EFFECT OF RARE EARTH ADDITION TO MOLTEN CARBONATE ON THE SOLUBILITY OF NiO

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ABSTRACT

For the commercial application of molten carbonate fuel cells (MCFCs) under high-pressure operation, Ni shorting might be a problem to be solved. To improve the MCFC cathode stability, the solubility of rare earth elements and the effects of the addition of these rare earth elements to the molten carbonates have been studied. The solubility of Y in molten carbonate was $9.5 \times 10^{-5}$ (mole fraction) at 923 K and $P_{O_2}/P_{CO_2} = 0.3/0.7$ atm. The NiO solubility was reduced by the Y addition. However, the effect of the Y addition is much smaller than that of La. This difference might be caused by the small solubility of Y compared with that of La ($=1.3 \times 10^{-2}$ (mole fraction)). The relationship between the solubility of NiO and the composition of the carbonate melt with a cation additive is also discussed. The addition of a smaller radius and higher valence cation with large solubility would effectively reduce the NiO solubility.

INTRODUCTION

Molten carbonate fuel cells (MCFCs) have long been expected as a new generation system that can be a substitute for thermal power generation and dispersed power generation. Recently, some demonstrative MCFC systems have been operating (1). However, Ni shorting by dissolution / Ni deposition on the NiO cathode is still a serious problem, because the MCFC combined cycle system with a gas turbine will be operated under highly-pressurized operating conditions.

The most effective procedure against Ni shorting is to reduce the solubility of the NiO in the molten carbonates, because the Ni$^{2+}$ ion plays an essential role in all of the processes for Ni shorting. More specifically, the stabilization of the cathode material itself and the stabilization of NiO by control of the basicity of an electrolyte have been investigated regarding the decrease of NiO solubility. As a latter example, alkaline earth metal carbonate additives to the alkaline metal molten carbonates reduced the NiO solubility (2).

In order to improve the performance and lifetime, investigations into more advanced materials are required. From the viewpoint of NiO stability and the oxygen reduction acceleration, lanthanum oxide as a new additive in these electrolytes has been studied (3-4). The solubility of NiO with the La additive in the molten carbonates was drastically reduced compared to melts with no additive, and the effect of the La additive on the solubility of NiO has been studied.
NiO was greater than that with any other alkali earth metal additives in the Li/Na carbonates. The molten carbonates might become more basic by adding the La additive.

The acid-base condition of molten carbonates has explained by $pO^2$ (-log [O$^2$]) as basicity which was defined by the Lux-Flood concept (4-5). The inter-relation between the basicity of the melts and the solubility of NiO has been discussed (6). However, it is difficult to completely estimate the NiO solubility in molten carbonates due to its complicated characteristics (7-8). The basicity, $[O^2] = [M_2O]$, that was assumed from the equilibrium of the $M_2CO_3$ decomposition, the NiO solubility as a function of $-\log [M_2O]$, would not provide a clear relationship between the NiO solubility and the type of carbonate. For this reason the acid-base equilibrium on the NiO solubility in molten carbonates has been evaluated by the dependence of carbon dioxide partial pressure (10). Therefore, the effect of various additives on the NiO solubility in molten carbonates should be investigated for the purpose of the basicity evaluation, and the factor that controls the basicity of the melt should also be considered.

In this paper, the solubility of rare earth elements in molten carbonates and the effects of the rare earth additives in the molten carbonates on the NiO solubility have been investigated. The relationship between the solubility of NiO and various additives in molten carbonates already investigated has also been discussed.

**EXPERIMENTAL**

**The evaluation of stable phase of rare earth elements in molten carbonates**

The stable phase of rare earth oxides was determined by X-ray diffraction (Shimadzu XRD-6000). $Y_2O_3$, $CeO_2$ and $Gd_2O_3$ (99.99%, Kojundo Chemical Laboratory) were used as starting materials of rare earth metal oxides. 52 mol% $Li_2CO_3$ - 48 mol% $Na_2CO_3$ (Li/Na eutectic carbonate) was used as molten carbonate. The carbonate were mixed in a dry box and refined by vacuum drying and CO$_2$ bubbling (9). The rare earth oxide of pellet ($Y_2O_3$ and $Gd_2O_3$) or powder ($CeO_2$) form was immersed in the molten carbonate at 923K under $PCO_2/P_{O2}$ - 0.7/0.3 atm for several hours. After immersion, the pellets or powder was washed with acetic acid, and the stable phase identified by XRD.

**The evaluation of the rare earth elements solubility in molten carbonates**

In order to evaluate the solubility of the rare earth metal oxides, the solubility was measured in 51.2 mol% $Li_2CO_3$ - 47.3 mol% $Na_2CO_3$ - 1.5 mol% $Y_2O_3$ (Li/Na eutectic carbonate + 3 mol % Y); 49.9 mol% $Li_2CO_3$ - 46.1 mol% $Na_2CO_3$ - 4 mol% $CeO_2$ (Li/Na eutectic carbonate+ 4 mol % Ce); and 51.7 mol% $Li_2CO_3$ - 47.8 mol% $Na_2CO_3$ - 0.5 mol% $Gd_2O_3$ (Li/Na eutectic carbonate+ 1 mol % Gd). The mixture was refined as described above. The solubility of the rare earth elements was measured in the $PCO_2$ range from 0.1 to 0.7 atm and in the temperature range 823-1023 K, respectively. A small melt sample for quantitative analysis was collected at appropriate intervals and dissolved in 3M HNO$_3$. The Y, Ce, and Gd concentrations were measured by ICP-AES (Seiko Instrument SPS30000).
In order to evaluate the solubility of NiO, the solubility was measured in the Li/Na eutectic carbonate containing the rare earth element. The lithiated NiO was prepared by a sintering method (10). The solubility of NiO was determined in the same manner as that of the rare earth oxide in the Li/Na eutectic carbonate. A small amount of carbonate was dissolved in 2M HCl for the Y addition or 3M HNO₃ for the Ce or Gd addition for determination by ICP-AES.

RESULTS

The stable phase and solubility of rare earth element in molten carbonates.

Figure 1 shows the XRD pattern of yttrium oxide before and after immersion in the Li/Na eutectic carbonate under PCO₂/P0₂ = 0.7/0.3 atm at 923 K for 100 h. The peaks detected before and after immersion were essentially Y₂O₃. Therefore, the stable phase of yttrium oxide in molten carbonates was Y₂O₃. Figure 2 shows the XRD pattern of cerium oxide before and after immersion in the Li/Na eutectic carbonate under PCO₂/P0₂ = 0.7/0.3 atm at 923 K for 400 h. The peaks detected before and after the immersion corresponded closely to CeO₂. Therefore, the stable phase of cerium oxide in molten carbonates would be CeO₂. Figure 3 shows the XRD pattern of gadolinium oxide before and after immersion in the Li/Na eutectic carbonate under PCO₂/P0₂ = 0.7/0.3 atm at 923 K for 75 h. The peaks detected after immersion were corresponded closely to Gd₂O₂CO₃, and no peak of Gd₂O₃ was detected. Therefore, the stable phase of gadolinium oxide in the molten carbonates should be Gd₂O₂CO₃.

Figure 4 shows the solubility of the rare earth elements in the molten carbonates as a function of the PCO₂ in the molten carbonates at 923 K vs. the solubility of La (11) at 923 K. The solubilities of Y, Ce and Gd under PCO₂/P0₂ = 0.7/0.3 atm were 9.5 x 10⁻⁵, 9.5 x 10⁻⁸ and 1.8 x 10⁻³ (mole fraction), respectively. These solubilities were lower than that of La. The solubility of Y and Gd increased with PCO₂. The slope of the plots for Y and Gd were ca. 1, and 1/2, respectively.

Figure 5 shows the logarithmic solubility of the rare earth elements in the molten carbonates as a function of the inverse temperature under PCO₂/P0₂ = 0.7/0.3 atm vs. the solubility of La (11) at 923 K. The solubility of Y and Gd in the molten carbonates was linear with the inverse temperature.

The dissolution reaction of the yttrium and the gadolinium oxides seemed to follow a simple acid dissolution, because the solubility was proportional to the PCO₂:

\[ \text{Y}_2\text{O}_3 (s) + \text{CO}_2 (g) \leftrightarrow 2\text{YO}^+ (l) + \text{CO}_3^{2-} (l) \]  \hspace{1cm} [1]  
\[ \text{Gd}_2\text{O}_2\text{CO}_3 (s) + 2\text{CO}_2 (g) \leftrightarrow 2\text{Gd}^{3+} (l) + 3\text{CO}_3^{2-} (l) \]  \hspace{1cm} [2]
Figure 1. X-ray diffraction pattern of yttrium oxide in molten carbonates before and after immersion at 923 K for 100h; $\text{Y}_2\text{O}_3(\text{°})$; a) after immersion, b) before immersion.

Figure 2. X-ray diffraction pattern of cerium oxide in the molten carbonates before and immersion at 923 K for 3000h; $\text{CeO}_2(\Delta)$; a) after immersion, b) before immersion.
Figure 3. X-ray diffraction pattern of gadolinium oxide in molten carbonates before and after immersion at 923 K for 75h; $\text{Gd}_2\text{O}_3$($\triangledown$), $\text{Gd}_2\text{O}_2\text{CO}_3$($\circ$), a) after immersion, b) before immersion.

Figure 4. Solubility of NiO in Li/Na eutectic carbonate with and without rare earth element addition as a function of $P_{\text{CO}_2}$ at 923K; La (11)($\circ$), Gd ($\circ$), Y($\circ$), Ce($\circ$).
Figure 5. Rare earth element solubility of NiO in Li/Na eutectic carbonate as a function of inverse temperature; La (11), Gd (○), Y (○).

Figure 6. NiO solubility in molten carbonates as a function of P$_{CO_2}$; No additive (10) (△), with Y (saturated) (●), with Gd (saturated) (○), with La (11) (0.5 mol%) (■).
The solubility of nickel oxide in molten carbonates with rare earth element

Figure 6 shows the solubility of NiO in the molten carbonates with the saturated rare earth elements addition as a function of the Pco2 in the molten carbonates at 923 K vs. the solubility of NiO with and without the La additive (0.5 mol%) (10-11) at 923 K. The solubilities of NiO with the Y, Ce or Gd additive under Pco2/Po2 = 0.7/0.3 atm were 1.2×10^{-5}, 1.5×10^{-5}, and 1.0×10^{-5} (mole fraction) in the molten carbonates. Since the solubilities of NiO in the molten carbonates with and without the La additive (0.5 mol%) under Pco2/Po2 = 0.7/0.3 atm were 6.3×10^{-4}, and 1.6×10^{-5} (mole fraction), respectively, the solubilities of NiO with the Y, Ce and Gd addition were approximately 25, 10, and 35 % less than without any additive, but these were greater than those with the La additive.

Figure 7 shows the logarithmic solubility of NiO in the molten carbonates with the rare earth addition as a function of the inverse temperature under Pco2/Po2 = 0.7/0.3 atm. The solubility of NiO in the molten carbonates with and without the rare earth element additive increased with the decrease of temperature. NiO dissolves by an acid dissolution mechanism at a high CO2 pressure as follows:

\[ \text{NiO (s)} + \text{CO}_2 (g) \leftrightarrow \text{Ni}^{2+} (l) + \text{CO}_3^{2-} (l) \]  

This equation was divided into two reactions as follows:

\[ K_{sp} \quad \text{NiO(s)} \leftrightarrow \text{Ni}^{2+} (l) + \text{O}^{2-} (l) \]  

\[ K_{dis} \quad \text{CO}_3^{2-} \leftrightarrow \text{CO}_2 (g) + \text{O}^{2-} (l) \]

According to this mechanism, the decrease in the NiO solubility with the rare earth additives would cause the basicity of the melt to decrease. The solubilities of NiO in molten carbonates with La addition drastically decreased. Since the solubility of La was much greater than that of Y, Ce, or Gd, the basicity of the melt with the La addition might be lower than that with the Y, Ce or Gd additive.

As the dissolution of the NiO into molten carbonates is an exothermic reaction in the acid dissolution region, the solubility of NiO will decrease with temperature. However, the slopes of the Ni solubilities in molten carbonates with the rare earth element additions were smaller than those without any additive due to the buffer effect of the rare earth oxides on the basicity. Therefore, the effect of the rare earth element addition to molten carbonates on the solubility of NiO was smaller at high temperatures than at low temperatures. This was attributed to the dissolution reaction of the Ce or Gd oxides in the molten carbonates and was similar to that of NiO as follows:

\[ \text{Gd}_2\text{O}_2\text{CO}_3 (s) \leftrightarrow 2\text{Gd}^{3+} (l) + \text{O}^{2-} (l) + \text{CO}_3^{2-} (l) \]  

\[ \text{CeO}_2 (s) \leftrightarrow \text{Ce}^{4+} (l) + 2\text{O}^{2-} (l) \]  

\[ \text{NiO(s)} \leftrightarrow \text{Ni}^{2+} (l) + \text{O}^{2-} (l) \]
Figure 7. NiO Solubility in molten carbonates as a function of inverse temperature. No additive (10) (△); with Y (saturated) (●); with Gd (saturated) (♦); with La (11) (0.5 mol%) (■).

The rare earth metal oxide solubility was greater than NiO, and the dependence of the rare earth metal oxide solubility on the temperature was same as the NiO. Therefore, a change in the rare earth metal oxide solubility would reduce the change of the NiO solubility and the basicity of the melt, in the manner of a buffer effect.

DISCUSSION

The solubility of the rare earth elements in molten carbonates

Each rare earth element has a different solubility in the molten carbonates. The effect of the rare earth element additive in molten carbonate on the NiO solubility per additive amount was much greater than the alkali earth metal carbonate additive. However, the rare earth additive would slightly decrease the solubility of NiO, if the solubility of the rare earth element itself was very low. Here, the reason why each kind of rare earth element has a different solubility in molten carbonate is considered. We defined $I_r$ as the ratio of the Coulomb force between the rare earth cation-carbonate ion ($F_b$) and bulk carbonate ions ($F_a$). $I_r$ was expressed as follows:
Figure 8. Rare-earth solubility in Li/Na eutectic carbonate as a function of $I_r$; La (11)$^{(1)}$, Gd $^{(1)}$, Ce$^{(1)}$.

Here, $Z$, and $r$ are the valence number and ion radius, and the subscripts of $a$, $Cn$, and $Ln$ are the alkali metal cation, carbonate anion, and the rare earth metal cation, respectively.

In other words, when the value of $I_r$ becomes small, the Coulomb force will be strong and the rare earth element will be hard to dissolve in the molten carbonates because of an oxide formation due to the strong Coulomb force. On the other hand, when the value of $I_r$ becomes large, the Coulomb force will be weaker, and the rare earth element will be easily dissolved in the molten carbonates. The $I_r$ of each melt was calculated using the ion radius (12-13) of their coordinate number (14) for the rare earth elements at 923 K, and then $I_r$ of the mixed melt was calculated for each amount of the melt. Figure 8 shows the solubility of the rare earth elements in the molten carbonates as a function of $I_r$. Based on this result, the solubility of rare earth elements increased with $I_r$. Therefore, the rare earth element that has the large ion radius and the small valance number might have large solubility in molten carbonates.

**The solubility of nickel oxide in molten carbonates with the additives**

There are two ways to decrease the solubility of NiO in molten carbonates: to stabilize the cathode material itself or to stabilize the NiO by the controlling of the basicity of the melt. Furthermore, the main factors to be stabilized in the cathode material itself are indicated by $K_{sp}$ from eq. [4] and the main factor to stabilize the NiO by controlling the
basicity of the melt is indicated by the $K_{\text{dis}}$ from eq. [5]. The basicity of the molten carbonate is also described in detail as follows from eq. [5]

$$pO_2^- = -\log [O_2^-] = \log \left[ \frac{P_{\text{CO}_2}}{K_{\text{dis}}} \right]$$  \[9\]

Figure 9. Effect of additive in molten carbonates on the solubility of NiO for Li/Na eutectic carbonate; No additive (10) (▲), La additive (■), Gd additive (●), Ba additive (2) (▲), Sr additive (2) (●).

We now consider the factor that influences the $K_{\text{dis}}$. Fig. 8 shows the effects of the additives in the molten carbonates on the NiO solubility. The effect of the rare earth elements was much greater than that of the alkali earth elements. Although this was caused by the acid-base equilibrium in the molten carbonates, this was also related to the cation valence number of the additive. Because the valence numbers of the rare earth element ion and alkali earth element ion were 3 and 2, respectively, these might lead in the difference of the effect on the solubility of the NiO. However, even if the valence number of the cation in the molten carbonates was the same as in the case of the Li/Na system and the Li/K system, the solubility of NiO in Li/Na system was lower than that in the Li/K system (9). This might indicate that the ion radius of cation in molten carbonates was related to the effect on the NiO solubility. Therefore, the valence number and the ionic radius of the cation of the melt were the essential factors to decrease the NiO solubility. We then defined the parameter ($\varepsilon'$), the amount of the electrostatic parameter of the cation that is used for conversion into the lattice enthalpy of the ionic crystal and also estimated the index for the molten salts (15). In other words, the larger values $\varepsilon'$ has, the more dissociative the carbonate. The $\varepsilon'$ value was expressed as follows:

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Here $N_c$, $Z$, and $r$ are expressed as the number of cations per unit volume, the valence number and the ion radius of the cation, respectively. The equation (10) was involved in an arithmetic mean of the charge account. Fig. 10 shows the NiO solubility in molten carbonates and that with an alkali earth element (Ba, Sr, Ca) (2) and rare earth element (La (16), Y, Gd, Ce) additive as a function of $\varepsilon'$ under $\text{P}_{\text{CO}_2}/\text{P}_{\text{O}_2} = 0.7/0.3$ atm at 923 K.

The relationship between the solubility of NiO and the $\varepsilon'$ appeared linear, not only for the Li/K carbonate system, but also for the Li/Na carbonate system, the Li/Na/K carbonates system and the all those with additives. According to this figure, the $\varepsilon'$ parameter seems to be useful for evaluating the basicity of the melt and the solubility of NiO. In order to decrease the solubility of NiO from this parameter, it seems that the melt required the following: a smaller radius and higher valence cation with large solubility to be effective.

CONCLUSIONS

The stable phases of the rare earth metal oxides in the Li/Na eutectic carbonate under $\text{P}_{\text{CO}_2}/\text{P}_{\text{O}_2} = 0.7/0.3$ atm at 923 K were CeO$_2$, Y$_2$O$_3$, and Gd$_2$O$_2$CO$_3$. The solubilities

\[
\varepsilon' = \sum_{i_c} \frac{Z_c}{r_c}^2
\]
of Y, Ce, or Gd in the Li/Na eutectic carbonate under $P_{CO_2}/P_{O_2} = 0.7/0.3$ atm at 923 K were $9.5 \times 10^{-5}$, $9.5 \times 10^{-8}$ and $1.8 \times 10^{-3}$ (mole fraction), respectively. These solubilities were lower than that of La.

The solubilities of NiO with the Y, Ce or Gd additive under $P_{CO_2}/P_{O_2} = 0.7/0.3$ atm were $1.2 \times 10^{-5}$, $1.5 \times 10^{-5}$ and $1.0 \times 10^{-5}$ (mole fraction) in the molten carbonates. These were approximately 25, 10, and 40% less than that without an additive, but had a larger solubility than that with the La additives. Since the solubility of La was much greater than that of Y, Ce or Gd, the basicity of the melt with the La additive might be lower than that with Y, Ce or Gd.

To predict the solubility of rare earth element in the molten carbonates, we defined the parameter $I_r$ as the ratio of the Coulomb force of the rare earth element in the molten carbonates. The solubility of the rare earth elements increased with $I_r$. To obtain a large solubility in the molten carbonates, the rare earth element that has a large ion radius and small valence number is required.

To evaluate the effects of the additives in the molten carbonates on the NiO solubility, we defined the parameter $\epsilon'$ that represented the amount of the electrostatic parameter of the cation. The relationship between the NiO solubility and $\epsilon'$ appeared linear for all the alkaline metal carbonate mixtures and all of them with additives. In order to decrease the NiO solubility, a smaller radius and higher valence cation with a large solubility would be effective.

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