

Novel Preparation Method of  
Manganese (II) Manganese (IV) Oxide ( $Mn_2Mn_3O_8$ ,  $Mn_5O_8$ ) 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 ( $Mn_2Mn_3O_8$ ,  $Mn_5O_8$ ). This manganese oxide was first prepared by Feitknecht<sup>1)</sup> as follows; (1) by thermal decomposition of  $\gamma$ -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.<sup>2)</sup> Shortly afterward Yamamoto et al. proposed an alternative method to prepare the well-crystallized  $Mn_5O_8$  by hydrothermal reaction of  $\gamma$ -MnOOH.<sup>3)</sup> Since the transformation of  $Mn_5O_8$  from  $\gamma$ -MnOOH shows topotactic change, some crystallographic studies have been reported in recent years.<sup>4,5)</sup>

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.<sup>6)</sup>

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.

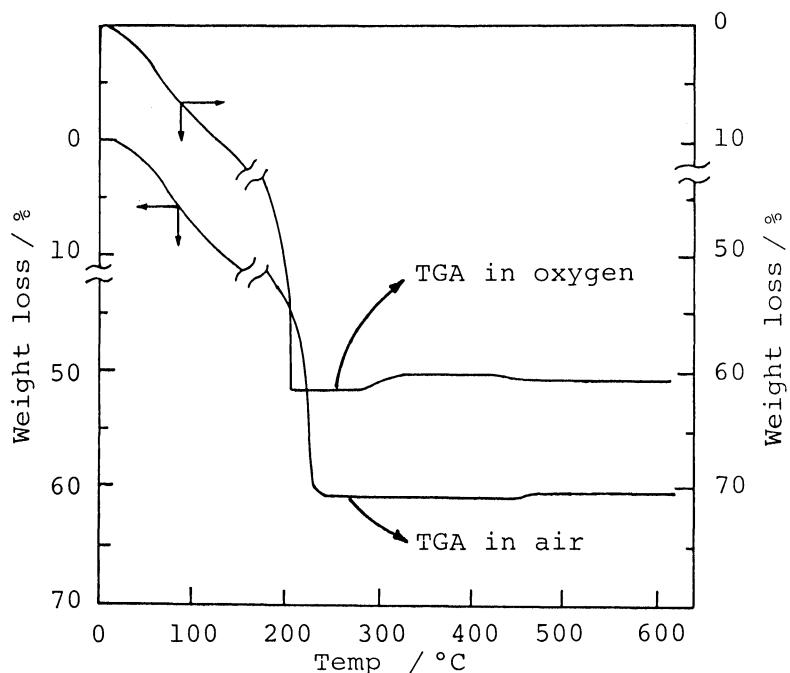


Fig.1. Thermogravimetric analysis(TGA) of citrate precursor in air and oxygen atmospheres.

On the basis of the thermal analysis, the products formed at various temperatures were characterized by XRD measurement<sup>7)</sup> 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.

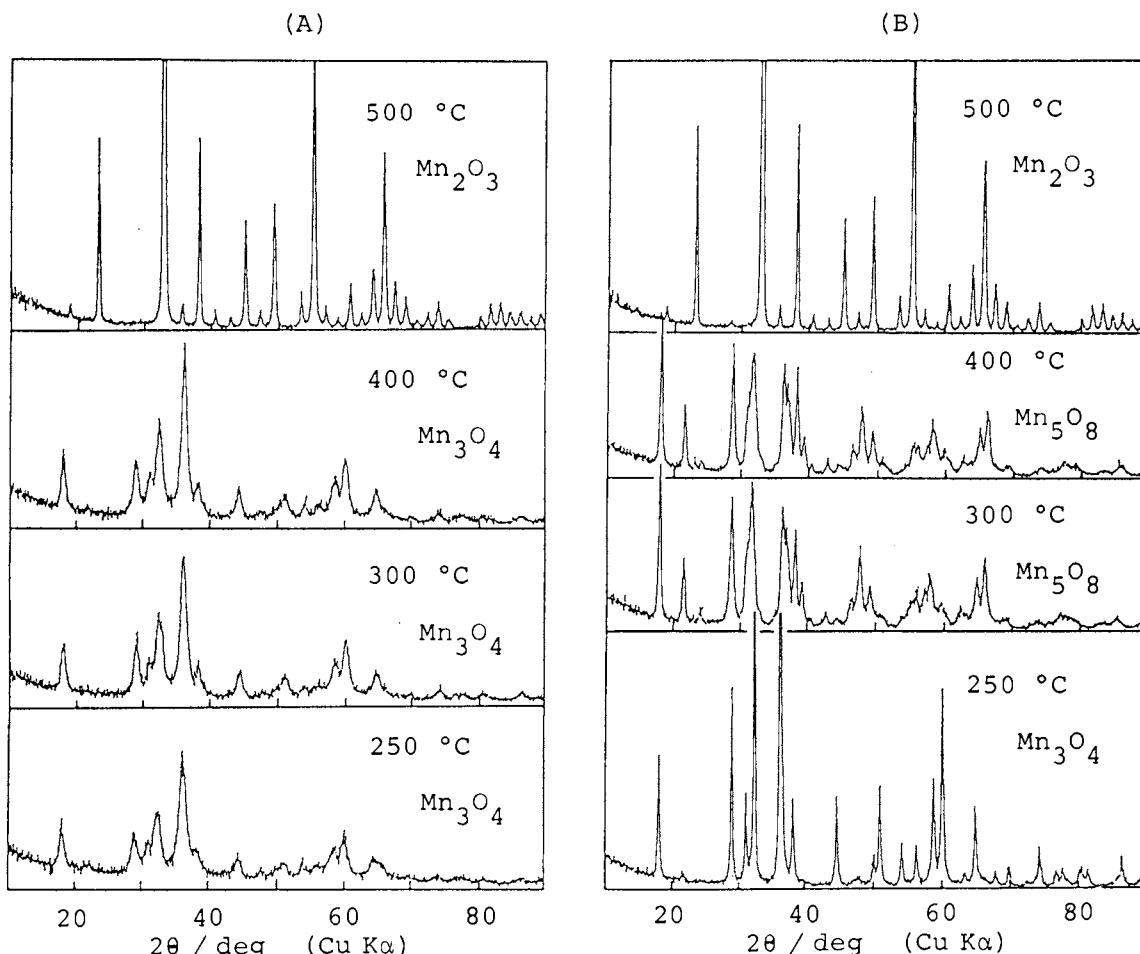
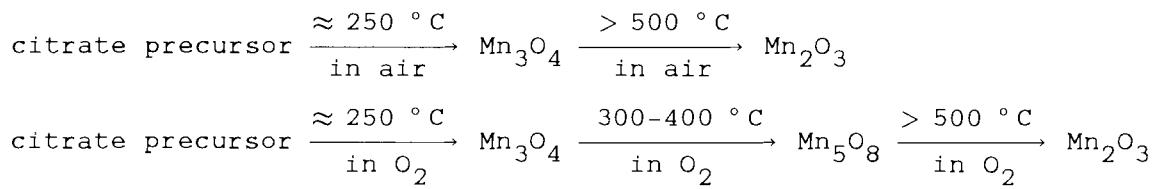


Fig.2. XRD profiles of the oxides formed by thermal treatment of citrate precursor at various temperatures in air (A) and oxygen (B) atmospheres.

In the both atmospheres, the initial decomposition product formed from the citrate precursor was  $\text{Mn}_3\text{O}_4$ . However, the  $\text{Mn}_3\text{O}_4$  formed in air did not yield  $\text{Mn}_5\text{O}_8$  by the further thermal treatment at  $300-400 \text{ }^\circ\text{C}$  in oxygen. The difference between the two  $\text{Mn}_3\text{O}_4$  can be seen in their XRD patterns. Thus, the  $\text{Mn}_3\text{O}_4$  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

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