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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 $(Li_{0.52}/Na_{0.48})_2CO_3$ 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.

Keywords: Molten carbonate; Fuel cell; Rare earth oxide; Solubility

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 $P_{CO_2}/P_{O_2} = 0.7$ atm/0.3 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 $P_{CO_2}/P_{O_2} = 0.7$ atm/0.3 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 $(Li/Na)_2CO_3$ 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, $Nd_2O_2CO_3$ was detected; however, this sample should be a mixture of the multiphase. Therefore, the stable phase of Nd oxide might be oxycarbonate. $La_2O_2CO_3$ and $Gd_2O_2CO_3$ were stable phases in the previous study [6]. The stable phases of lager 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 $(Li/Na)_2CO_3$ under $P_{CO_2}/P_{O_2} = 0.7$ atm/0.3 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} 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:

$$MO = M^{2+} + O^{2-} \tag{1}$$

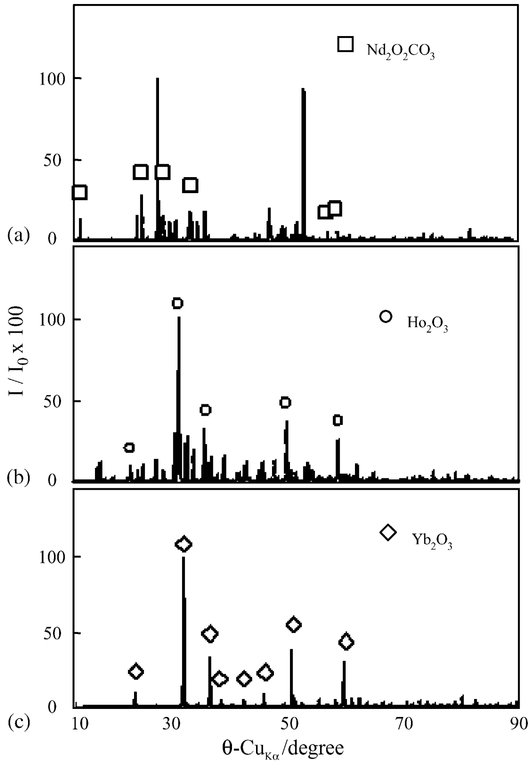

Fig. 1. X-ray diffraction pattern of (a) Nd_2O_3, (b) Ho_2O_3 and (c) Yb_2O_3 in molten carbonate for 4000 h.

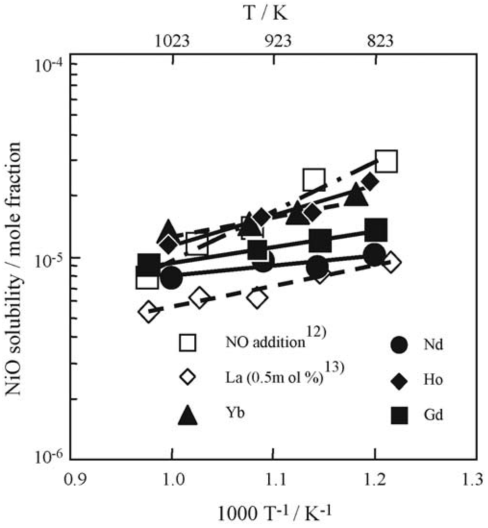

Fig. 2. Dependence of NiO Solubility in molten carbonates with and without rare earth additives as a function of inverse temperature in $CO_2/O_2 = 0.7$ atm/0.3 atm.