

Solubility and deposition of LiCoO_2 in a molten carbonate

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Abstract

The solubility and deposition of LiCoO_2 in carbonate melts have been studied under the cathode condition (1–7 atm, CO_2 –air or CO_2 – O_2 – N_2 working atmosphere). The solubility of LiCoO_2 in the $(\text{Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3$ melt for the applied pressure of 1 atm was found to be directly proportional to $P_{\text{CO}_2}^{1.5}$ and $P_{\text{O}_2}^{-0.25}$, while in the case when applied pressure was 7 atm it was proportional to $P_{\text{CO}_2}^{1.7}$ and $P_{\text{O}_2}^{-0.3}$. Although the dependence of P_{CO_2} and P_{O_2} on the solubility at 7 atm was a little different from the result at 1 atm, it was thought that the dissolution of LiCoO_2 at the elevated pressure would be regarded as the acidic dissolution mechanism. The solubility of LiCoO_2 in the $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ melt was less than half of that in the $(\text{Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3$ melt and this trend was the same as that of NiO. Moreover the deposition rate of LiCoO_2 in the $(\text{Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3$ melt was smaller than that of NiO and was about one-thirtieth. © 1998 Elsevier Science S.A.

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1. Introduction

In developing the molten carbonate fuel cells (MCFCs) for practical use, a short circuit of cell by means of dissolution and deposition of a cathode material is a big problem. The life of the MCFCs considerably depends on the solubility and deposition rate of the cathode material and it is thought that the MCFCs in which NiO is used as a cathode material are not able to operate over 40 000 h. Recently, owing to suppressing the dissolution of the cathode material, alkaline earth metal salts have been added to the molten carbonate electrolyte [1] and new cathode materials have been developed [2–5]. Veldhuis et al. [3] have reported that LiCoO_2 was one of the most stable material in a carbonate melt and could be used for a new cathode material. It is necessary to investigate the solubility and deposition of the new cathode material for practical use. The solubility of the new material at atmospheric pressure was reported by some researchers [3,5–7]. However, there are almost no reports about the solubility at the elevated pressure. The results of that at the elevated pressure are important because of operating of MCFCs in pressurized condition. It is also necessary that deposition properties of new materials are

clarified because of needs of long-term operation over 40 000 h. The aim of the present work is to confirm that LiCoO_2 can be applied as an alternate cathode material. We measured the solubility of LiCoO_2 at the elevated condition and define CO_2 and O_2 pressure dependence on the solubility of LiCoO_2 . The deposition rate of LiCoO_2 and NiO were also measured by the electrochemical method.

2. Experimental

LiCoO_2 powders supplied from the Nikko Fine Products Corporation Ltd. were uniaxially pressed at 30 MPa and then isostatically pressed at 300 MPa to the pellets (20 mm diameter). The pellets were sintered at 900°C and LiCoO_2 samples (12 × 5 × 5 mm) were obtained by cutting the sintered pellet. NiO samples, as a reference material, were also prepared by sintering the pellets at 850°C. The Ni powder made by the Inco Corporation Ltd. was used as a starting material. The samples were immersed into the 62 mol% (m/o) Li_2CO_3 –38 m/o K_2CO_3 ($(\text{Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3$) and 52 m/o Li_2CO_3 –48 m/o Na_2CO_3 ($(\text{Li}_{0.52}\text{K}_{0.48})_2\text{CO}_3$) melt at 650°C at various atmosphere (1–7 atm, CO_2 –air or CO_2 – O_2 – N_2). Fig. 1 shows the autoclave type apparatus (Chino Corporation Ltd.) used for the immersed test at the elevated pressure. Co or Ni concentration dissolved into a carbonate

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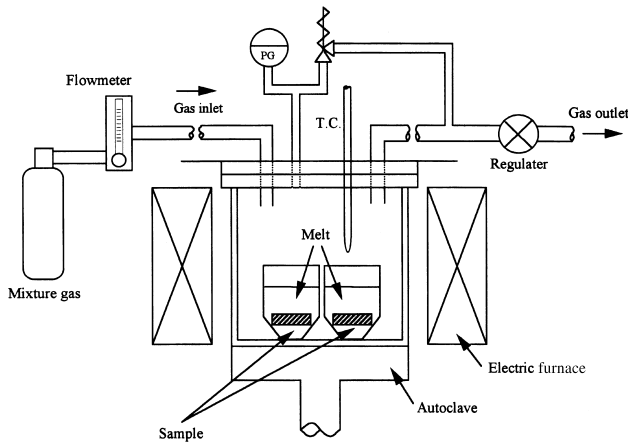


Fig. 1. Schematic diagram of the autoclave type apparatus.

melt were analyzed by ICP–AES (Nippon Jarrell-Ash Corporation Ltd.) and the saturation concentration of Co or Ni was regarded as the solubility. The composition of LiCoO_2 before and after the immersed test was also analyzed by ICP–AES.

Deposition properties of LiCoO_2 and NiO were evaluated by the constant potentiometric technique using an electrochemical measurement system (Hokuto Denko Ltd. HB-105, HA-1030G and Solatron 1250). The deposition test apparatus is schematically illustrated in Fig. 2. LiCoO_2 or NiO samples were immersed in 62 m/o Li_2CO_3 –38 m/o K_2CO_3 melt under 30% CO_2 –70% air for 250 h to reach the saturated solubility. A sample was taken out from the melt after 250 h and after that constant potential was loaded between a working electrode and an oxygen reference electrode (33% CO_2 –66% O_2) for 48 h. The precipitate on the

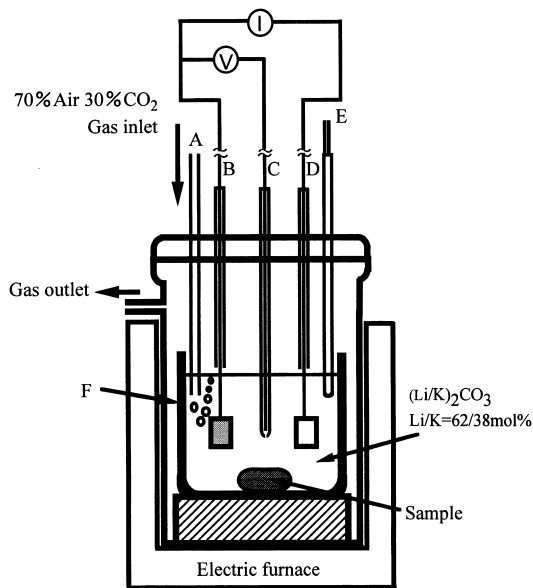


Fig. 2. Schematic diagram of the deposition test apparatus; (A) ceramics tube bubbler (Al_2O_3), (B) working electrode (Au), (C) reference electrode (Au: $\text{CO}_2/\text{O}_2 = 2:1$), (D) counter electrode (Au), (E) thermocouple, (F) alumina crucible.

Table 1

Solubility of LiCoO_2 and NiO under 30% CO_2 –70% air atmosphere at 650°C

Sample	P_{total} (atm)	Solubility (molar fraction)	
		In $(\text{Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3$	In $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$
LiCoO_2	1	4×10^{-6}	3×10^{-6}
	7	40×10^{-6}	20×10^{-6}
NiO	1	12×10^{-6}	4×10^{-6}
	7	45×10^{-6}	25×10^{-6}

working electrode was dissolved into HCl solution and the precipitate value was determined by ICP–AES measurement. Dissolution of the sample in the melt after the test was also measured by ICP–AES.

3. Results and discussion

3.1. Solubility

The dissolution of LiCoO_2 and NiO in a carbonate melt under gas a mixture of 30% CO_2 –70% air at 650°C increased with time and reached constant value after 200 h. These saturation concentrations of Co and Ni were regarded as the solubilities of LiCoO_2 and NiO , respectively. Table 1 shows solubilities of LiCoO_2 and NiO in $(\text{Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3$ and $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ melt at 650°C . The solubility of NiO in 30% CO_2 –70% air atmosphere at 1 atm is 12×10^{-6} (mole fraction). This value approximately corresponds to the result of Ota et al. [8]. The solubility of LiCoO_2 at 1 atm is 4.2×10^{-6} , it is about one third of that of NiO . This result is similar to previous work [3,6,7], whereas, solubilities of LiCoO_2 and NiO at 7 atm are 40×10^{-6} and 45×10^{-6} , respectively. Though the difference of solubility between LiCoO_2 and NiO decreases with increasing pressure, the solubility of LiCoO_2 is lower than that of NiO used under the practical cathode condition in the MCFC. On the other hand, the solubility of them in $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$ melt is about half of that for the experiments performed under atmosphere of 30% CO_2 –70% air. It is thought that the difference obtained in the solubility is caused by the difference of basicity of the melt.

Fig. 3 shows the dependence of CO_2 partial pressure (P_{CO_2}) and O_2 partial pressure (P_{O_2}) on the solubilities of LiCoO_2 and NiO under the total pressure of 1 and 7 atm. It is obvious from this figure that the solubility of NiO is proportional to P_{CO_2} at both applied pressures and these results support the acidic dissolution, as shown in previous work [8–10]. However, the solubility of LiCoO_2 at 1 atm is directly proportional to $P_{\text{CO}_2}^{1.5}$ and $P_{\text{O}_2}^{-0.25}$ (Fig. 1a). This result agreed with the result of Ota et al. [6]. Therefore, we proved that the dissolution of LiCoO_2 will be regarded as the acidic dissolution mechanism as shown in the following Eq. (1) and the solubility can be described by the experimental Eq. (2).

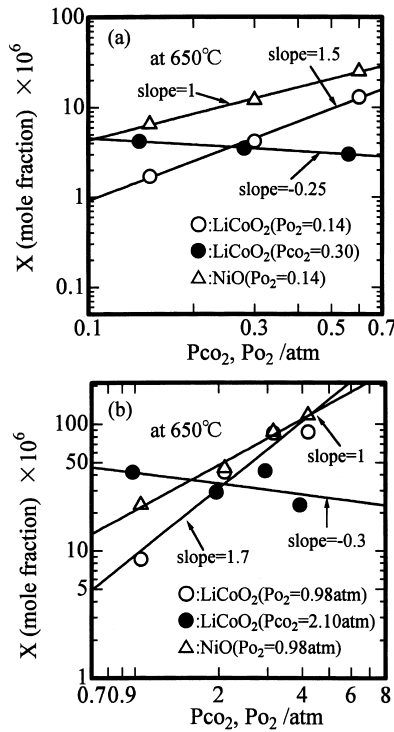
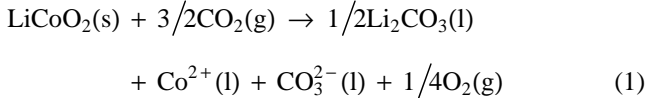


Fig. 3. Dependence of P_{CO_2} and P_{O_2} on the solubility of $LiCoO_2$ and NiO (a) 1 atm and (b) 7 atm.



($LiCoO_2$ solubility/mole fraction)

$$= 1.60 \times 10^{-5} \times P_{CO_2}^{1.5} \times P_{O_2}^{-0.25} \quad (2)$$

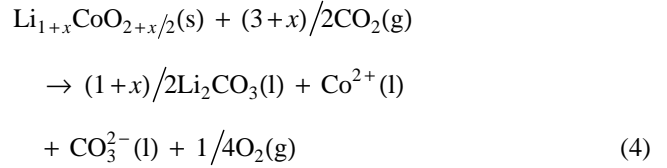
On the other hand, the dependence of the solubility of $LiCoO_2$ at 7 atm is slightly different from the result at 1 atm. The solubility of $LiCoO_2$ at 7 atm is directly proportional to $P_{CO_2}^{1.7}$ and $P_{O_2}^{-0.3}$ (Fig. 3b) and can be described as follows:

($LiCoO_2$ solubility/mole fraction)

$$= 1.26 \times 10^{-5} \times P_{CO_2}^{1.7} \times P_{O_2}^{-0.3} \quad (3)$$

It is thought that this difference of the solubility between 1 atm and 7 atm is caused by (a) increase of the basicity in the carbonate melt due to increasing of CO_2 and O_2 gas solubilities and (b) change in composition of $LiCoO_2$ under pressurized condition. Gas solubilities in the carbonate melt obeyed Henry's law: $c = Hp$, where c is the solubility of gas in the carbonate melt, H is Henry's constant and p is the partial pressure of gas. CO_2 and O_2 gas solubilities at 7 atm hardly differ from those at 1 atm and they are 10^{-5} and 10^{-7} (mol/cm³ per atm), respectively, because Henry's constant of their gases in Li/K carbonate melt at 650°C are very small [11]. Therefore, we surmise that the increase of gas solubility scarcely influences the basicity of the melt and is

not a main cause of this difference of the solubility between 1 and 7 atm. On the other hand, it is expected that the shift of the equilibrium of the dissolution reaction due to the change in the composition of $LiCoO_2$ influences the partial pressure dependence of the solubility. If the composition of $LiCoO_2$ changes in Li rich composition under the elevated pressure in Li/K carbonate melt, the dissolution reaction and the solubility can be described as follows:



($LiCoO_2$ solubility/mole fraction)

$$= K \times P_{CO_2}^{1.5+x/2} \times P_{O_2}^{-0.25} \quad (5)$$

where x is the deviation factor from stoichiometric composition of $LiCoO_2$ and K is the solubility constant. Li/Co ratio of $LiCoO_2$ sample before and after immersed test at 7 atm analyzed by ICP-AES were 0.67 and 1.10, respectively. It is regarded that the solubility is proportional to $P_{CO_2}^{1.55}$ by means of this result of Li/Co ratio and this CO_2 partial pressure dependence ($P_{CO_2}^{1.55}$) is nearly similar to the experimental result at 7 atm ($P_{CO_2}^{1.7}$). Therefore, the dissolution of $LiCoO_2$ at the elevated pressure will be regarded as the acidic dissolution mechanism. Moreover, it is speculated that Li/Co ratio on the surface of $LiCoO_2$ samples is higher than that of the average composition because the surface directly contacting the Li/K carbonate melt and the CO_2 partial pressure dependence of the solubility might be higher.

Fig. 4 shows the solubilities of $LiCoO_2$ and NiO calculated using experimental Eq. (3) under the cathode condition of the Kawagoe 1 MW plant. It is confirmed that this solubility of $LiCoO_2$ is less than half of that of NiO at 7 atm pressure.

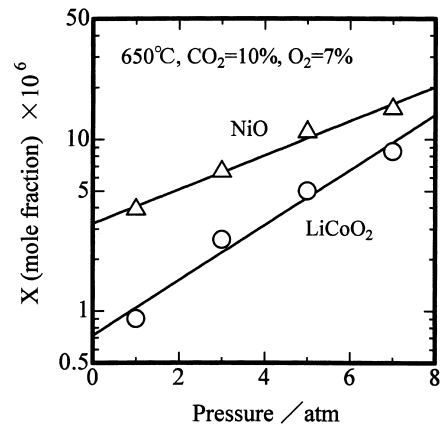


Fig. 4. Solubility of $LiCoO_2$ and NiO vs. pressure at 650°C in Li/K carbonate melt.

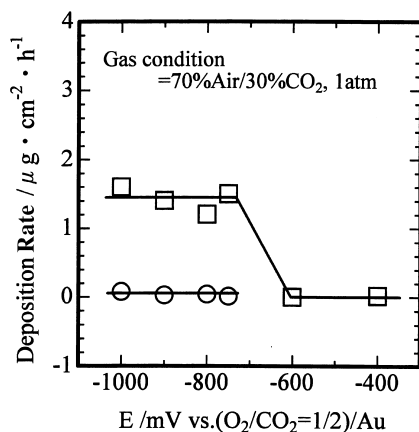


Fig. 5. Deposition rate of (○) LiCoO₂ and (□) NiO vs. potential difference at 650°C in Li/K carbonate melt.

3.2. Deposition

Fig. 5 shows the deposition rate of LiCoO₂ and NiO in the (Li_{0.62}K_{0.38})₂CO₃ melt at 650°C. It is obvious from this Fig. 5 that the deposition rate of LiCoO₂ is smaller than that of NiO and is about one-thirtieth. The deposition rate of NiO decreases rapidly over about -0.8 V. This potential nearly corresponds to the standard electrode potential ($E_{\text{Ni}^{2+}} = -0.84$ V) of Ni oxide formation in the carbonate melt under cathode condition [11]. Ni metal is stable under -0.84 V ($E_{\text{Ni}^{2+}}$), while Co metal is stable under -0.91 V ($E_{\text{Co}^{2+}}$) in the carbonate melt [11].

Deposition rate depends on the dissolution, diffusion and deposition reaction of the cathode material. In this test, the dissolution reaction can be ignored because cathode material is taken out from the melt just before the starting test. Moreover, the deposition reaction can occur very fast when the potential under $E_{\text{Ni}^{2+}}$ and $E_{\text{Co}^{2+}}$ values is used during the constant potentiometric test. Therefore, it is considered that the diffusion of metal ion is regarded as the rate determining step. Table 2 shows the measured deposition rate and the dissolution amount of LiCoO₂ and NiO after and before test. The dissolution of the cathode material should decrease with precipitation on the working electrode. However, the dissolution of cathode material after test nearly corresponded to the solubility. It is thought that small amount of precipitation due to the short test time causes this result.

Table 2

Deposition rate and solubility of LiCoO₂ and NiO

Sample	Potential (mV) vs. reference	Deposition rate (μg/cm ² h)	Dissolution (molar fraction)	
			After test	Before test (solubility)
LiCoO ₂	-750	0.01	5×10^{-6}	4×10^{-6}
	-800	0.04	3×10^{-6}	
NiO	-750	1.5	12×10^{-6}	12×10^{-6}
	-800	1.2	10×10^{-6}	

In general, the diffusion rate can be described by Fick's law as follows:

$$(\text{Diffusion rate}) = -Ddc(x,t)/dx \quad (6)$$

where D is diffusion coefficient, $dc(x,t)/dx$ is a gradient of concentration at some distance and time. In this case, $dc/dx(x,t)$ is regarded as constant because the dissolution of cathode material in the melt is almost constant during this test. Therefore we guess that the difference of deposition between LiCoO₂ and NiO is caused by the difference of the solubility of the cathode materials and the appearance diffusion coefficient of metal ion in the melt. However, we need more examinations which contain the measuring of the diffusion coefficient for clarifying this statement of the deposition property of LiCoO₂ and NiO.

4. Conclusions

The solubility of LiCoO₂ and NiO in (Li_{0.62}K_{0.38})₂CO₃ and (Li_{0.52}Na_{0.48})₂CO₃ melt were measured by immersed method under the cathode conditions (1–7 atm, CO₂–air or CO₂–O₂–N₂) at 650°C. The deposition property of them in (Li_{0.62}K_{0.38})₂CO₃ melt was also evaluated by the constant potentiometric method. The following main results are listed.

1. The solubility of LiCoO₂ was lower than that of NiO at the elevated pressure. The solubility of LiCoO₂ was found to be proportional to $P_{\text{CO}_2}^{1.7}$ and $P_{\text{O}_2}^{-0.3}$ and that of NiO was proportional to P_{CO_2} at the elevated pressure.
2. The dependence of P_{CO_2} on the solubility of LiCoO₂ at the elevated pressure was a little differ from that at atmospheric pressure. It was estimated that the composition deviation of LiCoO₂ at the elevated condition caused this change. Therefore, we supposed that the dissolution of LiCoO₂ at the elevated pressure obeyed the acidic dissolution mechanism.
3. The deposition rate of LiCoO₂ was smaller than that of NiO and was about one-thirtieth. We could speculate that this difference of the deposition property was mainly caused by the difference of the solubility of the cathode materials and the appearance diffusion coefficient of the metal ion in the melt.

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References

- [1] K. Tanimoto, Y. Miyazaki, M. Yanagida, T. Kojima, N. Ohtori and T. Kodama, *Denki Kagaku*, 63 (1995) 316.
- [2] L. Plomp, E.F. Sitters, C. Vessies and F.C. Eckes, *J. Electrochem. Soc.*, 138 (1991) 629.
- [3] J.B.J. Veldhuis, F.C. Eckes and L. Plomp, *J. Electrochem. Soc.*, 139 (1992) L6.
- [4] L. Giorgi, M. Carewska, S. Scaccia, E. Simonetti and F. Zarzana, *Denki Kagaku*, 64 (1996) 482.
- [5] C. Lagergren, A. Lundbland and B. Bergman, *J. Electrochem. Soc.*, 141 (1994) 2959.
- [6] K. Ota, Y. Takeishi, S. Shibata, H. Yoshitake, N. Kamiya and N. Yamazaki, *J. Electrochem. Soc.*, 142 (1995) 3322.
- [7] M. Higashino, M. Yanagida, K. Tanimoto, T. Kojima, Y. Tamiya, H. Matsumoto, T. Asai, Y. Miyazaki and Y. Takigawa, *Proceedings of Intersociety Energy Conversion Engineering Conference* (1997) 779.
- [8] K. Ota, S. Mitsushima, S. Kato, S. Asano, H. Yoshitake and N. Kamiya, *J. Electrochem. Soc.*, 139 (1992) 667.
- [9] C.E. Baumgartner, *J. Am. Ceram. Soc.*, 69 (1986) 162.
- [10] J.D. Doyon, T. Gilbert, G. Davies and L. Paetsch, *J. Electrochem. Soc.*, 134 (1987) 3035.
- [11] J.R. Selman and H.C. Maru, *Adv. Molten Salt Chem.*, 4 (1982).