

# The Effect of La Oxide Additive on the Solubility of NiO in Molten Carbonates

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## 1. Introduction

Fuel cells are known for their capability of high energy conversion efficiency in electric power generation, because they can directly convert chemical energy to electrical energy. Molten carbonate fuel cells (MCFCs) have been expected for a long time to become a new generation system that has good suitability for the environment and high power generation efficiency. However, some technical problems still remain for practical applications. Ni shorting by NiO cathode dissolution is one of these problems. During atmospheric pressure operation, the lifetime should be almost 40,000 hours, which is the projected lifetime using the present materials [1], however, the durability of the present materials is insufficient to operate for 40,000h under pressurized conditions that produce a higher efficiency, because the Ni shorting then becomes quite serious. The Ni shorting takes place via the following processes [2, 3].

1. The NiO cathode dissolves in the electrolyte as  $\text{Ni}^{2+}$  ion.
2. The  $\text{Ni}^{2+}$  ion diffuses into the electrolyte.
3. The  $\text{Ni}^{2+}$  ion is reduced by  $\text{H}_2$  that diffused from the anode and deposits as Ni.
4. The deposited Ni develops a reaction path, and Ni shorting occurs.

Here, the solubility of  $\text{Ni}^{2+}$  may affect all of these processes. Therefore, in order to prevent Ni shorting, reducing the solubility of NiO is very important, and various ways to reduce the NiO solubility have been investigated [4, 5].

There are two ways to decrease the solubility of NiO. The first one is decreasing the activity of the Ni in the cathode by the formation of a solid solution with other metal oxides. The other one is to change the composition of the molten carbonates to basic, because the solubility of NiO increases in an acidic melt. As a former example, the solid solution of NiO-MgO [6] and NiO- $\text{Fe}_2\text{O}_3$  [7] has a lower solubility than NiO, but they do not have the ability to operate for over 40,000 hours under pressurized conditions [8]. As a latter example, Li/Na carbonate and the additives of alkaline earth metals reduce the NiO solubility from the Li/K carbonate [9, 10], and the performance of an MCFC with a Li/Na carbonate electrolyte was high and stable [11, 12]. However, these changes are also insufficient for operation over 40,000 hours under pressurized conditions [13].

For practical use, the reduction of the overpotential of the oxygen reduction reaction is one of the important issues. The overpotential decreased when using a rare earth metal additive, especially the La additive, in the ternary alkaline metal carbonate system [14]. The La impregnated lithiated NiO showed a higher catalytic activity for oxygen reduction and lower dissolution of Ni based on the fuel cell measurement [15].

The solubility of NiO decreased in the lithium-rich alkaline metal carbonate [16], and the alkaline earth metal additive [9, 10]. These results should show that the high valent cation with a smaller radius produces a lower Ni solubility. Therefore, the La should be one of the better additives for the MCFC electrolyte in terms of both the stability and overpotential of the NiO cathode. In this study, to determine the feasibility of La as an additive to the electrolyte of the MCFC, the solubility of La in the molten carbonate and the effect of the additive on the NiO solubility were investigated.

## 2. Experimental

### 2-1 The Solubility of La in Molten Carbonates

$\text{La}_2\text{O}_3$  (99.99%, Kojundo Chemical Laboratory) was used as the starting material of the La oxide. In order to evaluate the La solubility, the solubility was measured in 50.2 mol%  $\text{Li}_2\text{CO}_3$  - 46.4 mol%  $\text{Na}_2\text{CO}_3$  - 3.4 mol%  $\text{La}_2\text{O}_3$  (Li/Na eutectic carbonate + 7 mol % La) and 42.65 mol%  $\text{Li}_2\text{CO}_3$  - 30.88 mol%  $\text{Na}_2\text{CO}_3$  - 24.51 mol%  $\text{K}_2\text{CO}_3$  - 1.96 mol%  $\text{La}_2\text{O}_3$  (Li/Na/K eutectic carbonate + 4 mol % La). The Li/Na/La carbonate and Li/Na/K/La carbonate were made on a weight basis for a total of 100 g and mixed in a dry box. The mixture was placed in a high-purity alumina crucible [16] and dried in a vacuum for 12 h at 673 K. It was melted at 973 K and then  $\text{CO}_2$  gas was bubbled through the melt for 24 h. The solubility was measured in  $\text{Pco}_2/\text{Po}_2 = 0.7/0.3$  atm at 923 K, and then the  $\text{CO}_2$  pressure was varied from  $10^{-5}$  to 1 atm while the  $\text{O}_2$  pressure was constant during the measurements. The total pressure was 1 atm and Ar was used as the balance gas. A small amount of the melt as a sample for quantitative analysis was collected at appropriate intervals. The sample was dissolved in 3 mol  $\text{dm}^{-3}$  of  $\text{HNO}_3$ . The La concentration was measured by ICP-AES (Seiko Instrument SPS3000).

### 2-2 The Stable Phase of La Oxide in Molten Carbonates

The stable phase of La oxide was determined by thermogravimetry and X-ray diffraction.  $\text{La}_2\text{O}_3$  in 52 mol%  $\text{Li}_2\text{CO}_3$  - 48 mol%  $\text{Na}_2\text{CO}_3$  (Li/Na eutectic carbonate) was measured by thermogravimetry (Shimadzu TGA 50) at 923K under  $\text{Pco}_2/\text{Po}_2 = 0.7/0.3$  atm and  $\text{Pco}_2/\text{Po}_2 = 0.9/0.1$  atm.

After the measurements, the sample, which was washed with acetic acid to remove the carbonates, was also identified by XRD (Shimadzu XRD-6000).

### 2-3 The Solubility of NiO in Molten Carbonate with La Oxide

The lithiated NiO powdered was first prepared, then NiO powder was immersed in the molten carbonate for 24 hours, and finally made into a pellet after washing, except for the surrounding molten carbonate, with acetic acid. The pellet was then sintered at 1373 K for 12 hours. Composition of 51.87 mol%  $\text{Li}_2\text{CO}_3$  - 47.88 mol%  $\text{Na}_2\text{CO}_3$  - 0.25 mol%  $\text{La}_2\text{O}_3$  (Li/Na eutectic carbonate + 0.5 mol % La), 43.34 mol%  $\text{Li}_2\text{CO}_3$  - 31.19 mol%  $\text{Na}_2\text{CO}_3$  - 24.87 mol%  $\text{K}_2\text{CO}_3$  - 0.50 mol%  $\text{La}_2\text{O}_3$  (Li/Na/K eutectic carbonate + 1 mol % La), and 43.07 mol%  $\text{Li}_2\text{CO}_3$  - 31.19 mol%  $\text{Na}_2\text{CO}_3$  - 24.75 mol%  $\text{K}_2\text{CO}_3$  - 0.99 mol%  $\text{La}_2\text{O}_3$  (Li/Na/K eutectic carbonate + 2 mol % La) were prepared in 100 gram quantities and mixed in a dry box. They were then evaluated as described in section 2-1.

A small amount of the melt as a sample for quantitative analysis was collected at appropriate intervals. The sample was dissolved in 1 mol  $\text{dm}^{-3}$  of HCl. The Ni concentration was measured by ICP-AES.

## 3. Results and Discussion

### 3-1 The Stable Phase and Solubility of La Oxide in Molten Carbonates

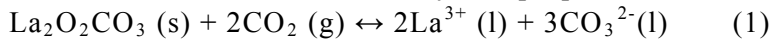
The stable phase of La oxide is reported to be  $\text{La}_2\text{O}_2\text{CO}_3$  below 973 K and  $\text{La}_2\text{O}_3$  in the temperature range from 973 K to 1023 K in air [17], and  $\text{La}_2\text{O}_2\text{CO}_3$  [18] under  $\text{Pco}_2/\text{Po}_2 = 0.7/0.3$  atm and  $\text{Pco}_2/\text{Po}_2 = 0.9/0.1$  atm at 923 K and are shown in Fig. 1. Although the weight gain would

be  $135 \text{ mg} \cdot \text{g}^{-1}$  if it was totally converted from  $\text{La}_2\text{O}_3$  to  $\text{La}_2\text{O}_2\text{CO}_3$ , the amounts for 100 hours were approximately  $50 \text{ mg} \cdot \text{g}^{-1}$  under  $\text{Pco}_2/\text{Po}_2 = 0.7/0.3 \text{ atm}$ , and  $90 \text{ mg} \cdot \text{g}^{-1}$  under  $\text{Pco}_2/\text{Po}_2 = 0.9/0.1 \text{ atm}$ , respectively. Figure 2 shows the XRD pattern of the La oxide in the Li/Na eutectic carbonate after 3000h. The detected peaks almost agreed with those of  $\text{La}_2\text{O}_2\text{CO}_3$ , and the peak of  $\text{La}_2\text{O}_3$  was not detected. Therefore, the stable phase of lanthanum oxide in the molten carbonate must be  $\text{La}_2\text{O}_2\text{CO}_3$  (at 923 K), and the kinetics of the reaction from  $\text{La}_2\text{O}_3$  to  $\text{La}_2\text{O}_2\text{CO}_3$  was slow.

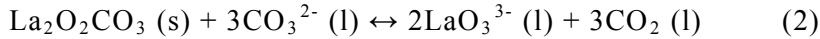
Figure 3 shows the solubility of La in the molten carbonates as a function of  $\text{Pco}_2$  in the molten carbonates at 923 K. The solubility of La under  $\text{Pco}_2/\text{Po}_2 = 0.7/0.3 \text{ atm}$  was  $1.0 \times 10^{-2}$  (mole fraction) in the Li/Na molten carbonates while it was  $2.3 \times 10^{-2}$  (mole fraction) in the Li/Na/K molten carbonates. The dissolution mechanism of La would be similar to that of Ni, because the solubility increased with  $\text{Pco}_2$  in the higher  $\text{Pco}_2$  region than in  $\text{Pco}_2 = 10^{-2} \text{ atm}$  and decreased with  $\text{Pco}_2$  in the lower  $\text{Pco}_2$  region. The values of the slope were ca. 1 in the higher  $\text{Pco}_2$  region and ca.  $-0.6$  in the lower  $\text{Pco}_2$  region.

Figure 4 shows the solubility of La in the molten carbonates as a function of the inverse temperature for  $\text{Pco}_2/\text{Po}_2 = 0.7/0.3 \text{ atm}$ . The solubility of La in both the Li/Na eutectic carbonate and Li/Na/K eutectic carbonate were proportional to the inverse of the temperature.

The dissolution reaction of La oxide in the higher  $\text{Pco}_2$  region seemed to be a simple acid dissolution, because the solubility was proportional to the  $\text{Pco}_2$ .

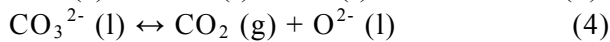
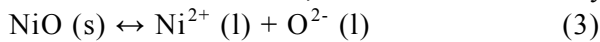


In the lower  $\text{Pco}_2$  region, the dissolution reaction is not yet clarified, because the solubility was proportional to the  $-0.6^{\text{th}}$  power of the  $\text{Pco}_2$ , but the following typical reaction of a simple basic dissolution shows the  $-1.5^{\text{th}}$  power of the  $\text{Pco}_2$ .



### 3-2 The Solubility of NiO in Molten Carbonates with La Oxide

Figure 5 shows the solubility of NiO in the molten carbonates with the La additive as a function of the  $\text{Pco}_2$  in the molten carbonates at 923 K. The solubility of NiO under  $\text{Pco}_2/\text{Po}_2 = 0.7/0.3 \text{ atm}$  were  $6.3 \times 10^{-6}$  (mole fraction) in the Li/Na molten carbonates with the 0.5 mol% La additive and  $4.1 \times 10^{-6}$  (mole fraction) in the Li/Na/K molten carbonates with the 2 mol% La additive. The solubility of NiO at  $\text{Pco}_2/\text{Po}_2 = 0.7/0.3 \text{ atm}$  were  $1.6 \times 10^{-5}$  (mole fraction) in the Li/Na eutectic carbonate and  $4.3 \times 10^{-5}$  (mole fraction) in the Li/Na/K eutectic carbonate. The slopes in the higher  $\text{Pco}_2$  region were ca. 1, and those in the lower  $\text{Pco}_2$  region were ca.  $-0.3$  for all the compositions of the carbonates. These behaviors were the same for the solubility of NiO in the molten alkaline metal carbonates with or without the alkaline earth metal carbonate additive [9, 16]. The dissolution reaction in the higher  $\text{Pco}_2$  region is understood based on the following acid dissolution mechanism, because the solubility of NiO is proportional to  $\text{Pco}_2$ .



Here, eq. (3) and (4) are the acid dissolution reaction and the acid-base equilibrium reaction, respectively. On the other hand, the dissolution reaction in the lower  $\text{Pco}_2$  region is still unclear, because, if the reaction follows a simple basic dissolution mechanism, the slope for the lower  $\text{Pco}_2$  region in Fig. 5 must be  $-1$ .



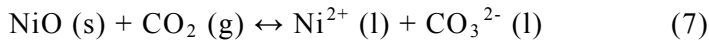
Here, eq. (5) is a basic dissolution reaction, and the dissolution behavior will be controlled by the acid-base equilibrium reaction, eq. (4). The slope cannot be explained by this reaction, however, the solubility of NiO increases with the decrease in the  $\text{Pco}_2$ . This may suggest that the dissolution species must be of the anion form, and the dissolution reaction will be similar to this

simple basic dissolution reaction. Here, we discuss the minimum value in Fig. 5 based on the assumption of the simple basic dissolution reaction.

$$[\text{Ni}^{2+}]^2 = [\text{NiO}_2^{2-}]^2 = 2 \cdot K_{\text{spa}} \cdot K_{\text{spb}} \quad (6)$$

In other words, the minimum value of the NiO solubility is independent of  $K_{\text{dis}}$  that is determined by the composition of the molten carbonate. The minimum value of the NiO solubility was ca.  $10^{-6}$  (mole fraction) for both the La-added molten carbonate and additive-free one. This shows that the solubility change in the mechanism by the La additive mainly corresponds to the change in the acid-base of the molten carbonate, and no Ni complex oxide was detected from the NiO sample after the solubility measurements.

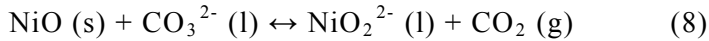
Figure 6 shows the solubility of NiO in the molten carbonates with and without the La additive as a function of the inverse temperature under  $P_{\text{CO}_2} = 0.7$  atm. The solubility of NiO in molten carbonates with and without the La additive increased with the decrease in temperature. The acid mechanism can be described as follows:



Since the dissolution of NiO into the molten carbonate is an exothermic reaction in the acid dissolution region, the solubility of NiO will decrease with temperature. The logarithm of the solubility was a reciprocal linear function of the temperature. However, the slopes of the Ni solubility in the molten carbonates in the La additive were smaller than that without the additive. The effect of the La additive to the molten carbonates on the solubility of NiO was smaller at high temperature than at low temperature.

As a result, the equilibrium dissolution of NiO in molten carbonates was influenced by the La oxides. Therefore, it is considered that the slight slope in the NiO solubility with the La additives was due to this effect.

Figure 7 shows the solubility of NiO in the molten carbonates with and without the La additive as a function of the inverse temperature under  $P_{\text{CO}_2} = 1 \times 10^{-4}$  atm. The solubility of NiO in the molten carbonates with and without the La additive decreased with the temperature in the lower  $P_{\text{CO}_2}$  region. The logarithm of the solubility was also a reciprocal linear function of the temperature. In the lower  $P_{\text{CO}_2}$  region, the slope of the Ni solubility in the molten carbonate with the La additive was also lower than that without the additive.



Since the dissolution of NiO into the molten carbonate is an endothermic reaction in the basic dissolution region, the solubility of NiO will decrease with temperature. However, the slopes of the NiO solubility in the molten carbonates with the La additive were greater than that without the additive, that is, the effect of the La additive in the molten carbonates on the solubility of NiO was greater at high temperature than at low temperature. This was attributed to the dissolution reaction of the La oxides in the molten carbonates that was similar to that of NiO, and the dissolved La seemed to weaken the acid-base equilibrium in the molten carbonates. Therefore, it is considered that the steep slope of the NiO solubility with La additives was due to this reason.

Figure 8 shows the NiO solubility as a function of the concentration of the additives in the Li/Na eutectic carbonate under  $P_{\text{CO}_2}/P_{\text{O}_2} = 0.7/0.3$  atm at 923 K. The data for the alkali earth additions to molten carbonates measured by Tanimoto et al. [11] are also shown in Fig. 8. The decrease in the NiO solubility due to the La additive was much greater than that by the Ca and Sr additives. This effect could be explained by the acid-base equilibrium.

Here, the equilibrium constant of eq. (3) is set equal to  $K_{\text{sp}}$ . The solubility of  $\text{Ni}^{2+}$  can then expressed as follows.

$$[\text{Ni}^{2+} \text{ (l)}] = 1 / (K_{\text{sp}} [\text{O}^{2-} \text{ (l)}]) \quad (9)$$

The equilibrium constant of eq. (2) is set to  $K_{\text{dis}}$ , and then  $K_{\text{dis}}$  will be defined as follows:

$$K_{\text{dis}} = P_{\text{CO}_2} [\text{O}^{2-} \text{ (l)}] \quad (10)$$

From eq. (7) and (8), the NiO solubility can be expressed as follows.

$$[\text{Ni}^{2+}(\text{l})] = 1 / (\text{K}_{\text{sp}} [\text{O}^{2-}(\text{l})]) \quad (11)$$

Assuming that the interaction between the cation in the molten carbonate can be disregarded, the decomposition equilibrium constant of the mixed salt can be expressed as that of a single salt. In short, when the total carbonate amount of La in the Li/Na system is set equal to x, it can be expressed as follows.

$$\text{K}_{\text{dis}} (\text{La} / (\text{Li}/\text{Na}) = x / 1-x) = \{\text{K}_{\text{dis}} (\text{La})\}^x \{\text{K}_{\text{dis}} (\text{Li}/\text{Na})\}^{1-x} \quad (12)$$

If eq. (10) and (11) are substituted into eq. (9),

$$\log [\text{Ni}^{2+}(\text{l})] = x \log \{\text{K}_{\text{dis}} (\text{Li}/\text{Na}) / \text{K}_{\text{dis}} (\text{La})\} + \{\text{Pco}_2 / \text{K}_{\text{sp}} \text{K}_{\text{dis}} (\text{Li}/\text{Na})\} \quad (13)$$

then, the basic index can be defined as follows:

$$\log \text{K}_{\text{dis}} = \text{pK}^{-1} \quad (14)$$

Assuming that  $\text{K}_{\text{sp}}$  is independent of the composition of the molten carbonate, the basic index can be calculated from the slope of Fig. 8 as follows.

$$\text{pK}^{-1} (\text{K}) : \text{pK}^{-1} (\text{Na}) : \text{pK}^{-1} (\text{Li}) : \text{pK}^{-1} (\text{Sr}) : \text{pK}^{-1} (\text{Ba}) : \text{pK}^{-1} (\text{La}) = 0.1 : 1.6 : 2 : 4 : 4 : 30 \quad (15)$$

The base-index of La on the NiO solubility in the molten carbonate was much greater than the alkali earth elements and found to be quite large compared with Li, Na, K, Sr and Ba. The greater the value of the base-index, the more the basicity of the melt might decrease.

#### 4. Conclusion

The stable phase of La oxide in the molten carbonates was found to be  $\text{La}_2\text{O}_2\text{CO}_3$ , and its solubility under  $\text{Pco}_2/\text{Po}_2 = 0.7/0.3$  atm at 923 K were  $1.0 \times 10^{-2}$  and  $2.3 \times 10^{-2}$  (mole fraction) in the Li/Na carbonates and in the Li/Na/K carbonates, respectively. The solubility of NiO under  $\text{Pco}_2/\text{Po}_2 = 0.7/0.3$  atm at 923 K were  $6.3 \times 10^{-6}$  and  $4.1 \times 10^{-6}$  (mole fraction) in the Li/Na carbonates with 0.5 mol% La additive and in the Li/Na/K carbonates with 2 mol% La additive. The solubility of NiO with the La additive in the molten carbonates was drastically reduced compared to that which was the additive free, and the effect of the La additive on the solubility of NiO was greater than that of any other alkali earth metal additives in the Li/Na carbonates. The solubility curve of NiO with the La additive was shift to the high  $\text{Pco}_2$  region as compared to those that were additive free. These results indicated that the molten carbonates might be become more basic by adding the La additive. Therefore, the more basic molten carbonate with the La additive produced a decrease in the solubility of NiO that was additive free. This effect could be explained by the acid-base equilibrium, and the base index value of La ( $\text{pK}^{-1}(\text{La})$ ), which is related to the solubility of NiO in molten carbonates, was 1-2 orders greater than the alkali and alkali earth metals.

#### 5. Acknowledgments

This work was partly supported financially by the New Energy and Industrial Technology Development Organization (NEDO) and Japan Fine Ceramic Center (JFCC).

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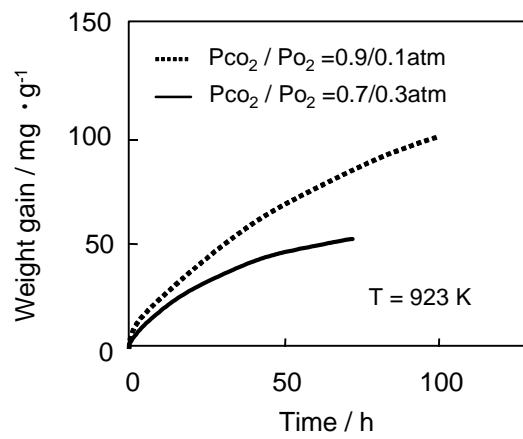


Fig. 1 TGA of  $\text{La}_2\text{O}_3$  for Li/Na carbonate.

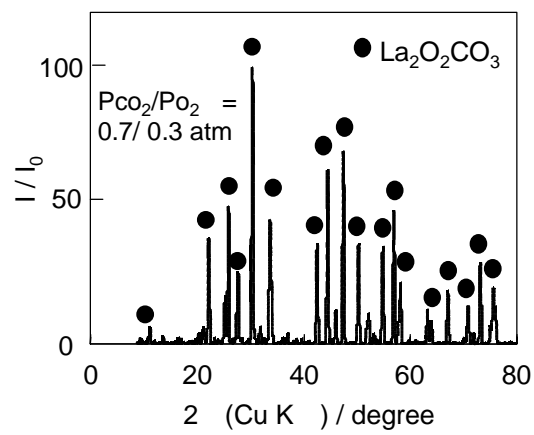


Fig. 2 X-ray diffraction pattern of  $\text{La}_2\text{O}_3$  in molten carbonate for 3000h.

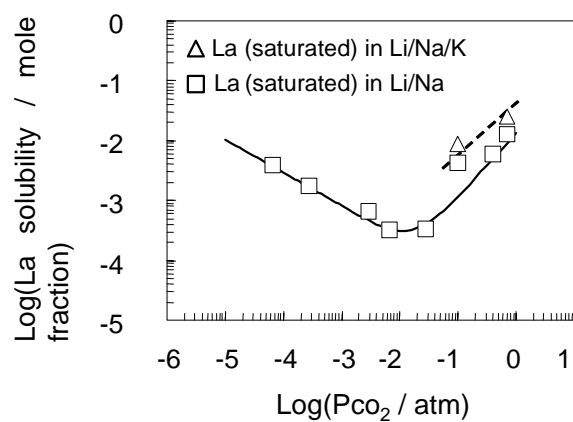


Fig. 3 Solubility of La as a function of  $P_{CO_2}$  in molten carbonate at 923 K.

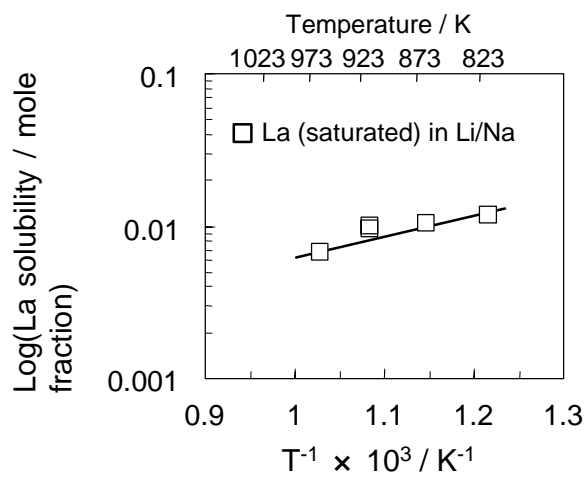


Fig. 4 Solubility of La as a function of the inverse temperature in molten carbonate for  $P_{CO_2}/P_{O_2} = 0.7/0.3$  atm.



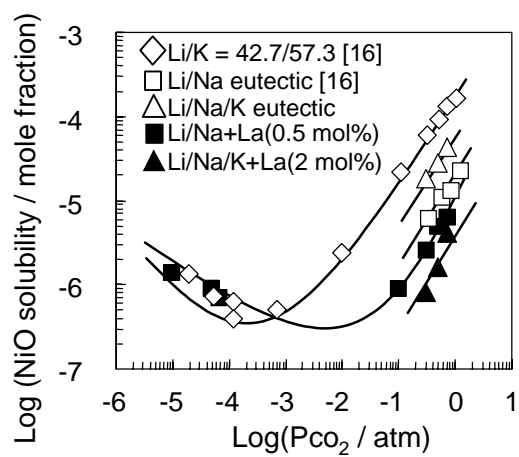


Fig. 5 Solubility of NiO in molten carbonate with and without La addition as a function of  $P_{CO_2}$  at 923K.

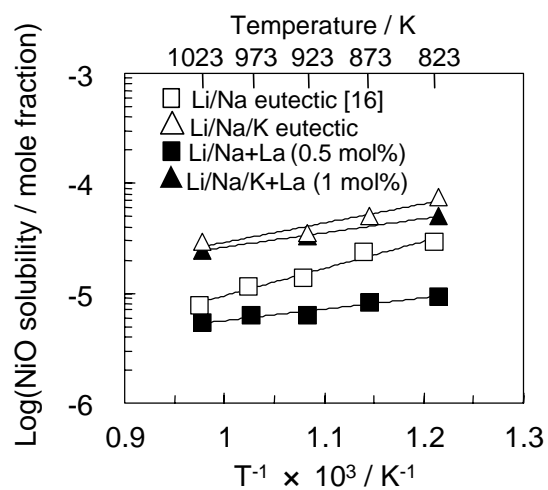


Fig. 6 Solubility of NiO in molten carbonate with and without La addition as a function of the inverse temperature for  $P_{CO_2} = 0.7$  atm.

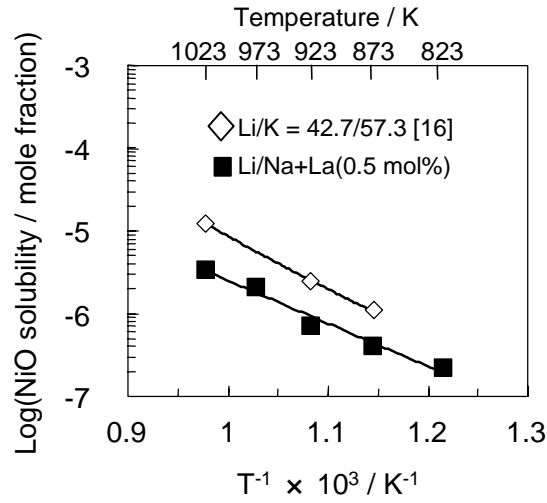


Fig. 7 Solubility of NiO in molten carbonate with and without La addition as a function of the inverse temperature for  $P_{CO_2} = 1 \times 10^{-4}$  atm.

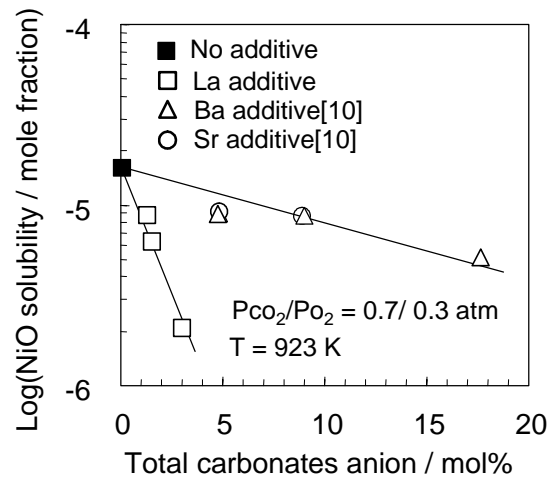


Fig. 8 The effect of the addition to NiO or carbonate on the solubility of NiO in Li/Na eutectic carbonate.