

Short Communication

Effect of rare earth oxides for improvement of MCFC

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Abstract

The solubility of rare earth metal oxides and their effect on the NiO solubility have been discussed to stabilize the cathode of molten carbonate fuel cells. The solubility of Ho, Yb, and Nd oxides were 4.4×10^{-4} , 3.4×10^{-4} , and 1.3×10^{-3} (mole fraction) at 923 K, respectively. The solubilities of NiO in $(\text{Li}_{0.52}/\text{Na}_{0.48})_2\text{CO}_3$ with the saturated Ho, Yb, and Nd were 1.57×10^{-5} , 1.41×10^{-5} , and 9.5×10^{-6} , respectively. Among these three, Nd, which has the highest solubility in the carbonates, reduced the NiO solubility most; although, the La reduced the NiO solubility more than Nd.

The logarithm of the solubility of the rare earth metal oxides has a linear relation to the Coulomb force ratio between the rare earth metal and the alkaline metal. Following this relation, the La should have the highest solubility among all the lanthanides. The basicity which NiO solubility closely relates has a linear relationship to the Coulomb force parameter of the melts. Based on these two models, the La would be the best additive to reduce the NiO solubility in Li/Na eutectic carbonate melt, among all the lanthanides.

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1. Introduction

Molten carbonate fuel cells (MCFCs) are using a fused mixture of alkaline metal carbonates as the electrolyte, and have been expected as a new generation system that can be a substitute for thermal power generations and dispersed power generations [1]. Some demonstrative MCFC systems have been operating since several years; however, the Ni shortening by dissolution/Ni deposition of the NiO cathode is still a serious problem, especially for the MCFC combined cycle system with a gas turbine that will operate under highly pressurized operating conditions.

The most effective procedure against Ni shorting is to reduce the solubility of NiO in the molten carbonate, because the Ni^{2+} ion, which is the dissolution specie of nickel, plays an essential role in all the steps of the Ni shorting. To reduce the solubility, the development of a new stable cathode material and the stabilization of NiO by the control of the basicity of an electrolyte have been investigated regarding the prevention of shorting. As a later example, alkaline earth metal carbonate additive to the alkaline metal molten carbonates reduced the NiO solubility [2]. As an

advanced additive, the rare earth metal oxides have been studied for both, the decrease of the NiO [3–6] and the enhancement of the oxygen reduction reaction [7,8]. The lanthanum oxide is the most effective additive to reduce the NiO solubility at present.

The acid–base concept [9,10] was applied to discuss the dependence of the NiO solubility on carbon dioxide partial pressure and the composition of alkaline metal carbonate [11,12]. The solubility of NiO is not only important for the application of MCFC, but also important as an index of the acid–base equilibrium, because NiO dissolves by the acid dissolution mechanism and forms oxide ion in higher carbon dioxide partial pressure region [5,12]. The relationship between the cation species and the basicity had been discussed from the NiO solubility point of view [5]. The electrostatic parameter might explain the relationship of alkaline metal carbonate with and without alkaline earth metal carbonate; however, the effect of the rare earth metal oxide, which has +3 or +4 valence, on the basicity from the NiO solubility point of view could not be clarified.

In this study, in order to improve the activity of MCFCs we have investigated a new additive to the electrolyte and clarified the effect of the additives on the solubility of NiO. The solubility of Ho, Yb, and Nd and their effect on the solubility of the NiO have been determined. These results were also discussed with the dependences of the size, the valence, and the stable phase of the rare earth metal cation on the solubility of the NiO.

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2. Experimental

2.1. Evaluation of stable phase of rare earth oxides in molten carbonates

The stable phase of rare earth oxides was determined by X-ray diffraction (Shimadzu XRD-6000). Ho_2O_3 (99.9%), Yb_2O_3 (99.99%), and Nd_2O_3 (99.9%, Kojundo Chemical Laboratory) were used as start materials of rare earth metal oxides. Fifty mole percent Li_2CO_3 –48 mol% Na_2CO_3 (Li/Na eutectic carbonate) was used as molten carbonate. The molten carbonate were made up to a total weight of 100 g and mixed in 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 [12]. Powder of the rare earth oxide was immersed in molten carbonates under $P_{\text{CO}_2}/P_{\text{O}_2} = 0.7 \text{ atm}/0.3 \text{ atm}$ for 4000 h. After the immersion, the powder was washed out from the carbonate by acetic acid, and identified by XRD to evaluate the stable phase.

2.2. Evaluation of the rare earth oxides solubility in Li_2CO_3 – Na_2CO_3

The solubilities of the stable phase of the Ho, Yb, and Nd oxides were determined in 52.0 mol% Li_2CO_3 –48.0 mol% Na_2CO_3 . Excess amount of the rare earth metal oxide was added in the alkaline metal carbonate. The mixture was refined as described above. The solubility of the rare earth elements was measured in the temperature range from 913 to 1023 K under $P_{\text{CO}_2}/P_{\text{O}_2} = 0.7 \text{ atm}/0.3 \text{ atm}$. The Ho, Yb, and Nd concentrations were determined by ICP-AES (Seiko Instruments Inc. SPS3000).

2.3. Evaluation of the nickel oxide solubility in molten carbonates with rare earth oxides

The solubility of NiO was measured in the Li/Na eutectic carbonate containing the saturated Ho, Yb, or Nd. The lithiated NiO was prepared by the sintering method [12]. The solubility of NiO was determined in the same manner as that of the rare earth oxide in the Li/Na eutectic carbonate.

3. Results and discussions

The XRD patterns of the Ho_2O_3 , Yb_2O_3 , and Nd_2O_3 after 4000 h solubility measurement in $(\text{Li}/\text{Na})_2\text{CO}_3$ are shown in Fig. 1. Ho_2O_3 or Yb_2O_3 was stable phase in this condition for these elements. For Nd_2O_3 , $\text{Nd}_2\text{O}_2\text{CO}_3$ was detected; however, this sample should be a mixture of the multiphase. Therefore, the stable phase of Nd oxide might be oxycarbonate. $\text{La}_2\text{O}_2\text{CO}_3$ and $\text{Gd}_2\text{O}_2\text{CO}_3$ were stable phases in the previous study [6]. The stable phases of larger cation radius elements were oxy-carbonate, and those of smaller cation radius elements were oxide.

The logarithm of the solubility of the rare earth metals in $(\text{Li}/\text{Na})_2\text{CO}_3$ under $P_{\text{CO}_2}/P_{\text{O}_2} = 0.7 \text{ atm}/0.3 \text{ atm}$ as a function of the inverse temperature is shown in Fig. 2. The solubility of Ho, Yb, and Nd were 4.4×10^{-4} , 3.4×10^{-4} , and 1.3×10^{-3}

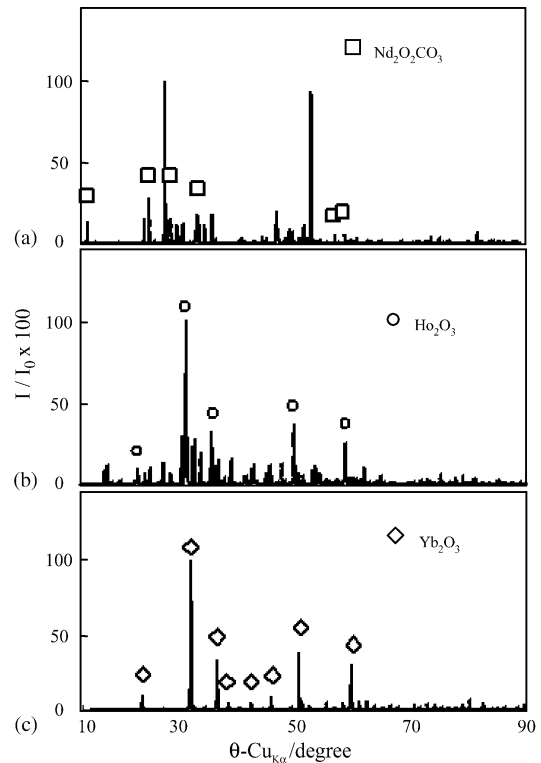


Fig. 1. X-ray diffraction pattern of (a) Nd_2O_3 , (b) Ho_2O_3 and (c) Yb_2O_3 in molten carbonate for 4000 h.

at 923 K, respectively. Their logarithms of the solubility were linear to the inverse temperature. This behavior is the same as the solubility of NiO; however, the solubility dependence of the Nd on temperature was very small. When the dissolution species is a cation, the dissolution reaction follows the acid dissolution mechanism. At this moment, the solubility is proportional to the carbon dioxide partial pressure and the solubility increases with the decrease in temperature. The acid dissolution mechanism of a metal oxide MO is as follows:

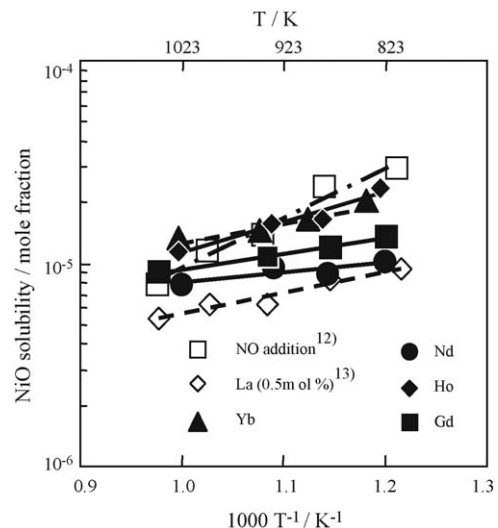


Fig. 2. Dependence of NiO Solubility in molten carbonates with and without rare earth additives as a function of inverse temperature in $\text{CO}_2/\text{O}_2 = 0.7 \text{ atm}/0.3 \text{ atm}$.

Table 1
Ionic radius and coordination number of ions (ionic radius $\times 10$ nm (coordination number))

Alkaline metal		Alkaline earth metal		Rare earth metal		Anion	
Li ⁺	0.76(6)	Ca ²⁺	1.00(6)	Y ³⁺	0.90(6)	CO ₃ ²⁻	1.85 ^a
Na ⁺	1.02(6)	Sr ²⁺	1.18(6)	La ³⁺	1.22(9)	O ²⁻	1.40(6)
K ⁺	1.51(8)	Ba ²⁺	1.42(8)	Ce ⁴⁺	0.97(8)		
				Nd ³⁺	0.98(6)		
				Gd ³⁺	1.11(9)		
				Ho ³⁺	0.90(6)		
				Yb ³⁺	0.87(6)		

^a Evaluated by Kapustinskii equation.



Here, (1) is the dissolution equilibrium and (2) is the acid–base equilibrium [12]. The dependence of the solubility on temperature should be the summation of the dissolution equilibrium and the acid–base equilibrium; however, the temperature dependence of the each equilibrium has not been clarified.

The relationship between the solubility of the rare earth metal and the ionic radius has been discussed from the ratio of the Coulomb force between the alkali metal cation-carbonate anion and the rare earth metal cation-carbonate anion [6]:

$$I = \frac{F_A}{F_L} = \frac{Z_A Z_C / (r_A + r_C)^2}{Z_L Z_C / (r_L + r_C)^2} \quad (3)$$

here, Z and r are the valence number and the ion radius, and the subscripts A, C, and L are the alkali metal cation, carbonate anion, and the rare earth metal cation, respectively.

The ionic radii that we used are shown in Table 1 with their coordination number [13,14]. The ionic radii of the elements were from the solid data of the stable phases [13]. The ionic radius of the carbonate anion was calculated from the Kapustinskii equation [14].

Fig. 3 shows the logarithm of the rare earth metal solubility as a function of the ratio of the Coulomb force: I . The logarithm

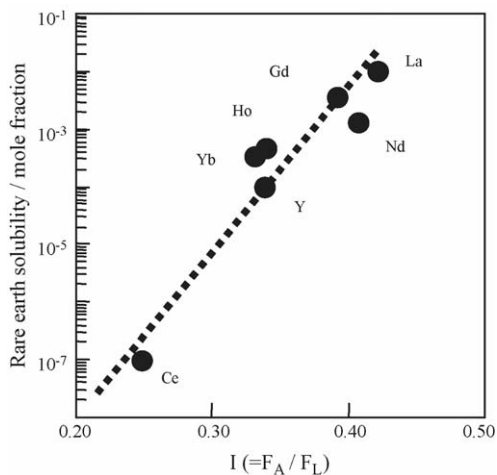


Fig. 3. Solubility of rare earth metal at 923 K in $\text{CO}_2/\text{O}_2 = 0.7$ atm/0.3 atm as a function of the Coulomb force ratio between the rare earth metal cation-carbonate anion and the alkaline cation-carbonate anion.

of the solubility was linear to the ratio of the Coulomb force. Therefore, a cation that had larger radius with smaller valence should be easier to dissolve in the melt. In other words, a cation that had a relative weak Coulomb bond and has larger radius and smaller valence, should be easy to dissolve. In this theory, the La would have the highest solubility in all the lanthanides.

The acid–base equilibrium has been discussed from the NiO solubility point of view. The solubility of NiO with and without rare earth metals as a function of temperature under $P_{\text{CO}_2}/P_{\text{O}_2} = 0.7$ atm/0.3 atm is shown in Fig. 3. NiO solubility decreased with the increase of temperature. The dependence of NiO solubility on temperature decreased by additive. The solubility of NiO in $(\text{Li}/\text{Na})_2\text{CO}_3$ without any additive was 1.60×10^{-5} in mole fraction [12]. The solubilities of NiO in $(\text{Li}/\text{Na})_2\text{CO}_3$ with the saturated Ho_2O_3 , Yb_2O_3 , and Nd_2O_3 were 1.57×10^{-5} , 1.41×10^{-5} , and 9.5×10^{-6} . In these three, the Nd, which has the highest solubility in them, reduced best; however, the La reduced NiO solubility more than Nd.

These orders might be predicted by the electrostatic parameter of the melt [5]; however, the NiO solubility as a function of the electrostatic parameter with the alkaline earth metal carbonate additive had smaller slope than that with rare earth metal oxide additive. Therefore, a basicity model by a new parameter based on the Coulomb force has been proposed. The assumptions of the Coulomb force parameter are as follows:

1. The solubility of NiO is small enough not to affect the property of the melt.
2. The melt consist of the alkaline, the alkaline earth, and the rare earth metal cations, oxide anions, and carbonate anions.
3. The ionic radii are in Table 1.
4. The Coulomb force parameter of the multi species of cation and the anion is an average of cations as follows:

$$F_A = \frac{1}{N_C} \sum_{i=1}^{N_C} \frac{Z_{C,i} Z_A}{(r_{C,i} + r_A)^2} \quad (4)$$

Here, N_C , i , $Z_{C,i}$, Z_A , $r_{C,i}$, and r_A are the total number of cations in the system, the ordinal number of the cation, the valence of cation “ i ”, the valence of anion, the radius of cation “ i ”, and the radius of anion.

5. The fraction of oxide anion in all anion can be determined as a nominal value that can be calculated from dissociation of the stable phase of the lanthanide by using their solubility

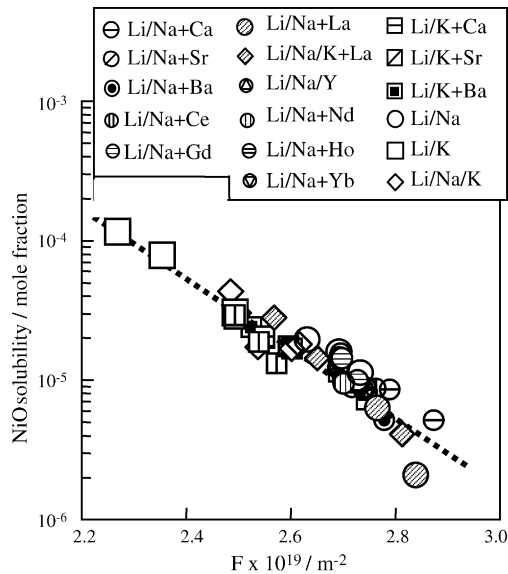
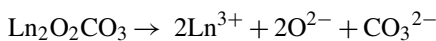


Fig. 4. Solubility of NiO at 923 K in $\text{CO}_2/\text{O}_2 = 0.7 \text{ atm}/0.3 \text{ atm}$ as a function of the Coulomb force parameter.

when Ln shows the rare earth elements as follows:



6. The Coulomb force parameter of the melt is the summation of the products of their fraction and the F_A of Eq. (4).

Therefore, the Coulomb force parameter F , can be determined by the following equation:

$$\begin{aligned}
 F &= f_{\text{CO}_3^{2-}} F_{\text{CO}_3^{2-}} + f_{\text{O}^{2-}} F_{\text{O}^{2-}} \\
 &= \frac{f_{\text{CO}_3^{2-}}}{N_C} \sum_{i=1}^{N_C} \frac{Z_{C,i} Z_{\text{CO}_3^{2-}}}{(r_{C,i} + r_{\text{CO}_3^{2-}})^2} \\
 &\quad + \frac{f_{\text{O}^{2-}}}{N_C} \sum_{i=1}^{N_C} \frac{Z_{C,i} Z_{\text{O}^{2-}}}{(r_{C,i} + r_{\text{O}^{2-}})^2}
 \end{aligned} \quad (5)$$

Fig. 4 shows the logarithm of the NiO solubility as a function of the Coulomb force parameter. This figure includes the NiO solubilities in binary [6,12] and ternary [6] alkali metal carbonate with and without additives [2,6]. The logarithm of the NiO solubility decreased with the increase in the Coulomb force, and this relationship was almost linear for all the solubility data. Therefore, the basicity of the molten carbonate might be a function of the size of the ions. To reduce the NiO solubility, the smaller ion radius and larger valence would be better; however, if the Coulombs force of an additive is too strong in a melt by its small cation radius and large radius, its solubility in the melt would be very small, and the effect of the additive on the NiO solubility might be very small. One of these examples is Ho_2O_3 in $(\text{Li}/\text{Na})_2\text{CO}_3$. By the solubility model for the

rare earth metal and the basicity model from the NiO solubility point of view, the La would be the best additive to reduce the NiO solubility in Li/Na eutectic carbonate melt for all the lanthanides.

4. Conclusion

MCFCs have excellent characteristics for the distributed power generation systems. However, the durability with the presence of molten carbonate should be improved. The Ni shortening caused by the dissolution of NiO cathode would be most serious especially at a high pressure operation. In order to protect the Ni shortening the solubility of NiO in molten carbonate should be reduced.

To reduce the NiO solubility in molten carbonate, the solubility of rare earth metal oxides and the effect of the rare earth metal oxide on the NiO solubility have been discussed. The solubility of Ho, Yb, and Nd oxides were 4.4×10^{-4} , 3.4×10^{-4} , and 1.3×10^{-3} (mole fraction) at 923 K, respectively. The solubilities of NiO in $(\text{Li}_{0.52}/\text{Na}_{0.48})_2\text{CO}_3$ with the saturated Ho, Yb, and Nd were 1.57×10^{-5} , 1.41×10^{-5} , and 9.5×10^{-6} , respectively. Among these three, Nd, which has the highest solubility in the carbonates, reduced the NiO solubility most; although, the La reduced the NiO solubility more than Nd.

The logarithm of the solubility of the rare earth metal oxides has a linear relation with the Coulomb force ratio between the rare earth metal cation and the alkaline metal cation by using ionic radii of solid phase. Following this relation, the La should have the highest solubility among all the lanthanides. The basicity which NiO solubility closely relates has a linear relationship to the Coulomb force parameter of the melts. Based on these two models, the La would be the best additive to reduce the NiO solubility in Li/Na eutectic carbonates melt among all the lanthanides.

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