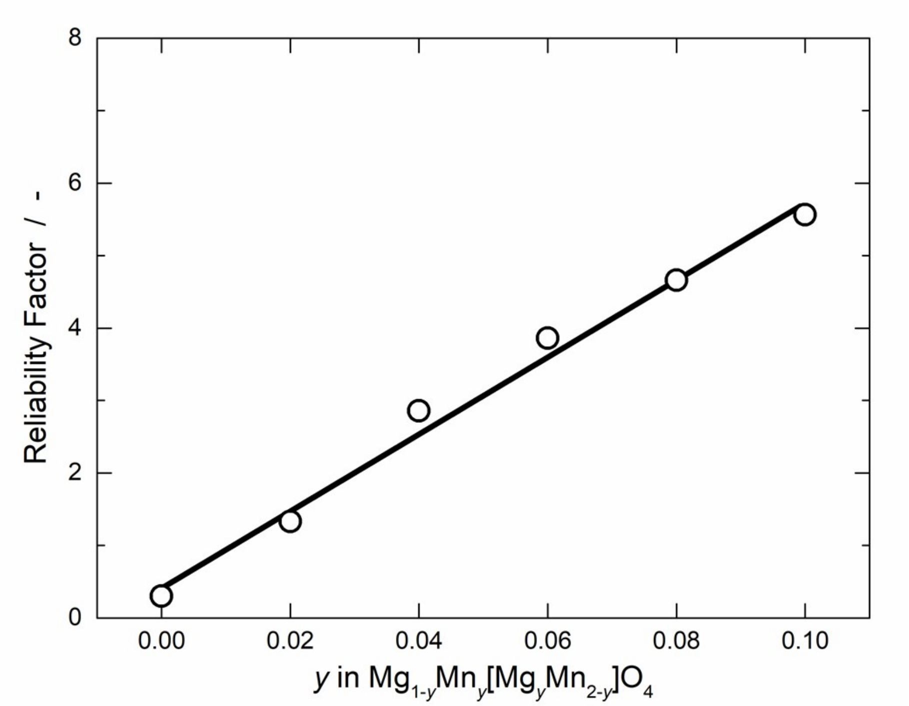


Figure S3. Results of the structural refinement of $MgMn_2O_4$ assuming the replacement with Mn and Mg ions at the tetrahedral and octahedral sites, respectively, i.e., $Mg_{1-y}Mn_y[Mg_yMn_{2-y}]O_4$. The structural refinement was performed by using 112, 200, and 211 diffraction lines. The reliability factor is given by $\Sigma|I_{obs} - I_{calc}|/\Sigma I_{obs}$, where $I_{obs}$ and $I_{calc}$ are the observed and calculated integrated intensities, respectively.

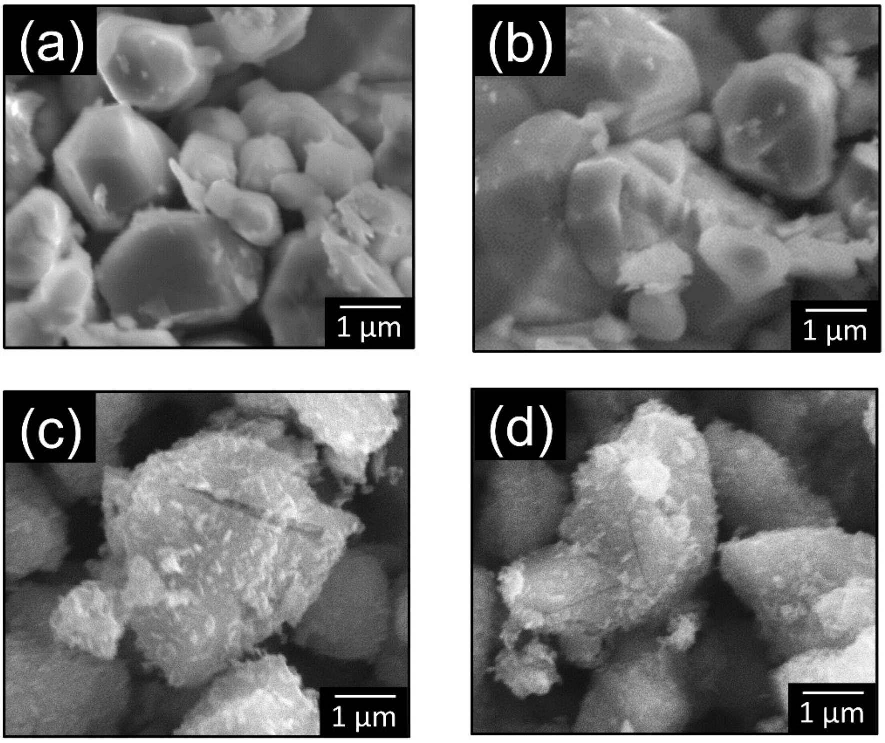


Figure S4. SEM images of $MgMn_2O_4$ (a, b) before and (c, d) after digestion in 1 M $HNO_3$ solution for 16 h.

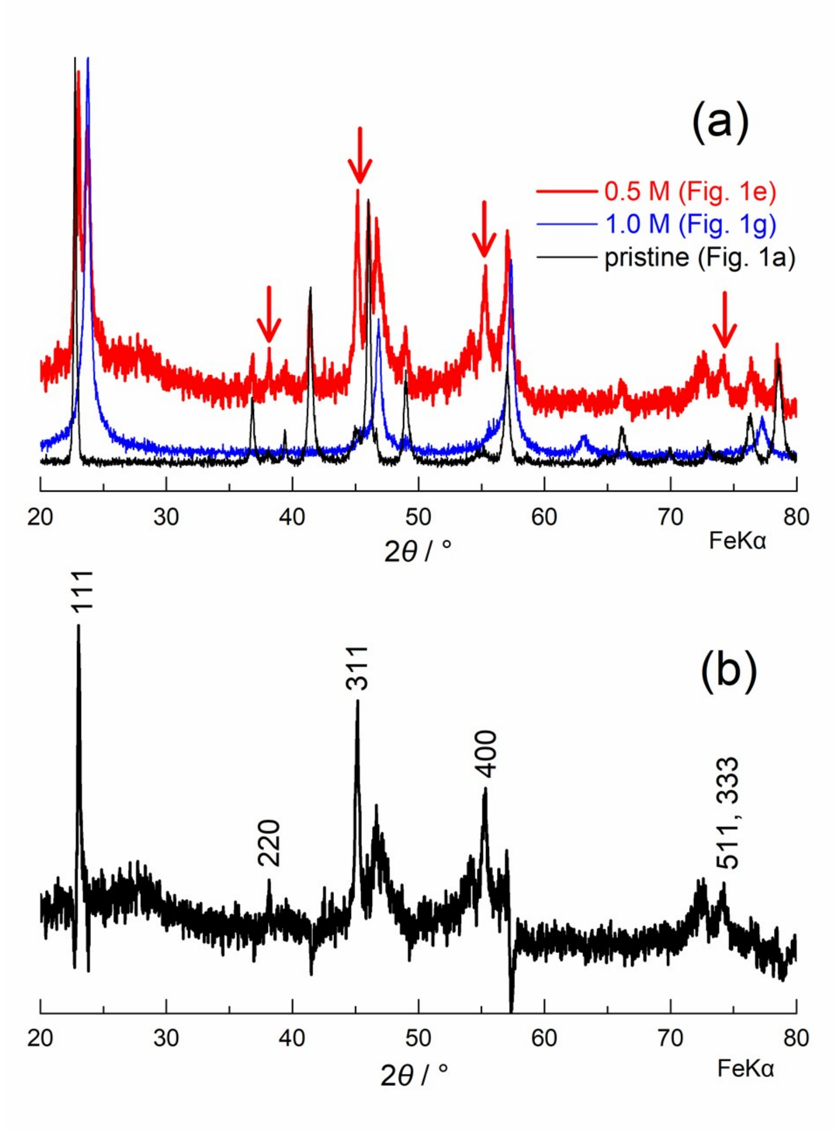


Figure S5. (a) Powder X-ray diffraction patterns of $MgMn_2O_4$ in the pristine state (black) and after acid digestion in 0.5 M (red) and 1.0 M (blue) $HNO_3$ solutions. (b) Difference XRD patterns obtained by point-by-point subtraction of the patterns in Fig. 1a and 1g from that in Fig. 1e.

The calibration curve for determining the phase fraction was produced using the ratio of integrated intensity for the strongest XRD lines of $MgMn_2O_4$ and λ-$MnO_2$.

1. First, XRD patterns were collected for physically mixed samples of the pristine $MgMn_2O_4$ and single-phase λ-$MnO_2$ at a ratio of 3:1, 1:1, or 1:3 by weight. The λ-$MnO_2$ was obtained by treating $MgMn_2O_4$ in 1.0 M $HNO_3$.

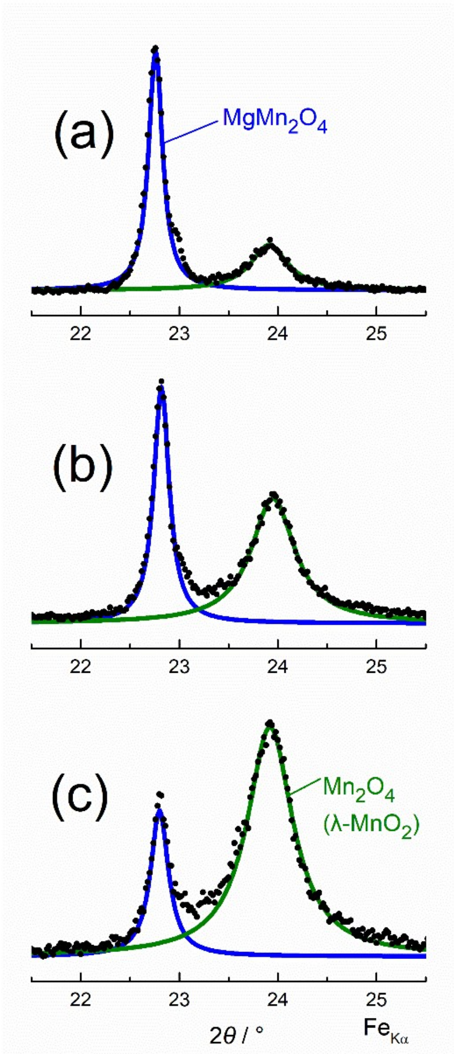


Figure S6. Peak fitting of the XRD lines for mixtures of $MgMn_2O_4$ and λ-$MnO_2$ in the weight ratio of (a) 3:1, (b) 1:1, and (c) 1:3. Black circles: experimental values. Coloured lines: $MgMn_2O_4$ (blue) and λ-$MnO_2$ (green).

2. After peak separation (Figure S6), the integrated intensity was estimated for the main peak of each phase (111 for both $MgMn_2O_4$ and λ-$MnO_2$) in the mixed sample.

3. When the mole fraction of λ-$MnO_2$ in the mixed sample was $x_A$, the relative integrated intensity for λ-$MnO_2$ ($f_A$) was calculated from the integrated intensity of the main peaks of λ-$MnO_2$ and $MgMn_2O_4$ ($I_A$ and $I_B$, respectively).

$$f_A = \frac{x_A I_A}{x_A I_A + (1 - x_A) I_B}$$

The obtained $f_A$ is plotted against $x_A$ in Figure S7.

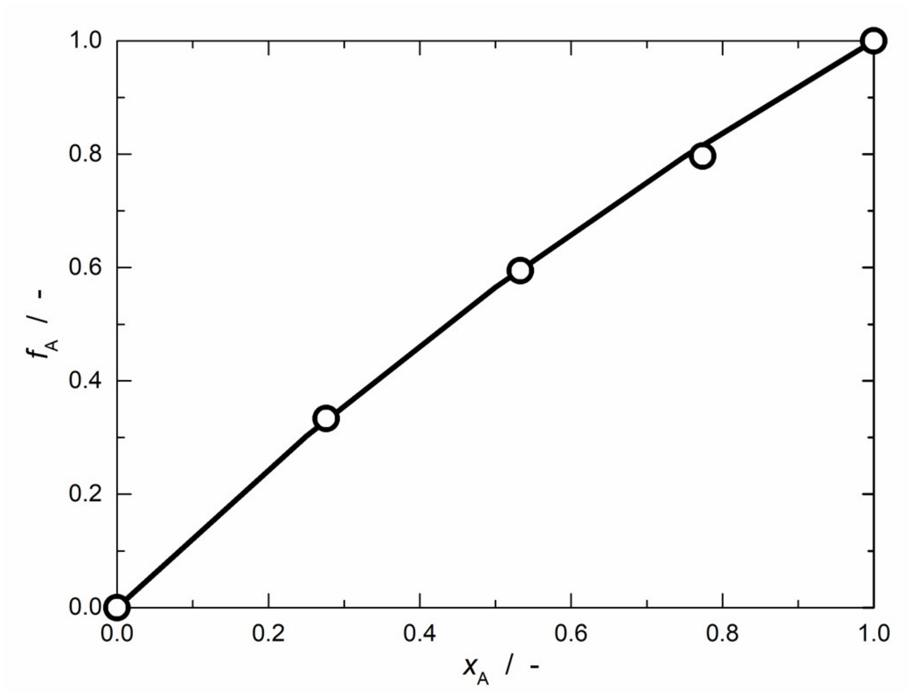


Figure S7. Relative integrated intensity of the 111 diffraction line of λ-$MnO_2$ ($f_A$) determined from the XRD data in Figure S7, versus the mole fraction of λ-$MnO_2$ ($x_A$).

4. To determine the calibration curve, the above equation was rewritten using $\alpha = I_A/I_B$ as follows

$$f_A = \frac{\alpha x}{1 + (1 - \alpha)x}, \quad \alpha = \frac{I_A}{I_B}$$

The calibration curve with a value of $\alpha = 1.3$ (black line in Fig. S8) best describes the data observed for the three mixed samples.

5. Using this calibration curve, the fraction of phases in the acid-digested samples shown in Figs. 7 & 9 was determined from the integrated intensity ratio of the strongest lines.
6. Since single-phase $Mg_{0.5}Mn_2O_4$ could not be obtained, its fraction was calculated in the same manner by assuming that the integrated intensity of its strongest line is intermediate between $MgMn_2O_4$ and $\lambda$-$MnO_2$ ($\alpha = 1.15$)."

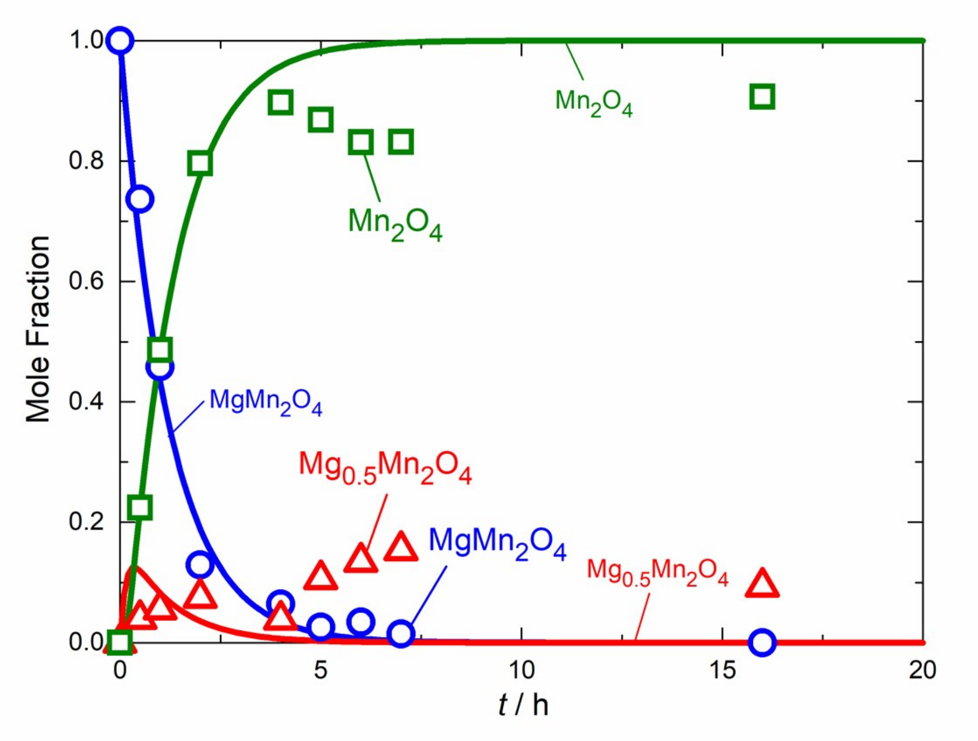


Figure S8. The mole fractions of $MgMn_2O_4$ (blue circles), $Mg_{0.5}Mn_2O_4$ (red triangles), and $Mn_2O_4$ (green squares) as a function of the acid digestion time. Solid curves indicate the fraction of each phase calculated by assuming two-step two-phase reactions (pathways 1 and 2). The data were analysed based on the following differential equations, which were solved numerically.

$$\mathrm{d}f(MgMn_2O_4)/\mathrm{d}t = -k_1 f(MgMn_2O_4)$$

$$\mathrm{d}f(Mg_{0.5}Mn_2O_4)/\mathrm{d}t = k_1 f(MgMn_2O_4) - k_2 f(Mg_{0.5}Mn_2O_4)$$

$$\mathrm{d}f(Mn_2O_4)/\mathrm{d}t = k_2 f(Mg_{0.5}Mn_2O_4)$$

Table S1. Summary of the acid digestion of $MgMn_2O_4$ powder in $HNO_3$ solutions with various concentrations.

| $HNO_3$ | $H^+$ in solution | $Mn^{2+}$ in solution | Residual mass | Fraction by XRD | | | $x$ in $Mg_xMn_2O_4$ |
|---|---|---|---|---|---|---|---|
| M | mmol | mmol | mg | $MgMn_2O_4$ | $Mg_{0.5}Mn_2O_4$ | $□Mn_2O_4$ | |
| 0.1 | 3 | 6.8 | 911 | 94.0 | 6.0 | 0 | 0.97 |
| 0.25 | 7.5 | 19.3 | 774 | 71.4 | 9.3 | 19.3 | 0.76 |
| 0.3 | 9.0 | 25.1 | 729 | 62.9 | 8.6 | 28.4 | 0.67 |
| 0.4 | 12 | 31.7 | 662 | 37.7 | 18.4 | 43.9 | 0.47 |
| 0.5 | 15 | 36.3 | 605 | 14.6 | 24.5 | 60.9 | 0.27 |
| 0.6 | 18 | 42.8 | 512 | 0 | 9.8 | 90.2 | 0.05 |
| 1.0 | 30 | 42.6 | 503 | 0 | 8.2 | 91.8 | 0.04 |