

## Effect of Rare Earth Addition to Molten Carbonate on the Solubility of NiO

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### Introduction

Recently, some of demonstrative plants of Molten Carbonate Fuel Cells (MCFCs) have been operated<sup>1)</sup>. In Japan, the combined generation system with a pressurized MCFC and a gas turbine developing to get higher energy efficiency than ambience pressure MCFC system. This leads to the high-pressured operation condition, and the Ni shortening by dissolution of a NiO cathode in still remains as a serious problem. Since the Ni<sup>2+</sup> ion plays an essential role in the Ni shortening, the most effective way to protect against the shorting is the reduction of the solubility of NiO in molten carbonates. The stabilization of NiO has investigated in order to decrease the NiO solubility by the control of basicity of an electrolyte. The effects of alkaline earth metal carbonate addition to molten carbonates on reducing the NiO solubility was reported<sup>3)</sup>. We have also reported the effect of La and some other rare earth element<sup>4)</sup>.

In this study, the effect of the Y addition as a rare earth element to molten carbonates on the NiO solubility has been studied in order to protect the Ni shortening in MCFC.

### Experimental

The solubility of rare earth oxides in molten carbonate was measured in 52 mol% Li<sub>2</sub>CO<sub>3</sub> - 48 mol% Na<sub>2</sub>CO<sub>3</sub> (Li/Na eutectic carbonate). The molten carbonates were refined by the usual method<sup>2)</sup>. 99.99 % Y<sub>2</sub>O<sub>3</sub> was used as rare earth oxide. The solubility was measured firstly at 923 K under P<sub>O<sub>2</sub></sub>/P<sub>CO<sub>2</sub></sub> = 0.3/0.7 atm. After an appropriate time interval, a small portion of the melt was extracted and was dissolved in 3M HNO<sub>3</sub>. The concentration of Y was measured by ICP-AES (Seiko Instruments SPS3000). After the solubility measurements, the solid oxide in the melt was also identified by XRD (Shimadzu XRD-6000).

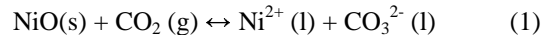
50.1 mol% Li<sub>2</sub>CO<sub>3</sub> - 47.0 mol% Na<sub>2</sub>CO<sub>3</sub> - 1.9 mol % Y<sub>2</sub>O<sub>3</sub> (Li/Na eutectic carbonate + 4 mol% (saturated) Y) was used as molten carbonates. Lithiated NiO was used as a NiO sample. The solubility of NiO was measured same as mentioned above. The P<sub>CO<sub>2</sub></sub> and the temperature were varied between 0.1~0.7 atm. A small amount of carbonates was extracted, and dissolved in 1M HCl. Ni concentration was measured by ICP-AES.

### Results and discussion

The solubility of Y in molten carbonates at 923K under P<sub>O<sub>2</sub></sub>/P<sub>CO<sub>2</sub></sub> = 0.3/0.7 atm were 9.5 × 10<sup>-2</sup> (mole fraction). The stable phase of yttrium oxide in molten carbonate was identified as Y<sub>2</sub>O<sub>3</sub> by XRD measurement.

Figure 1 shows the solubility of NiO in the molten carbonates with and without additives<sup>2-4)</sup> as a function of P<sub>CO<sub>2</sub></sub> in molten carbonates at 923 K. The solubility of NiO with the Y addition was approximately 25 % less than that without addition, but this number is small compared with those of La, Sr and Ba addition. Since the

dissolution reaction of NiO in molten carbonate follows the acid dissolution mechanism, the dissolution mechanism with rare earth additive would be also followed the acidic dissolution mechanism as follows:



Therefore, the decrease of the solubility of NiO by Y addition might be mainly attributed to the acid-base equilibrium of molten carbonates.

Figure 2 shows that the NiO solubility as a function of the concentration of additives in Li/Na eutectic carbonate under P<sub>CO<sub>2</sub></sub>/P<sub>O<sub>2</sub></sub> = 0.7/0.3 atm at 923 K. The decrease of NiO solubility per the amount of additive by Y addition was much greater than that by Sr, Ba and La addition. This effect would be explained by the acid-base equilibrium. The relation between the mixture of carbonate and the acid-base equilibrium of molten carbonate can be expressed as follows<sup>2)</sup>:

$K_{\text{dis}}(M_1/M_2 = x/1-x) = \{K_{\text{dis}}(M_1)\}^x \{K_{\text{dis}}(M_2)\}^{1-x}$  (2) where M is a cation. The basic index was defined as follows.

$$\text{Log } K_{\text{dis}} = \text{pK}^{-1} \quad (3)$$

From the view of acid-base equilibrium of molten carbonates related to the solubility of NiO, the basic index would be obtained from inclination of Fig. 2 as follows.

$$\text{pK}^{-1}(\text{Na}) : \text{pK}^{-1}(\text{Li}) : \text{pK}^{-1}(\text{Sr}) : \text{pK}^{-1}(\text{Ba}) : \text{pK}^{-1}(\text{La}) : \text{pK}^{-1}(\text{Y}) = 1.6 : 2 : 4 : 4 : 30 : 90 \quad (4)$$

The addition of a smaller radius and higher valence cation with large solubility would be important to reduce the NiO solubility.

### Acknowledgements

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### Reference

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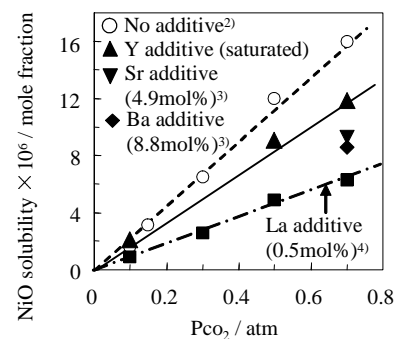


Fig. 1 The Solubility of NiO in molten carbonate with and without additives as a function of P<sub>CO<sub>2</sub></sub> at 923K.

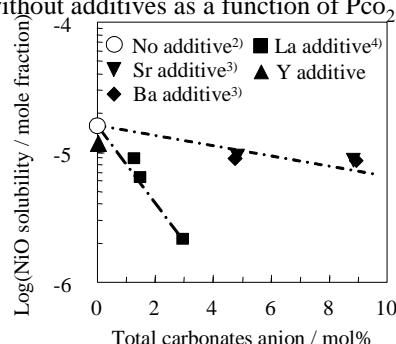


Fig. 2 The effect of additives to molten carbonate on the solubility of NiO in Li/Na eutectic carbonate.