SOLUBILITY AND CORROSION OF COBALT IN MOLTEN CARBONATES

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ABSTRACT

The solubility of Co oxide and the corrosion of Co in the presence of \((\text{Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3\) melt have been studied in \(\text{CO}_2\cdot\text{O}_2\) atmosphere at 873 \(-\) 1073 K. The stable phase of Co oxide in the melt was \(\text{LiCoO}_2\) coexisting with \(\text{O}_2\) and \(\text{CO}_2\) and the solubility of was proportional to \(P_{\text{CO}_2}\) \(-\) 1.5 and \(P_{\text{O}_2}\) 

\[\text{LiCoO}_2 + 3/2\text{CO}_2 \rightarrow \text{Li}^+ + \text{Co}^{2+} + 3/2\text{CO}_3^{2-} + \text{1/4O}_2.\]

In spite of the low solubility of the Co oxide in the carbonate melt, the hot corrosion of Co metal occurred when the thin film of the melt was present on the metal. The weight gain curve could be divided into two regions: (1) the first stage of severe corrosion and (2) the second stage of slow corrosion rate. The corrosion products at the first stage were \(\text{CoO}\) and \(\text{Co}_3\text{O}_4\), and those of the second stage were \(\text{Co}_3\text{O}_4\) and \(\text{LiCoO}_2\). The low solubility of \(\text{LiCoO}_2\) might affected the corrosion reaction and suppressed the corrosion rate.

INTRODUCTION

The molten carbonate fuel cell (MCFC) is expected to be one of the most promising power generation systems for the coming century owing to the high efficiency, the excellent characteristics to the environment and the ability of utilization of wide variety fuels.

In this system, the durability is quite important for the long time operation. Especially, the solubility of the cathode material under the cathodic condition and the metallic corrosion in the presence of molten carbonate are thought to be very important factors for the commercialization. Recently, Veldhuis reported that the solubility of
LiCoO₂ is very low compared to NiO². In this paper the solubility of Co oxide was measured and the result was compared with that of NiO². If the solubility of Co oxide is low, Co metal might be stable with the carbonate melt. In this paper the corrosion of Co has also been studied in the presence of molten carbonate.

EXPERIMENTAL

(1) Solubility measurement

The solubility of LiCoO₂ was measured in the binary eutectic melt of \((Li_{0.62}K_{0.38})_2CO_3\). High purity LiCoO₂ powder was pressed to a pellet and sintered at 1073 K for 12 h. The sintered pellet was crushed to small particles and the particles whose size were about 1 mm were selected for the solubility measurement to ensure a large surface area. The particles of LiCoO₂ were immersed in the carbonate melt and the solubility measurement was started. The gaseous atmosphere was Ar-CO₂-O₂ mixture, where P_{CO_2} was varied from 0.1 to 0.7 atm (P_{O_2} is fixed with 0.3 atm) in order to measure the effect of P_{CO_2} and P_{O_2} was varied from 0.1 to 0.7 atm (P_{CO_2} is fixed with 0.3 atm) to check the effect of P_{O_2}. The cell temperature was varied from 873 K to 1023 K. A small portion of the melt (0.2~0.5 g) was taken out periodically by means of a pure alumina tube and weighed. The melt sample was dissolved in HCl solution and the content of Co was measured by atomic absorption spectroscopy.

(2) Corrosion study

99.9% Co sheet (thickness=1 mm) was cut to a rectangular size (6x12mm) and used for the corrosion test. Two types of corrosion test were carried out in a gold cell. One is the corrosion in the melt (immersed) and the other is the corrosion with carbonate melt coating. For the test of coated sample, the carbonates were put on the surface of the specimen by dipping the carbonate-ethanol mixture and dried. The amount of carbonate on the metal was determined by the weight change before and after the coating process. The corrosion tests were carried out at 923 K in CO₂-O₂ atmosphere with \((Li_{0.62}K_{0.38})_2CO_3\) melt. The weight gain of the specimen was monitored continuously by TGA (Shimazu DT-40). And after the corrosion test, the corrosion products were analyzed by X-ray diffraction.

758
RESULTS AND DISCUSSION

(1) Solubility of LiCoO$_2$

Figure 1 shows the dissolution curves of LiCoO$_2$ under P$_{CO_2}$=1 atm (without O$_2$) and P$_{CO_2}$=0.7 atm (P$_O_2$ was 0.3 atm) at 923 K. The concentrations are expressed in mole fraction. The Co content in the melt increased immediately after the start in both cases. Under P$_{CO_2}$=0.7 atm, the Co content in the melt reached a steady state after 150 h, and then kept constant for three weeks. The solubility was determined from this steady state concentration. The value was 1/3 of the NiO solubility at the same condition. Thus, from the point of the solubility under this condition, LiCoO$_2$ is more stable than NiO. However, under P$_{CO_2}$=1 atm and without O$_2$, the Co content in the melt did not reach a steady state even at 250 h. The content went up more than 70 ppm (mole fraction) at 250 h and still increased. Therefore, LiCoO$_2$ is considered to be unstable without O$_2$ gas.

Figure 2 shows the solubility of LiCoO$_2$ in (Li$_{0.62}$K$_{0.38}$)$_2$CO$_3$ as a function of P$_O_2$ at 923 K (P$_{CO_2}$ is fixed with 0.3 atm). The result of Veldhuis$^{1)}$ and the solubility of NiO$^{2)}$ are also shown for comparison. Although the NiO solubility was independent of P$_O_2$, the LiCoO$_2$ solubility decreased with increasing of P$_O_2$. This means that the difference of the solubilities of LiCoO$_2$ and NiO becomes smaller at low pressure of O$_2$. Although the tendency was similar, our results are smaller than that of Veldhuis. The slope of the line was -0.22 and this number is close to -0.25. Thus, the solubility of LiCoO$_2$ is considered to be proportional to P$_O_2^{-0.25}$.

Figure 3 shows the solubility of LiCoO$_2$ in (Li$_{0.62}$K$_{0.38}$)$_2$CO$_3$ at 923 K as a function of P$_{CO_2}$ (P$_O_2$ is fixed at 0.3 atm). The results of Veldhuis$^{1)}$ and the solubility of NiO$^{2)}$ at P$_O_2$=0.3 atm are also plotted. Our results are different from those of Veldhuis as of Fig.2. This might be caused by the difference in the analytical method of Co in the melt. Veldhuis used the electrochemical reaction in the melt that is indirect method. In this study the Co content in the melt was obtained directly by the atomic adsorption spectroscopy. The solubility of LiCoO$_2$ increased with P$_{CO_2}$. The solubility is proportional to P$_{CO_2}^{-1.5}$. The dependence of the solubility on P$_{CO_2}$ is larger than that of NiO, since the solubility of NiO was proportional to P$_{CO_2}$. Although the solubility of LiCoO$_2$ was lower than that of NiO in the low pressure range of CO$_2$, the difference becomes smaller at high pressure of CO$_2$. 

759
Considering the dependences of the solubility of LiCoO₂ on Pco₂ and Po₂, the
dissolution reaction in this study is considered as follows.

\[ \text{LiCoO}_2 + 3/2\text{CO}_2 \rightarrow \text{Li}^+ + \text{Co}^{2+} + 3/2\text{CO}_3^{2-} + 1/4\text{O}_2 \] (1)

Figure 4 shows the temperature dependence of the LiCoO₂ solubility under
Pco₂=0.7 atm and Po₂=0.3 atm. The NiO solubility decreased with the increase of
temperature, but the LiCoO₂ solubility increased with the increase of temperature. The
effect of temperature on the solubility of LiCoO₂ was smaller than that of NiO. And the
solubility of LiCoO₂ above 1023 K was larger than that of NiO.

From these results the solubility can be expressed as follows.

For LiCoO₂
\[ X=621\times10^{-6} \cdot P_{\text{co}_2}^{1.5} \cdot P_{\text{o}_2}^{-0.25} \cdot e^{3061/T} \]

For NiO
\[ X=0.187\times10^{-6} \cdot P_{\text{co}_2} \cdot e^{5163/T} \]

where X is the solubility (mole fraction) of metal oxide and T is absolute temperature. Using these equations, the solubilities of metal oxides can be calculated at the actual
MCFC cathode inlet or outlet conditions at 923 K. Followings are calculated results.

a) solubility under 1 atm (Air/CO₂=70/30, gas utility:30%)
- LiCoO₂: \( X_{\text{in}}=17\times10^{-6}, X_{\text{out}}=11\times10^{-6} \)
- NiO: \( X_{\text{in}}=34\times10^{-6}, X_{\text{out}}=24\times10^{-6} \)

b) solubility under 8 atm (Air/CO₂=70/30, gas utility:30%)
- LiCoO₂: \( X_{\text{in}}=227\times10^{-6}, X_{\text{out}}=146\times10^{-6} \)
- NiO: \( X_{\text{in}}=274\times10^{-6}, X_{\text{out}}=192\times10^{-6} \)

\( X_{\text{in}} \) means the solubility of the metal oxide (mole fraction) at the inlet condition of MCFC
cathode and \( X_{\text{out}} \) means that of outlet condition. At 1 atm, the solubility of LiCoO₂ is half
of NiO. However, at higher pressure system, the difference is almost negligible. In order
to apply LiCoO₂ to the cathode of MCFC, this point should be considered.
Corrosion study

Figure 5 shows the weight gain curves for the corrosion of Co under 33%O2-67%CO2 at 923 K. The amounts of corrosion were large with the presence of carbonate melt, either immersed or coated. The effect of the melt coating is larger than that in the melt. When Co was immersed in the melt, the weight gain after 50 h was 38.5 mg/cm2 and the amount was 1/3 of that with coating. The reaction products in the melt after 50 h were LiCoO2 and CoO. With 41 mg/cm2 coating the weight gain curve divided into two regions: (1) the first stage of severe corrosion, where the so-called hot corrosion occurred and (2) the second stage of slow corrosion rate. The high corrosion rate in the initial period is surprising, considering the small solubility of LiCoO2. The reaction products were CoO after 30 min, LiCoO2 and Co3O4 after 15 h, and LiCoO2 and Co3O4 after 50 h.

The formation of CoO and Co3O4 occurred mainly in the first stage of the corrosion. However, after 15 and 50 h CoO could not be detected. This is because the formation of CoO was very limited compared to other oxides and CoO could not be detected by the XRD. Once the formation of LiCoO2 started, the corrosion rate decreased. The low solubility of LiCoO2 might affect the corrosion reaction.

Figure 6 shows the effect of the coated amount on the corrosion of Co coated with (Li0.62K0.38)2CO3 at 923 K under 33%O2-67%CO2. The detected product after 50 h were LiCoO2 and Co3O4 in any case. The more the coated amount increased, the longer the first stage continued. The amount of corrosion until the turning point of the first stage to the second stage increased owing to the coating amount. This is the other reason why the turning point was affected by the solubility of Co oxide that was formed during the corrosion reaction. The initial corrosion rate decreased with the increase of the coated amount up to 27 mg/cm2. The increase of coating amount caused the increase of the thickness of the melt on the metal. Since the diffusion of O2 from gas phase to scale became smaller owing to the increase of the film thickness, the corrosion rate decreased during the first stage.

REFERENCES

1) J.B.J. Veldhuis, F.C. Eckes, and L. Plomp, J. Electrochem. Soc., 139, L6 (1992).
2) K. Ota et al, ibid, 139, 667 (1992)
Fig. 1 Solubilities of LiCoO$_2$ in (Li$_{0.62}$K$_{0.38}$)$_2$CO$_3$ under P$_{\text{CO}_2}$=1 and 0.7 atm at 923 K.

Fig. 2 Solubilities of LiCoO$_2$ and NiO in (Li$_{0.62}$K$_{0.38}$)$_2$CO$_3$ as a function of P$_{\text{O}_2}$ under P$_{\text{CO}_2}$=0.3 atm at 923 K.
Fig. 3 Solubilities of LiCoO$_2$ and NiO in (Li$_{0.62}$K$_{0.38}$)$_2$CO$_3$ as a function of P$_{CO_2}$ under P$_{O_2}=0.3$ atm at 923 K.

Fig. 4 Temperature dependence of solubilities of LiCoO$_2$ and NiO in (Li$_{0.62}$K$_{0.38}$)$_2$CO$_3$ under P$_{CO_2}=0.7$ atm and P$_{O_2}=0.3$ atm.
Fig. 5 Weight gain curves for the corrosion of Co at 923 K under 33%O₂-67%CO₂.

Fig. 6 Weight gain curves for the corrosion of Co coated with 1 ~ 51 mg/cm² of (Li₀.₆₂K₀.₃₈)₂CO₃ at 923 K under 33%O₂-67%CO₂.