Mechanochemical reduction of manganese dioxide by grinding in organic vapors

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Mechanochemical redox reactions of manganese dioxide with organic vapors have been studied to control the chemical valence (oxidation number) of manganese ions under grinding. Electrolytic-manganese dioxide (EMD) including double chains of edge-sharing MnO_6 -octahedra transforms into $\beta\text{-MnO}_2$ (Pyrolusite) consisting of the single chains under grinding in Ar. The mechanical dissociation of the double chains generates active sites to adsorb the atmospheric $(\text{CH}_3)_2\text{CO}$ vapor and the strongly adsorbed $(\text{CH}_3)_2\text{CO}$ molecules pull out the oxide ions from MnO_2 to reduce Mn^{4+} to Mn^{3+} ions, while $(\text{CH}_3)_2\text{CO}$ is oxidized to CO_2 and H_2O via the intermediate oxidation products, HCOH and CH_3COH . One $(\text{CH}_3)_2\text{CO}$ molecule can reduce 16 MnO_2 units to trivalent $\text{MnO}_{1.5}$ (Bixbyite). However, the decomposition products, CO_2 and H_2O , occupying the adsorption sites dominantly to $(\text{CH}_3)_2\text{CO}$ disturb the redox process. This mechanochemical reduction of MnO_2 can be applied to the synthesis of $\text{LiMn}^{\text{III}}\text{Mn}^{\text{IV}}\text{O}_4$ powder from both combinations of the starting mixtures of $\text{MnO}_2\text{--LiOH}$ and $\text{MnO}_2\text{--Li}_2\text{CO}_3$. Some alcohols and ketones also provide the similar reduction ability.

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1. Introduction

Mechanochemical process based on the enhanced chemical reactivity of finely ground and activated particles under grinding is expected as one of the candidate synthesis routes of inorganic powders.^{1)–3)} This process can be successfully applied to the synthesis of titanates,^{4)–6)} ferrites,^{7)–11)} manganates,¹²⁾ cobaltates,¹³⁾ and others. In these applications, the chemical valence (oxidation number) of the available starting materials is sometimes different from that of the desired products. For example, there are few trivalent nickel and cobalt compounds available for the synthesis of $\text{LiNi}^{\text{III}}\text{O}_2$ and $\text{LaCo}^{\text{III}}\text{O}_3$. For the synthesis of $\text{LiMn}^{\text{III}}\text{Mn}^{\text{IV}}\text{O}_4$, either the partial oxidation of the starting Mn_2O_3 or the partial reduction of the starting MnO_2 is required. Then, if we can control the redox reactions under grinding, the applicability of mechanochemical processes becomes wide.

For the redox processes, there are many available oxidizing reagents such as H_2O_2 , HClO_4 and HNO_3 ,^{8)–10)} but there are a few reducing reagents. Then, the possibility of some organic compounds as the reducing reagent to MnO_2 under grinding has been studied. Under the grinding processes, newly developed solid surface strongly adsorbs environmental gases, vapors and liquids (chemisorption).¹⁾ If the chemisorbed vapors can pull-out oxide ions, the solid materials are reduced. However, few papers describe the reactions of solids with gases under grinding. In the present paper, the effect of Acetone (boiling point, bp = 56.3°C), 2-Butanone (bp = 79.5°C), 3-Propanone (bp = 101.7°C), Methanol (bp = 64.7°C) and Ethanol (bp = 78.3°C) on the reduction of MnO_2 have initially been examined. Then, the process is applied to the synthesis of LiMn_2O_4 as the cathode material for lithium batteries.

2. Experimental

A reagent-grade MnO_2 powder (electrolytic- MnO_2 , EMD with the structural similarity to $\gamma\text{-MnO}_2$, Wako Pure Chemical, Industries, Ltd.) was used after drying for more than 24 h in an air convection oven. The specific surface area (SSA) of the EMD was 30.3 m^2g^{-1} . The EMD (10 g) was encapsulated into the grinding vessel (stainless steel, capacity: 420 cm^3) with grinding media ($\phi 2$ mm- YTZ balls). The fractional filling of the grinding media was fixed at 0.40. The air in the vessel was evacuated and the vapor of the organic compounds was charged from a vaporizer (80–100°C) attached to the gas line kept at 100°C by the use of an Ar gas as the carrier. The amount of distilled Acetone charged was 0 cm^3 (A0, Ar atmosphere), 0.1 cm^3 (A1), 0.2 cm^3 (A2), 0.3 cm^3 (A3), 0.4 cm^3 (A4), 0.5 cm^3 (A5) and 1.0 cm^3 (A10). The EMD powder was planetary-milled (Kurimoto-Tekko-Sho) in these atmospheres at the revolution frequency (f_{rev}) of 6.0 s^{-1} for 3 h with the cooling intervals for 15 min in every 1 h-grinding, where the temperature inside the vessel was kept at 45–50°C. On the assumption of the complete vaporization, partial pressure of Acetone inside the vessel is 11.5 kPa (A1)–115 kPa (A10) at 50°C, while the saturated vapor pressure calculated by Antoine's equation is 81.3 kPa corresponding to 0.71 cm^3 of the charged Acetone. Then, 0.29 cm^3 Acetone is condensed as liquid at the initial grinding stage of A10. The reduction ability of 2-Butanone (B3), 3-Pentanone (P3), Methanol (M3), and Ethanol (E3) was also examined by the same procedure (0.3 cm^3).

For the synthesis of LiMn_2O_4 , stoichiometric mixtures of EMD and the reagent-grade LiOH or Li_2CO_3 (15.0 g as LiMn_2O_4) were encapsulated into the vessel with the grinding media and the atmosphere was substituted to Ar containing 0.5 cm^3 -Acetone. After the mill-treatment at 6 s^{-1} for 3 h, the ground products were sieved (60 mesh) in a grove bag filled with a dry Ar gas and then heat-treated isothermally between 300 and

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900°C in air.

The ground powders were identified by X-ray diffractometry (XRD) with Cu K α radiation and X-ray photoelectron spectrometry (XPS) with Mg K α radiation. The specific surface area (SSA) was determined by a N₂-adsorption BET method. Thermal analyses (TG DTA) was performed at the heating rate of 10 K·min⁻¹ in a flowing air. The morphology was observed by SEM. The gaseous decomposition products were identified by GC-mass, where a small portion of the ground product was sealed into the glass-capsule quickly in the grove bag and the gases were released by heating in the equipment.

3. Results and discussion

3.1 Solid and gaseous products under grinding in Acetone-containing atmosphere

Figure 1 shows the XRD profiles of the ground MnO₂. The γ -MnO₂-like structure of EMD transformed to β -MnO₂ (Pyrolusite) in Ar without containing Acetone (A0). The small amounts of Acetone (A1 and A2) did not reduce MnO₂, but the amorphization of β -MnO₂ progressed. The reduction of MnO₂ to Mn₂O₃ (Bixbyite) was observed when the Acetone content exceeded 0.3 cm³ (A3). The crystallinity of Mn₂O₃ improved with an increase in the Acetone content. The transformation of γ -MnO₂ to β -MnO₂ indicates the dissociation of the double chains of edge-sharing MnO₆-octahedra of EMD and the rearrangement to the single chains as indicated in **Fig. 2**. It is considered that the reduction was caused by Acetone molecules adsorbed on the breakage of the double chains. If the oxide ions at the corner of the octahedra are removed by Acetone, the MnO₆-octahedra can be rearranged to the structure of Mn₂O₃. Under the thermal processes, the transformation occurs at 200–400°C and the reduction progresses at 561°C with the mass loss of 9.2%.¹¹⁾ Contrary, the ambient temperature inside the vessel was 45–50°C and the increase in temperature was mostly due to the heat of friction of the bearing supporting the vessel. Then, the mechanically induced breakage of the double chains is strongly suggested, although the heat of friction of the grinding media and

the mechanical-thermal activation are the alternative mechanisms to be considered.

The Mn3p XPS spectra are shown in **Fig. 3**. The Mn3p spectra indicated the increase in Mn^{III} peak at 47.7 eV with the increase in Acetone content in compensation to the decrease in Mn^{IV} peak at 48.5 eV. The other peak at 51.0 eV indicated the adsorbed H₂O on the surface. The valence of surface manganese ions for A5 was determined as 3.37 by referring the peak intensities of standard MnO₂ and Mn₂O₃ powders. The thermogravimetric curves of the ground products illustrated in **Fig. 4** also showed the reduction of MnO₂ under grinding. The mass loss at 560°C for the reduction of MnO₂ to Mn₂O₃ decreased from 9.20% for the stoichiometric reaction, $\text{MnO}_2 \rightarrow \text{MnO}_{1.5} + 1/2\text{O}_2$, to 8.03% for A0 and 3.51% for A5. The surface valence obtained from the XPS and the bulk valences calculated from the mass loss are plotted against the molar ratio of Acetone to MnO₂ in **Fig. 5**. Both values decreased with the increase in the Acetone content and terminated at 3.36 for A5 and A10. The trivalent Mn₂O₃ phase appeared when the average valence was reduced to 3.6 (A3).

The gas chromatogram and the mass spectra of the gaseous

Fig. 2. Phase transformation and reduction of MnO₂ under grinding.

Fig. 1. X-ray diffraction (XRD) profiles of the ground products in a pure Ar gas (A0) and in the atmosphere containing 0.1 (A1), 0.2 (A2), 0.3 (A3), 0.4 (A4), 0.5 (A5), or 1.0 cm³ (A10) Acetone.

Fig. 3. X-ray photoelectron spectra (Mn3p) of the ground products.

Fig. 4. Thermogravimetric (TG) curves of the ground products. Heating rate: 10 K·min⁻¹, Atmosphere: flowing air (100 cm³·min⁻¹).

Fig. 5. Chemical valence of surface and bulk manganese ions in the ground products determined by XPS and TG, respectively.

products for A5 are shown in **Fig. 6**. The gaseous products indicating the short retention time had the two mass numbers of 40 and 44. One of them having the mass number of 40 was Ar occluded in the ground products. There are two possibilities for the other gas with the mass number of 44, CH₃COH and CO₂.

3.2 Discussion on reduction mechanism

The initial process of the reduction is supposed to be the pull-out of O²⁻ ions by the strongly adsorbed Acetone molecules on the breakage sites of the double chains, where the Acetone molecule disproportionated into CH₃CHO and HCHO according to the following reaction (1). The Gibbs free energy change (ΔG) for the reaction (1) is -38.7 kJ·mol⁻¹.

One of the disproportionational products, HCHO, was not detected in the mass spectrum. Then, it was further oxidized to CO₂ and H₂O. The overall reactions with or without decomposi-

Fig. 6. Gas chromatogram and mass spectra of the gaseous product.

tion of CH₃CHO were represented by Eqs. (2) and (3).

The relations between the bulk valence and the molar ratio (CH₃)₂CO/MnO₂ according to Eqs. (2) and (3) are shown in **Fig. 4**. The observed relation agrees with Eq. (2) rather than Eq. (3). This is supported by the larger negative value of $\Delta G = -1320$ kJ·mol⁻¹ for reaction (2) than $\Delta G = -453$ kJ·mol⁻¹ for reaction (3). The Acetone molecules were completely oxidized to CO₂ and H₂O. Sixteen Mn⁴⁺ ions can be reduced to Mn³⁺ in compensation to the complete oxidation of one Acetone molecule. However, the formation of CO₂ and H₂O having higher adsorption ability decreased the efficiency by occupying the breakage sites of the double chains dominantly.

3.3 Morphology and surface area of ground products

The formation of H₂O suggested the increase in agglomeration ability of the ground products. The morphology of the ground products is shown in **Fig. 7** with SSA. The ground product was agglomerated even for A0 without containing Acetone. The increase of the Acetone content resulted in the decrease of the size of agglomerates, while SSA decreased once for A1 and A2 and then increased for A3 < A4 < A5. The SSA increased by the pulverization of the agglomerates when Mn₂O₃ was formed. **Figure 8** shows the integrated XRD peak intensity and the half-value width of the (222) reflection for Mn₂O₃ as the function of molar ratio (CH₃)₂CO/MnO₂ after calcination. The integrated intensity for A0, A1 and A2, where MnO₂ was thermally reduced to Mn₂O₃, was almost the same at 500 and 800°C. The half-value width for these ground products was low. Then, well-crystallized Mn₂O₃ was obtained by the thermal reduction. Contrary to this, the mechanochemically reduced Mn₂O₃ (A3–A5) indicated the poor crystallinity at 500°C. The SSA for the calcined products at 500°C was small for the thermally reduced Mn₂O₃ (15–13 m²·g⁻¹ for A0–A3), and increased for the mechanochemically reduced Mn₂O₃ (17, 18 and 20 m²·g⁻¹ for A3, A4 and A5, respectively). The peculiarity of mechanically enforced reduction products, fine particle size, agglomeration and the defected crystalline structure were preserved after calcination at 500°C.

Fig. 7. Morphology and specific surface area (SSA) of the ground products.

Fig. 8. Integrated XRD intensity (I) and half-value width (HW) of (222) reflection for Mn_2O_3 after calcination of the ground products in air.

3.4 Reduction ability of some ketones and alcohols

The reduction of MnO_2 can be induced by the other organic vapors. **Figure 9** shows the XRD profiles of the ground products in the atmosphere containing Acetone (A3), Methanol (M3), Ethanol (E3), 2-Butanone (B3), and 3-Pentanone (P3). The all ground products were the mixture of β - MnO_2 and Mn_2O_3 . The reduction to Mn_2O_3 was promoted for A3, B3 and E3. The XPS spectra in **Fig. 10** also indicated the higher peaks of Mn(III) for the 3 ground products. The surface and bulk valence of manganese ions were determined from the XPS and thermogravimetric data and listed in **Table 1**. On the assumption of the complete oxidation of the organic chemicals to CO_2 and H_2O , one mole of Acetone, 2-Butanone, 3-Pentanone, Methanol and Ethanol can reduce 16, 22, 28, 6 and 12 moles of Mn^{4+} ions to Mn^{3+} , respectively. The estimated bulk valence on this assumption was 3.44

Fig. 9. Effect of some organic compounds on the reduction of manganese ions under grinding. A3: Acetone, B: 2-Butanone, P: 3-Pentanone, M: Methanol, and E: Ethanol.

Fig. 10. XPS spectra (Mn3p) of the ground products in the atmosphere containing Acetone (A3), 2-Butanone (B), 3-Pentanone (P), Methanol (M) and Ethanol (E).

Table 1. Effect of Organic Compounds on Reduction of Manganese Ions

Sample	A3	B3	P3	M3	E3
Surface valence of Mn	3.51	3.48	3.62	3.54	3.49
Bulk valence of Mn	3.59	3.54	3.74	3.70	3.67

(A3), 3.36 (B3), 3.32 (P3), 3.62 (M3), and 3.47 (E3). The efficiency for the observed degree of reduction was 0.727 (Acetone), 0.718 (2-Butanone), 0.382 (3-Propanone), 0.781 (Methanol) and 0.618 (Ethanol). The evidently low efficiency of 3-Propanone would be due to the low vapor pressure relating to the high boiling point. The saturated vapor pressure calculated by Antoine's equation was 81.8, 36.2, 15.8, 55.6 and 29.4 kPa at 50°C for Acetone, 2-Butanone, 3-Propanone, Methanol, and Ethanol, respectively.¹⁴⁾ The difficulty for the disproportionational reaction as the initiation process of the redox process would also relate to the low efficiency.

Fig. 11. XRD profiles of the ground products in MnO₂-Li₂CO₃ system (PC/planetary mill, MC/mortar ground) and MnO₂-LiOH system (PH/planetary milled, MH/mortar ground).

3.5 Application to the synthesis of LiMn₂O₄

This redox process was applied to the synthesis of LiMn^{III}Mn^{IV}O₄ as a cathode material for lithium batteries. The XRD profiles of the ground products in LiCO₃-MnO₂ (PC) and LiOH-MnO₂ (PH) systems are shown in **Fig. 11** in comparison with those of mortar-ground ones (MC and MH). The Acetone content of 0.5 cm³ was a little higher than the requirement to reduce the half of MnO₂ to Mn₂O₃ according to Eq. (2), because the reaction products CO₂ from Li₂CO₃ (PC) and H₂O from LiOH (PH) should disturb the reduction. The mortar ground mixtures showed the reflections for the starting Li₂CO₃ and LiOH as well as those for γ-MnO₂. Contrary, for PC and PH, reflections for LiCO₃ and LiOH disappeared. The starting γ-MnO₂ remained for PC but it was transformed to β-MnO₂ and Mn₂O₃ for PH. Additionally, the broad peak for LiMn₂O₄ appeared at 2θ = 18.8° for PH. This strongly indicated the penetration of Li⁺ ions into the lattice of γ-MnO₂ to rearrange the lattice to LiMn₂O₄-like structure. The carbonate-derived PC had the deformed γ-MnO₂ structure suggesting the dissolution of Li⁺ ions. For both changes in the crystalline structure, parts of Mn⁴⁺ ions should be reduced to Mn³⁺.

These reactions were promoted by the reduction of MnO₂ with the assistance of Acetone vapor removing oxygen.

The ground products PC and PH can be converted to the crystalline LiMn₂O₄ completely without forming by-products by the post heat-treatment at 700°C as shown in **Fig. 12**. The BET-equivalent particle size of the calcined PC was 195, 293 and 459 nm at 600, 700, and 800°C, respectively. The powders obtained from PH were smaller than PC; 153, 214 and 399 nm at the same temperatures. As described in a separate paper,¹²⁾ the fine powders prepared by the mechanochemical method indicate the excellent cycle performances for the rechargeability.

Fig. 12. XRD profiles of the calcined PC, MC, PH and MH at 700°C for 3 h.

4. Conclusion

Mechanochemical reduction of MnO₂ under grinding in the atmosphere containing organic vapors has been studied. Organic vapors such as Acetone, 2-Butanone, 3-Pentanone, Methanol and Ethanol has the activity to reduce MnO₂ to Mn₂O₃. The reduction mechanism with the assistance of mechanical dissociation of edge-sharing MnO₆-double chains of γ-MnO₂ has been discussed. This redox process can be applied to the synthesis of LiMn₂O₄.

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