Solubilities of Manganese Oxide in Molten Carbonate

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Solubilities of manganese oxides in molten carbonates was investigated in relation to the stability of cathode material in molten carbonate fuel cell. Stable phase of manganate was found as $LiMnO_2$ or Li_2MnO_3 in Li/K=62/38-eutectic melt, according to P_{CO2}, which agreed with thermodynamical calculation. The solution mechanism was discussed in terms of the dependence of the partial pressures of gas atmosphere.

1 INTRODUCTION

The molten carbonate fuel cell(MCFC) is advantageous in the variation of the fuel, efficiency and cleanliness and it is under development as a fuel system of the next decades. There are many problems still left in the way of the development, especially the solution of components into melts. It is considered that by using NiO, most hopeful candidate for the cathode material at present, the life time of the cell is unlikely to attain by itself more than 40,000 h because of its high solubility under high pressure and high temperature. One solution for this difficulty is to develope a new cathode material that is more stable than NiO in the operating condition. From this view, many studies have been contributed to find new alternatives including $LaNiO_3$[1], $LiFeO_2$[1-3], CuO[1, 2, 4], ZnO[1, 2, 5], Li_2MnO_3[2] and La_2ZrO_3[5]. Better cathode materials, however, have not been proposed yet which complete the necessities in better stability and conductivity than those of NiO.

Among these candidates manganese is an element of stainless steel and its behavior in the melts are important in investigating the corrosion of stainless steel. But few report on the solubility of Li_2MnO_3[2, 6] has been published and we feel that more work is desirable especially in the relationship to the temperature and gas composition in Li/K = 62/38 eutectic melt.

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2 EXPERIMENTAL

The solubility was measured in 62 m/o Li_2CO_3-38 m/o K_2CO_3 eutectic melt (Li/K = 62/38 melt), since this composition is a standard for the conventional MCFC. The reagent grade alkaline carbonates were made up by weight to a total of 100 g and mixed in a dry box. The mixture was placed in a high purity alumina crucible and dried in vacuum for 12 h at 623 K. It was melted at 973 K and then CO_2 gas was bubbled through the melt for 24 h.

The oxide samples used were Mn_2O_3 powder purchased from Soekawa Chemicals Co., Ltd. and Li_2CO_3 powder from Wako Pure Chemical Industries Ltd. These were mixed in the ratio of Mn/Li = 1/2 or 1/0 and molded into pellets followed by calcination at 1,162 K for 25 h in air. The sintered pellet thus obtained was crushed into ca. 1 mm grain and immersed into the carbonate melt. Pressure of CO_2 and O_2 was varied from 7×10^{-5} to 7 x

10^{-1} atm and 1 x 10^{-1} to 7 x 10^{-1} atm, respectively. The atmosphere was balanced by argon. Experimental cell used in solubility mesurement was already reported [7]. A small portion of the melt was sampled in some interval by means of a pure alumina tube and weighed. Then it was dissolved into hydrochloric acid and the metal concentration was determined by atomic absorption spectrometry using Hitachi 180-80 spectrometer.

3 RESULTS AND DISCUSSION

The experiment began at the determination of the stable solid phase of manganate in the melt. After immersing Mn_2O_3 pellet at 923 K under P_{CO_2} = 7 x 10^{-1} atm and P_{O_2} = 3 x 10^{-1} atm for 10 days, the solid was extracted and analyzed by Cr-Kα x-ray diffraction. The pattern is shown in Fig. 1(a). Most of all peaks are assigned to be those of Li_2MnO_3 though a few peaks of low intensity are unclear. It is most probable to be concluded that the stable solid phase in the melt under this condition is Li_2MnO_3. This agrees with the previous study of Smith et al.[2]. The main composition of the sample for the solubility measurement was thus determined to be Mn/Li = 1/2 as described in the experimental section. In fact, after solubility measurement under several conditions, the residual solid was elucidated to be Li_2MnO_3 but in the form of hydrate as demonstrated in Fig. 1(b). It is likely that this hydrate was produced not in the melt but at some stage of powder preparation for the diffraction analysis, probably drying in the oven at 383 K after the removal of carbonates with HCl.

We also determined the stable phase of manganate under 1 atm CO_2, which was out of the condition of solubility measurement, and its diffration pattern (Fig. 1(c)) was identified as $LiMnO_2$. It is to be noted that the stable phase probably switches around 1 atm.

The dissolution behaviour of Mn_2O_3 at 923 K was given in Fig. 2. The maximum of the manganese concentration was observed just after the insert of the sample pellet but it was soon decreased to reach the terminal value (= 1.7 x 10^{-6}) at around 200 h. This peak is likely attributed to the dispersion of the sample grain into the melt. This

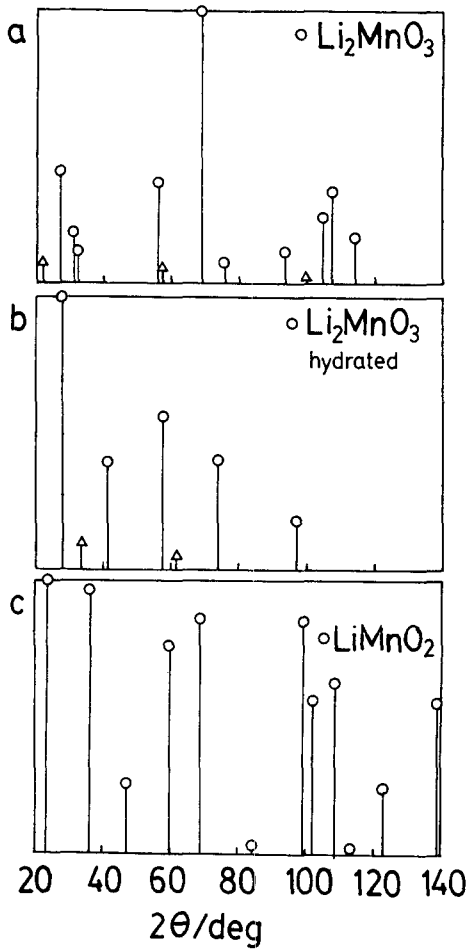

Fig. 1 X-ray diffraction pattern (a) of the solid in the melt ten days after immersing Mn_2O_3. The melt composition was Li/K = 62/38. The condition was P_{CO_2} = 7 x 10^{-1} atm and P_{O_2} = 3 x 10^{-1} atm. The temperature was 923 K. The peaks are attributable to Li_2MnO_3 except a few small unidentified ones. (b) of the solid in the melt measuring the solubility of Li_2MnO_3. The melt composition was Li/K = 62/38. The atomsphere was varied. The temperature was 923 K. The peaks are attributable to hydrated Li_2MnO_3 except a few small unidentified ones. (c) of the solid in the melt ten days after immersing Mn_2O_3. The melt composition was Li/K = 62/38. The condition was P_{CO_2} = 1 atm. The temperature was 923 K. The peaks are attributable to $LiMnO_2$ except a few small unidentified ones. △ : unidentified peak.

behavior was also observed as to Li_2MnO_3 but could be avoided by modifying the molding the pellet. The response of the solubility of Li_2MnO_3 was plotted in Fig. 3 against the change in atmosphere at 1,023 K. 300 h was generally needed for the stablization of the system after the change of the gas composition.

Figure 4 illustrates the influence of the temperature to the solubility of Li_2MnO_3 with other materials in the literature. It increased according to the temperature, and the factor is 50 comparing 1,023 K and 873 K. To evaluate the performance as an electrode material, comparison of the solubility with that of the other candidate materials makes one of the important criteria. At the present operating temperature (1,023 K) the

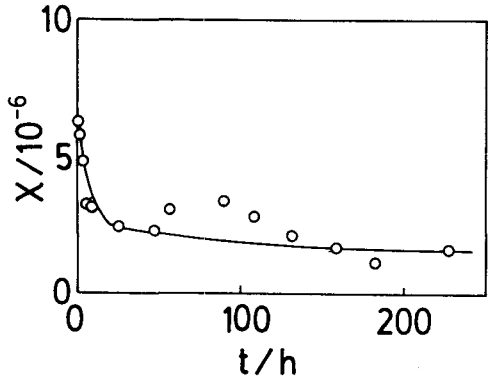

Fig. 2 Dissolution of Mn_2O_3 in Li/K = 62/38 melt at 923 K under P_{CO_2} = 7 x 10^{-1} atm and P_{O_2} = 3 x 10^{-1} atm. χ: mole fraction.

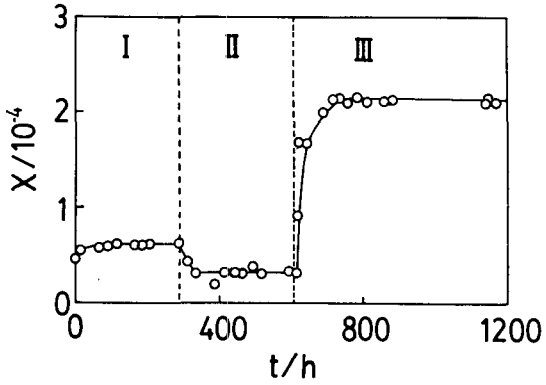

Fig. 3 Dissolution of Li_2MnO_3 in Li/K = 62/38 melt at 1,023 K under P_{CO_2} = 7 x 10^{-1} atm and P_{O_2} = 3 x 10^{-1} atm. χ: mole fraction. I: P_{CO_2} = 0.3 atm, II: P_{CO_2} = 0.1 atm and III: P_{CO_2} = 0.007 atm.

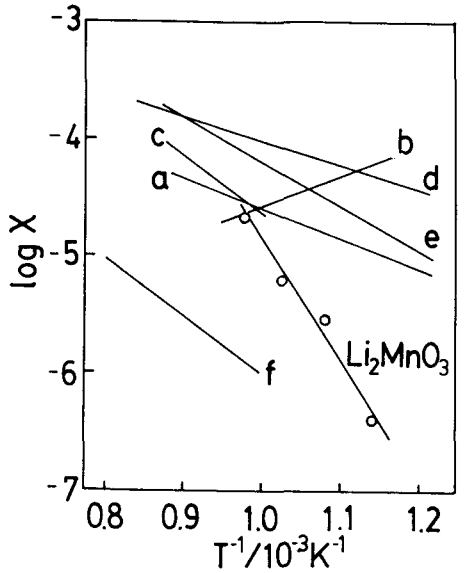

Fig. 4 Logarithmic solubility of Li_2MnO_3 in Li/K = 62/38 melt as a function of inverse temperature at 1,023 K under P_{CO_2} = 7 x 10^{-1} atm and P_{O_2} = 3 x 10^{-1} atm. χ: mole fraction. That of other various metal oxides for comparison in Li/K = 62/38 carbonate melts are shown. The gas compositions were P_{CO_2} = 7 x 10^{-1} atm and P_{O_2} = 3 x 10^{-1} atm for Li_2MnO_3, P_{CO_2} = 0.3 atm and air + H_2O for NiO (a), $LiFeO_2$ (c), ZnO (d), CuO (e), Li_2ZrO_3 (f) and P_{CO_2} = 1 atm for NiO(b), after reference 1, 4 and 6.

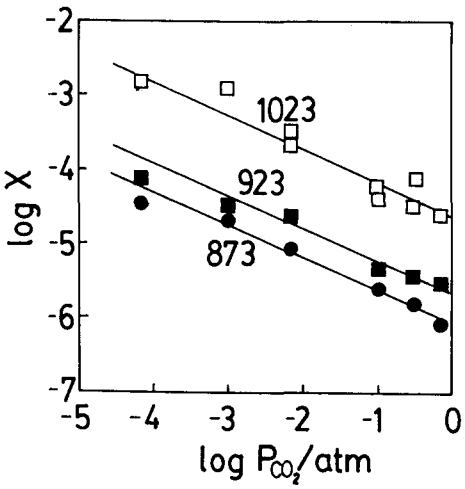

Fig. 5 Logarithmic solubility of Li_2MnO_3 in Li/K = 62/38 melt as a function of log P_{CO_2} at 873 K, 923 K and 1,023 K. P_{O_2} = 3 x 10^{-1} atm.

solubility of Li_2MnO_3 is almost the same as that of $LiFeO_2$ which has been reported hopeful against the corrosion [3, 4] and lower than that of NiO. Another feature for Li_2MnO_3 is large slope comparing other oxides. This implies that it would be the most stable material for MCFC cathode when the operating temperature is lower in the future.

The solubility also depends on the partial pressure of CO_2 and O_2 as shown in Figs 5 and 6, respectively. The logarithmic slopes against CO_2 was -1/2 and against O_2 was 1/4, which were independent of the temperature. Most probable mechanism which can explain these dependence is

$Li_2MnO_3 + 1/2CO_3^{2-} + 1/4O_2 = 2Li^+ + MnO_4^{3-} + 1/2CO_2$

since the solubility constant, K_d, of above equilibrium represented as

$K_d = [MnO_4^{3-}]\ P_{CO_2}^{1/2} / P_{O_2}^{1/4}$

i.e.

$\log[MnO_4^{3-}] = \log K_d - 1/2\log P_{CO_2} + 1/4\log P_{O_2}$

with the assumption of the activity of abundant Li^+ and CO_3^{2-} and solid Li_2MnO_3 equals unity.

The stable phase can be predicted by the drawing programme as shown in Fig. 7 though the enough thermodynamic data for lithium manganates are not available in the literature. Two assumptions were necessary for the evaluation of unknown Gibbs energy of lithium manganates formations. These are the additivity of the entropy and coefficient of the heat capacity (in the function of temperature) of the mother compouds at the standard state and the evaluated enthalpy of lithium manganates with those of related compounds. The mother compounds were chosen as $Li_2MnO_3 = Li_2O + MnO_2$ and $LiMnO_2 = 1/2\ Li_2O + 1/2\ Mn_2O_3$ in which the formal oxidation number of manganese did not change. The related compounds were $LiFeO_2$ and $LiCrO_2$ for which

$\Delta H_f(LiCrO_2) = 1/2\Delta H(Li_2O) + 1/2\Delta H(Cr_2O_3)$
$- 59.18\ kJ \cdot mol^{-1}$

$\Delta H_f(LiFeO_2) = 1/2\Delta H(Li_2O) + 1/2\Delta H(Fe_2O_3)$
$- 39.13\ kJ \cdot mol^{-1}$

Then we evaluated the residual enthalpy of $LiMnO_2$ for $-50\ kJ \cdot mol^{-1}$. There is no thermodynamic data for the relative compounds of Li_2MnO_3. We assume its residual enthalpy as $-75\ kJ \cdot mol^{-1}$ due to the stoichiometry. These assumptions make it possible to obtain the phase diagram. The other composites with high stoichiometric numbers have quite high ΔH_f and would not appear in the diagram.

If $\log P_{O_2}$ and $\log P_{CO_2}$ are around zero, it can be predicted in the diagram that two phases, Li_2MnO_3 and $LiMnO_2$, are very close. This is consistent with our experimental results which the stable phase can be obtainable when change the CO_2 pressure, say from 0.1 to 1 atm.

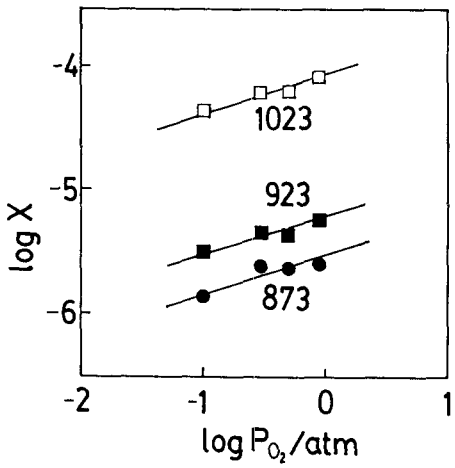

Fig. 6 Logarithmic solubility of Li_2MnO_3 in Li/K = 62/38 melt as a function of P_{O_2} at 873 K, 923 K and 1,023 K under $P_{CO_2} = 7 \times 10^{-1}$.

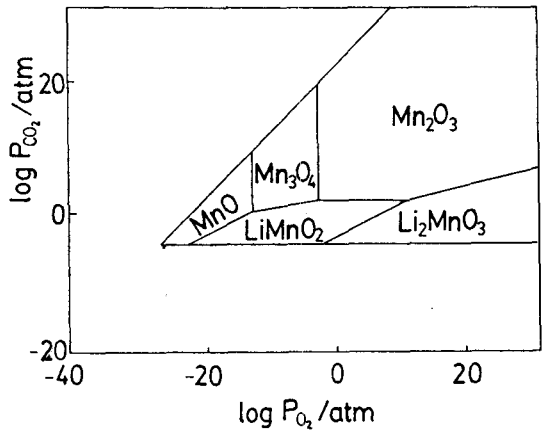

Fig. 7 Phase diagram of Li-K-C-O-Mn system at 923 K calculated in constant activity of Li_2CO_3, namely, $\log a(Li_2CO_3) = 0.30$.

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