

Novel Preparation Method of
Manganese(II) Manganese(IV) Oxide ($\text{Mn}_2\text{Mn}_3\text{O}_8$, Mn_5O_8) by Citrate Process

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The amorphous citrate precursor obtained by the reaction of manganese nitrate and citric acid resulted in the formation of single phase of Mn_5O_8 by the thermal decomposition at 300 - 400 °C in oxygen atmosphere.

A variety of manganese oxides are now being studied to apply for cathode active materials of batteries, catalysts and so on by many workers. Among these studies much attention has not been denoted to manganese(II) manganese(IV) oxide ($\text{Mn}_2\text{Mn}_3\text{O}_8$, Mn_5O_8). This manganese oxide was first prepared by Feitknecht¹⁾ as follows; (1) by thermal decomposition of γ - MnOOH at a low temperature, and (2) by slow oxidation of Mn_3O_4 particles with a characteristic surface area. Such reactions on the formation of Mn_5O_8 were also reported by Giovanori et al.²⁾ Shortly afterward Yamamoto et al. proposed an alternative method to prepare the well-crystallized Mn_5O_8 by hydrothermal reaction of γ - MnOOH .³⁾ Since the transformation of Mn_5O_8 from γ - MnOOH shows topotactic change, some crystallographic studies have been reported in recent years.^{4,5)}

These preparation methods described as above require certain restrict conditions to obtain a single phase of Mn_5O_8 . The authors have studied some manganese oxides as battery materials, and have found a suitable method to prepare easily Mn_5O_8 by a so-called citrate process.⁶⁾

An equimolar mixture of aqueous solutions of manganese nitrate and citric acid was evaporated at 60 °C under reduced pressure by a rotary evaporator. The resulting viscous liquid was further evaporated at 80 °C

to give powder of citrate complex with the evolution of nitrogen oxide. The powder thus obtained was dried under reduced pressure at room temperature, and then used as a starting citrate precursor to prepare manganese oxides by thermal decomposition.

Figure 1 shows the results of thermal analyses of the citrate precursor in air and oxygen atmospheres. The precursor decomposes rapidly by 250 °C, followed by the subsequent reaction with the different pathways in air and oxygen, respectively. The decomposition product formed by 250 °C undergoes the weight gain reaction in air. On the other hand, oxygen atmosphere causes the weight-gain reaction at 300 °C to give a stable phase at 300-400 °C, followed by the weight-loss reaction at 500 °C.

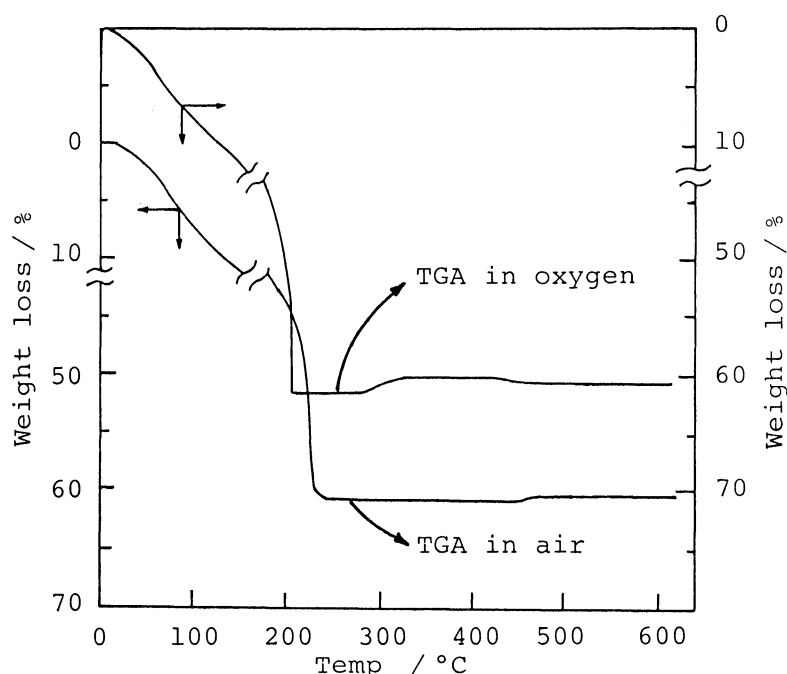


Fig.1. Thermogravimetric analysis(TGA) of citrate precursor in air and oxygen atmospheres.

On the basis of the thermal analysis, the products formed at various temperatures were characterized by XRD measurement⁷⁾ as shown in Fig.2. The precursor decomposes to Mn_3O_4 at first step reaction to give Mn_2O_3 over 500 °C in air. Such a series of reaction agrees with the thermogravimetric behaviors. The initial decomposition product in oxygen is also Mn_3O_4 , which is oxidized to Mn_5O_8 at 300 °C, followed by the formation of Mn_2O_3 over 500 °C. These oxides formed were also confirmed by

chemical analysis for the average valence of manganese in addition to the XRD measurement. Consequently, the thermal decomposition reaction may be shown as the following schemes.

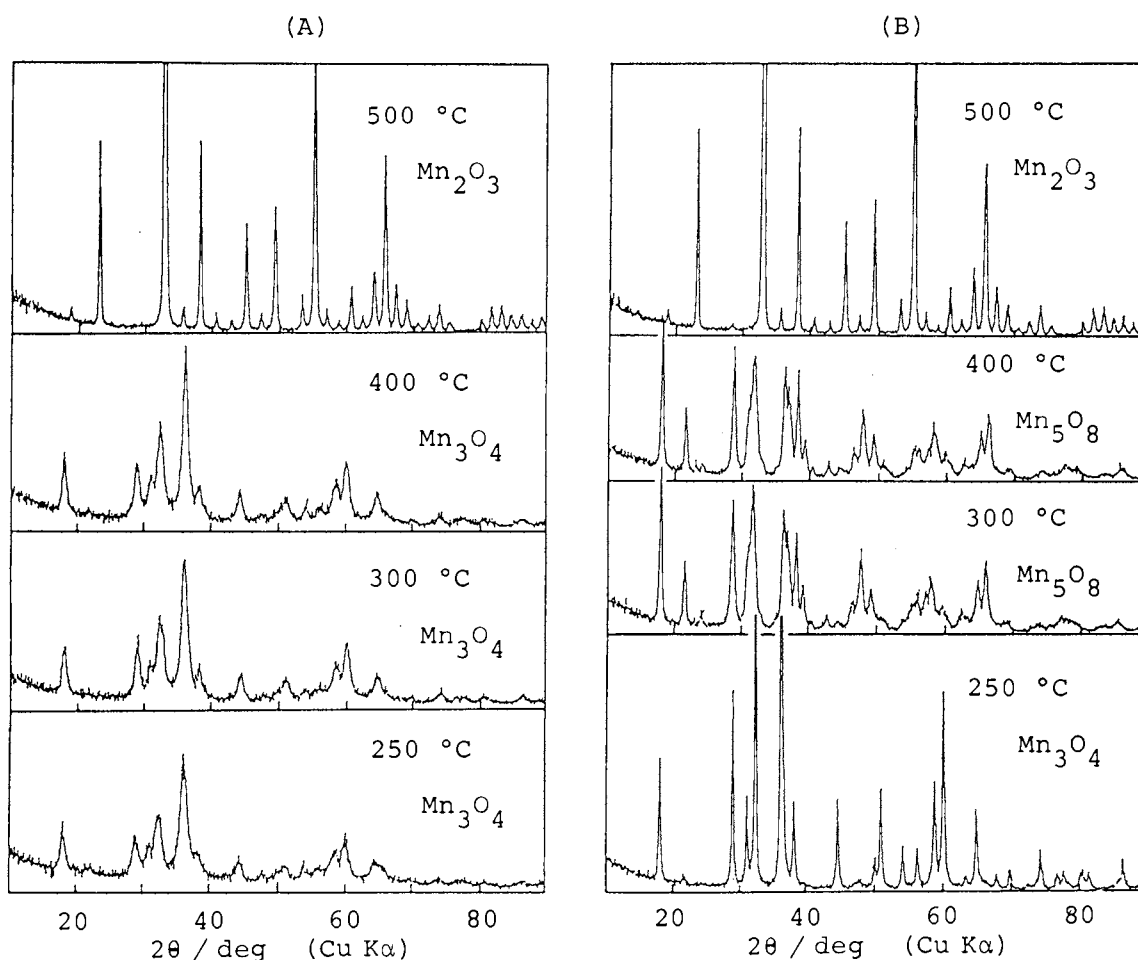
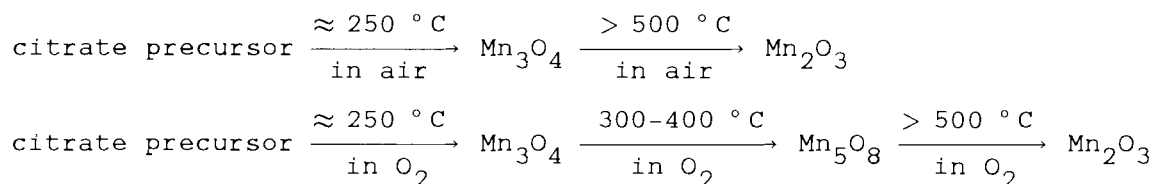


Fig.2. XRD profiles of the oxides formed by thermal treatment of citrate precursor at various temperatures in air(A) and oxygen(B) atmospheres.

In the both atmospheres, the initial decomposition product formed from the citrate precursor was Mn_3O_4 . However, the Mn_3O_4 formed in air did not yield Mn_5O_8 by the further thermal treatment at 300-400 °C in oxygen. The difference between the two Mn_3O_4 can be seen in their XRD patterns. Thus, the Mn_3O_4 formed in oxygen was a well-crystallized oxide compared

with that obtained in air. No other differences were observed in the measurement of surface area and SEM observation. The formation of Mn_5O_8 in this study is of interest at any event, and hence the further study on the reaction process is now being carried out together with the application for electrocatalysis.

References

- 1) W.Feitrknecht, Pure Appl. Chem., 9, 423 (1964) .
- 2) R.Giobanori and U.Leuenberg, Helv. Chim. Acta, 52, 2333 (1969) .
- 3) N.Yamamoto, M.Kiyama, and T.Takada, Jpn. J. Appl. Phys., 12, 1827 (1973) .
- 4) J.A.Lee, C.E.Newnham, F.S.Stone, and F.L.Tye, J. Solid State Chem., 31, 81 (1980) .
- 5) J.H.Rask and P.R.Buseck, Am. Mineral, 71, 805 (1986) .
- 6) C.Marcilly, P.Courty, and B.Delmon, J. Am. Ceram. Soc., 53, 56 (1970) ;
M.S.G.Baythoun and F.R.Sale, J. Mater. Sci., 17, 2757 (1982) .
- 7) H.R.Oswald and M.J.Wampetich, Helv. Chim. Acta, 50, 2023 (1967) .

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