Short communication

Solubilities of NiO and LaNiO₃ in Li/Na eutectic carbonate with rare-earth oxide

Koichi Matsuzawa *, Yoji Akinaga, Shigenori Mitsushima, Ken-ichiro Ota

Chemical Energy Laboratory, Graduate School of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama, Kanagawa 240-8501, Japan

ARTICLE INFO

ABSTRACT

For the commercial application of molten carbonate fuel cells (MCFCs) under high-pressure operation, the problem of Ni shorting should be solved that is closely related to the solubility of cathode material. In order to improve the MCFC cathode stability, effects of the addition of rare-earth metal oxides to the molten carbonates have been quantitatively investigated. Especially, La_2O_3 addition to the molten carbonate significantly decreased the solubility of NiO. Such low solubility of NiO was caused by effects of both the acid–base equilibrium of molten carbonate and the activity of Ni in solid by the formation of complex oxide. Solubilities of $LaNiO_3$ and Nd_2NiO_4 were also smaller than that of NiO in molten carbonate as the same reason as that of NiO in the molten carbonates with saturated La_2O_3. Based on the data of solubility, a new parameter was proposed to evaluate the solubility of metal ion in molten carbonates. This parameter concerned with the acid–base equilibrium of melts and the activity of solid for the metal oxide. A linear relationship with the measured solubility of metal oxide in molten carbonates was obtained by this parameter. It would be indicated that the parameter is useful for the prediction of metal oxide solubilities in molten carbonates.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Molten carbonate fuel cells (MCFCs) have been expected and developed for distributed power generation systems and substitute thermal power generation systems with high energy conversion efficiency. MCFCs have been reached to the entry of the commercialization in worldwide [1]. However, several problems still remain on the durability of the materials such as the dissolution/deposition of NiO cathode, and the corrosion of stainless steel separators. Especially, under the high pressure operation, dissolution of the cathode (NiO) finally leads to the internal short circuit that is called as the Ni shorting. There are several steps toward the Ni shorting. First, the cathode dissolves into electrolyte, and the Ni ion transports form cathode side to anode. Then, the Ni ion reduces to the Ni metal by the reaction with crossover hydrogen from anode. After that, the Ni metal deposits across electrodes, and the Ni shorting finally occurs. During these processes, the Ni ion is the important factor for all the process toward the Ni shorting so that the most essential approach against the Ni shorting is to decrease the solubility of Ni ion. There are mainly three procedures against the dissolution of NiO; the alternative cathode material [2–5], the stabilization of cathode material by the reduction of their activity in solid [6–8], and the optimization of the acid–base condition of molten carbonates [9–11]. We have focused on the third method,

effects of rare-earth metal oxide as the additive to the molten carbonates for the decrease of the solubility of NiO [12–15]. There are also other reports to improve of the cathode stability using by rare-earth materials [16–19]. Above all, our results of NiO solubility in molten carbonates with lanthanum oxide additives obtained the lowest solubility [12–15]. In addition, we also found that La_2O_3 addition to molten carbonates also accelerated the oxygen reduction reaction [20]. In spite of such productive contributions for the MCFC cathode material, effects of the solid and melt composition on the solubility of NiO have not been clarified yet [12–15].

In this study, in order to improve the cathode material of MCFCs, we have investigated the solubilities of $LaNiO_3$ and Nd_2NiO_4 as new materials for MCFCs. Based on our results of solubility in molten carbonates, we also considered effects of solid and melt composition to propose the parameter for the prediction of solubility of metal ion.

2. Experimental

2.1. Evaluation of solubilties of nickel oxide and lanthanum oxide in molten carbonates with lanthanum oxides

Solubilities of NiO and La_2O_3 were measured in the 52% Li_2CO_3–48 mol% Na_2CO_3 (Li/Na eutectic carbonate) and that with saturated La_2O_3. The molten carbonate was made up to a total weight of 100 g, and mixed in a dry box. Then the excess amount of La_2O_3 (99.9%, Kojundo Chemical Laboratory) were also added to the Li/Na eutectic carbonate. The mixture was placed in a high-purity

* Corresponding author. Tel.: +81 45 339 4022; fax: +81 45 339 4024.
  E-mail address: kmatsu@ynu.ac.jp (K. Matsuzawa).

alumina crucible, and dried in vacuum for 12 h at 623 K. Then, carbonate melt was refined at 973 K in CO_2 bubbled for 24 h [13,14]. The lithiated NiO was prepared by the sintering method [13,14]. Concentrations of Ni and La in the melt were analyzed by ICP-AES (SPS3000, Seiko Instruments Inc.). For the evaluation of the solubility of Ni in molten carbonate with saturated amount of La_2O_3, the concentration of La was measured until it reached its solubility, and then the lithiated NiO was immersed into molten carbonate. After the solubility measurement, the cross section of the immersed sample was also characterized by SEM-EDX (SM-200, Topcon Co.).

2.2. Preparation and evaluation of the solubility of $LaNiO_3$ and Nd_2NiO_4 in molten carbonate with rare-earth metal oxide

$LaNiO_3$ and Nd_2NiO_4 were prepared by a coprecipitation method [21]. The stoichiometric ratio of lanthanum nitrate hexahydrate (98.0% Guaranteed reagent, Junsei Chemical Co.) or neodymium nitrate hexahydrate (99.9% Guaranteed reagent, Junsei Chemical Co.) and nickel nitrate hexahydrate (98.0% Guaranteed reagent, Junsei Chemical Co.) were dissolved in highly pure water (Millipore, Milli-Q Element A10). Adding the excess amount of tetramethylammonium hydroxide, the metal oxy-hydroxides were precipitated out from the solution. Precipitates were washed within highly pure water, dried and sintered for 40–60 h at 1023 K to obtain the powder of $LaNiO_3$ or Nd_2NiO_4. The solubility of $LaNiO_3$ or Nd_2NiO_4 in Li/Na eutectic carbonate with rare-earth metal oxide was determined by ICP-AES as same method written in the last section.

3. Result and discussion

3.1. Solubilities of nickel oxide and lanthanum oxide in molten carbonates

Fig. 1 shows dissolution curves of NiO (C_{Ni}') and La_2O_3 (C_{La}') in Li/Na eutectic carbonate with excess amount of La_2O_3. The saturated La_2O_3 concentration was 0.5 mol% (=1 mol% La) under $p_{CO_2}/p_{O_2} = 0.7/0.3$ atm at 923 K. The concentration of La was almost same as the solubility of La at 500 h [12,13]. The C_{Ni}' had peak at around 1200 h, and then it was gradually come to a steady concentration. When C_{Ni}' was reached a steady concentration at 2000 h, this concentration of Ni was regarded as the solubility ($C_{Ni} = 2.1 \times 10^{-6}$ (mole fraction)), which was 80% lower than that of C_{Ni} in Li/Na eutectic carbonate without any addition. At that time, the C_{La}' of 2000 h was 10% lower than that of 500 h. In order to research why C_{La}' was decreased with time, the sample after solubility measurement was analyzed by SEM-EDX. Fig. 2 shows results of cross section of the sample. Both La and Ni were detected near
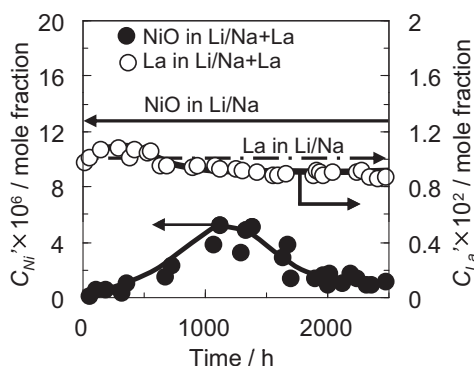

Fig. 1. Dissolution curves of C_{Ni}' and C_{La}' in Li/Na eutectic carbonate with saturated La_2O_3 under $p_{CO_2}/p_{O_2} = 0.7/0.3$ atm at 923 K.
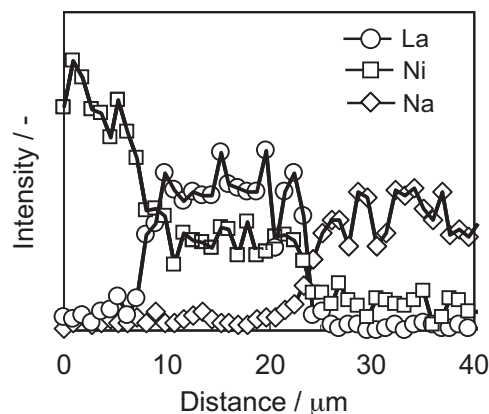

Fig. 2. EDX analysis of NiO section immersed for 2500 h in Li/Na carbonate with saturated La_2O_3 under $p_{CO_2}/p_{O_2} = 0.7/0.3$ atm at 923 K.

the interface between the sample and molten carbonates in Fig. 2. According to results of solubility measurement and SEM-EDX analysis, the surface of NiO would be reacted with La ion to $LaNiO_3$ in molten carbonate with saturated amount of La_2O_3 as shown in the following equation:

$$2La^{3+}(l) + 3CO_3^{2-}(l) + 2NiO(s) + 2O_0(g) \leftrightarrow 2LaNiO_3(s) + 3CO_2(g) \quad (1)$$
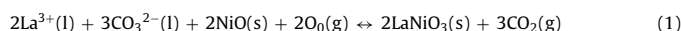
This solid solution layer on the NiO surface would decrease the activity of Ni in the solid. Therefore, one of the reasons why the solubility of Ni in molten carbonate with saturated La_2O_3 was lower than that in no additive can be explained by decreasing the activity of Ni.

On the other hands, the dissolution reaction of the La_2O_3 in Li/Na eutectic carbonate is a simple acid dissolution as follows [12,13]:

$$La_2O_2CO_3(s) + 2CO_2(g) \leftrightarrow 2La^{3+}(l) + 3CO_3^{2-}(l) \quad (2)$$
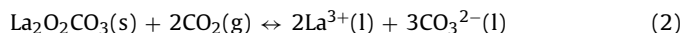
NiO in Li/Na eutectic carbonate with La_2O_3 addition dissolves with the acid dissolution mechanism above 10^{-2} atm of CO_2 partial pressure as follows:

$$NiO(s) + CO_2(g) \leftrightarrow Ni^{2+}(l) + CO_3^{2-}(l) \quad (3)$$
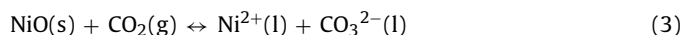
This equation was divided into two reactions as follows:

$$NiO(s) \leftrightarrow Ni^{2+}(l) + O^{2-}(l) \quad (4)$$

$$CO_3^{2-}(l) \leftrightarrow CO_2(g) + O^{2-}(l) \quad (5)$$
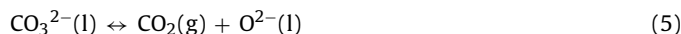
Following Eqs. (2), (4) and (5), the decrease C_{Ni} in Li/Na eutectic carbonate with La_2O_3 was explained by the acid–base equilibrium of molten carbonates [12,13]. The La solubility: C_{La} (=1.0×10^{-3} (−)) [13] was smaller than that of alkali-earth carbonates such as $CaCO_3$, $BaCO_3$ and $SrCO_3$ whose solubilities in Li/Na eutectic carbonates are 2.3×10^{-2} (−), 1.7×10^{-2} (−) and 8.8×10^{-3} (−), respectively under $p_{CO_2}/p_{O_2} = 0.7/0.3$ atm at 923 K [10]. In spite of the low solubility of La in molten carbonate, the La_2O_3 addition to molten carbonates was more effective than that of alkali-earth carbonates to decrease the solubility of NiO. Therefore, an exceptionally-small C_{Ni} in Li/Na eutectic carbonate with La_2O_3 addition could be explained by both effects; the activity of NiO and the acid–base equilibrium of molten carbonates.

3.2. The solubility of $LaNiO_3$ and Nd_2NiO_4 in molten carbonates with the rare-earth oxide

Fig. 3 shows XRD patterns of the $LaNiO_3$ and Nd_2NiO_4. Although small amount of Nd_2O_3 was detected in Nd_2NiO_4, samples were well identified to $LaNiO_3$ or Nd_2NiO_4 [22,23].

Fig. 4 shows dissolution curves of Ni (C_{Ni}') and La (C_{La}') of $LaNiO_3$ in Li/Na eutectic carbonate with saturated La_2O_3 under $p_{CO_2}/p_{O_2} =$
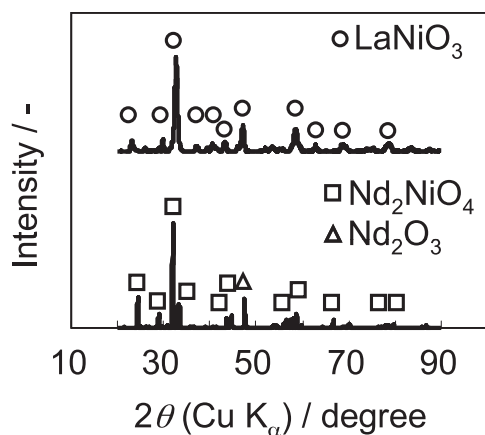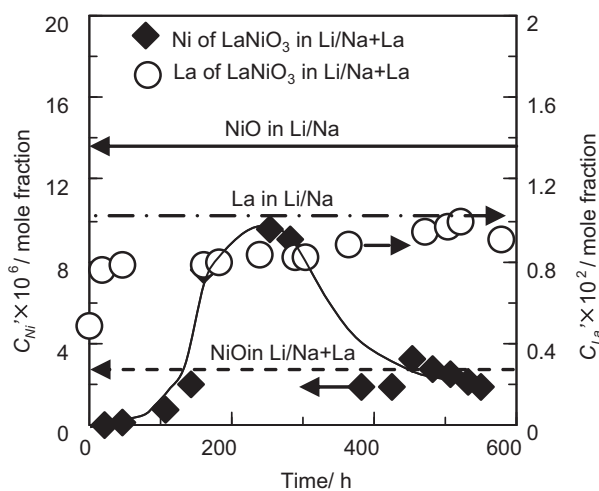
Fig. 3. XRD patterns of the LaNiO$_3$ and Nd$_2$NiO$_4$.

Fig. 4. Dissolution curves of C_{Ni}' of LaNiO$_3$ and C_{La}' in Li/Na eutectic carbonate with saturated La$_2$O$_3$ under p_{CO_2}/p_{O_2} = 0.7/0.3 atm at 923 K.

0.7/0.3 atm at 923 K. The C_{Ni}' had peak around 300 h, and then it was gradually came down to the solubility (C_{Ni} = 2.0 × 10^{-6} (mole fraction)) which was almost the same to C_{Ni} of NiO in Li/Na eutectic carbonate with La$_2$O$_3$. According to Fig. 4, C_{Ni} was archived almost 500 h, and that time was a quarter shorter than that of NiO in Li/Na eutectic carbonate with La$_2$O$_3$ in Fig. 1. In parallel,
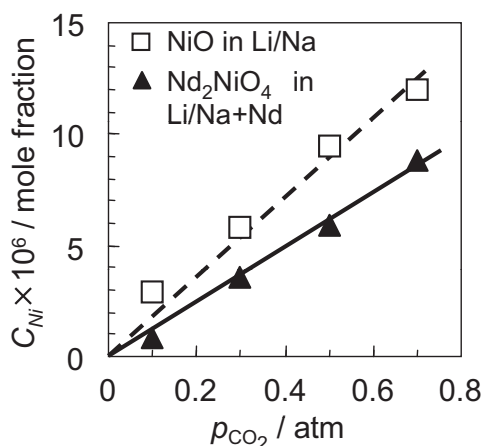

Fig. 5. C_{Ni} in Li/Na eutectic carbonates with and without Nd$_2$O$_3$ as a function of p_{CO_2} at 923 K.
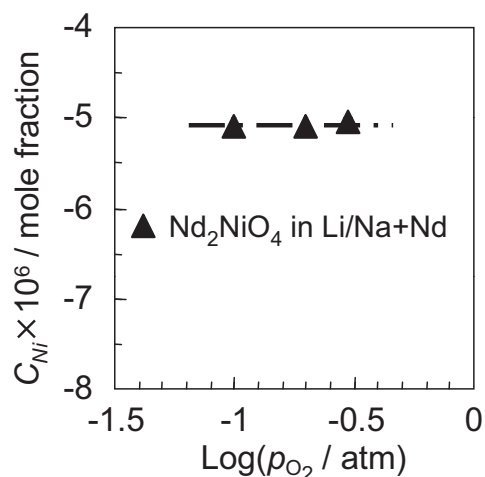

Fig. 6. C_{Ni} in Li/Na eutectic carbonates with and without Nd$_2$O$_3$ as a function of p_{CO_2} at 923 K.

the C_{La}' was gradually increased with time, and then archived to the solubility of La$_2$O$_2$CO$_3$. Because the saturated amount of La$_2$O$_3$ was added to molten carbonate, the C_{Ni} of LaNiO$_3$ was influenced by the acid–base equilibrium of molten carbonate. Moreover, the reason why the C_{Ni} of LaNiO$_3$ was extremely smaller than that of NiO in molten carbonate was also had the effect of the activity of Ni in LaNiO$_3$. Though the C_{Ni}' had peak around 300 h, the sample might be a mixture of LaNiO$_3$ and NiO or other Ni compound whose activity of Ni is larger than that of LaNiO$_3$.

Fig. 5 shows C_{Ni} of Nd$_2$NiO$_4$ and NiO in Li/Na eutectic carbonates with and without Nd$_2$O$_3$ as a function of p_{CO_2} at 923 K in p_{O_2} = 0.3 atm. C_{Ni} of both samples were proportional to the p_{CO_2}. When the condition of atmosphere was p_{CO_2}/p_{O_2} = 0.7/0.3 atm, the C_{Ni} of NdNiO$_4$ in Li/Na eutectic carbonates with Nd$_2$O$_3$ was ca. 35% lower than that of NiO in Li/Na eutectic carbonates without additives. Dependence of the both C_{Ni} on p_{O_2} at 923 K was shown in Fig. 6. The C_{Ni} was constant to p_{O_2} in p_{CO_2} = 0.7 atm as same as that of NiO. Hence, Nd$_2$NiO$_4$ dissolves with an acid dissolution mechanism at CO$_2$ pressure as follows:

$$Nd_2NiO_4(s) + CO_2(g) \leftrightarrow Ni^{2+}(l) + Nd_2O_3(s) + CO_3^{2-}(l) \qquad (6)$$
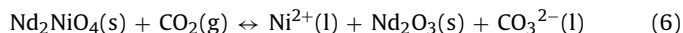
Fig. 7 shows the solubility of Nd (C_{Nd}) as a function of p_{CO_2} or p_{O_2} at 923 K. The C_{Nd} was proportional to $p_{CO_2}^{2/3}$ at p_{O_2} = 0.3 atm, and constant to p_{O_2} at p_{CO_2} = 0.7 atm. Thus, the dissolution reaction
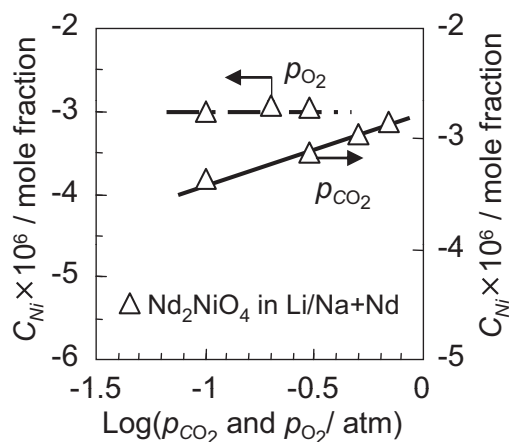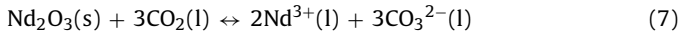

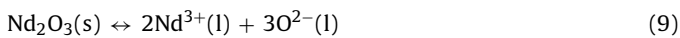**Fig. 7.** C_{Nd} in Li/Na eutectic carbonates with saturated Nd$_2$O$_3$ as a function of p_{O_2} and p_{CO_2} at 923 K.

of the neodymium oxides would be to a simple acid dissolution as follows:

$$Nd_2O_3(s) + 3CO_2(l) \leftrightarrow 2Nd^{3+}(l) + 3CO_3{}^{2-}(l) \qquad (7)$$

According to Eqs. (5)–(7), the decrease of C_{Ni} on Nd_2NiO_4 was explained by the acid–base equilibrium of molten carbonates.

3.3. Dependence of metal solubilities in molten carbonates on the acid–base of melt composition and the metal oxide

Several data of solubility in molten carbonate were shown in above section. Not only our results but also other results by several researchers were reported solubilities of metal in molten carbonates, so that there are a lot of data of solubility in molten carbonates. Because of these series of data of solubility, it is desirable to establish the index that can predict the solubility from the salt composition and materials. The parameter on NiO solubility had already reported as a function of the acid–base equilibrium of molten carbonates [14,15]. However, the solubility of the complex oxide of nickel and rare-earth metal could not be explained with the parameter. Thus a new parameter which includes both the activity of solid and the acid–base equilibrium of melts should be developed. Moreover, it should be better for a new parameter to predict not only the solubility of NiO but also other cathode materials. From those points of view, we tried to establish the new parameter as follows. First, we tried to improve the parameter of the acid–base equilibrium of molten carbonates. The parameter that we had reported [14] was based on the electrostatic parameter of the cation which is estimated the index for molten salts [24]. In other words, it focused only the cation in the melt. The relationship between the parameter and the measured C_{Ni} had the liner relation for mixed melts of alkaline and alkaline earth metals. However, in the case of the La oxide additives, the relationship between the predictive data and measured C_{Ni} was never liner. The difference of dissolution reactions of the La oxide and Nd oxide might be one of the reasons as follows [14,15]:

$$La_2O_2CO_3(s) \leftrightarrow 2La^{3+}(l) + 2O^{2-}(l) + CO_3{}^{2-}(l) \qquad (8)$$

$$Nd_2O_3(s) \leftrightarrow 2Nd^{3+}(l) + 3O^{2-}(l) \qquad (9)$$
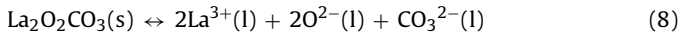
In a contrast, alkali-earth carbonate ($AeCO_3$) would be dissolved in molten carbonates as follows:

$$AeCO_3(s) \leftrightarrow Ae^{2+}(l) + CO_3{}^{2-}(1) \qquad (10)$$
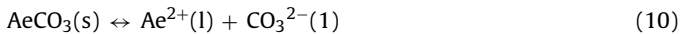
The oxide ion produces directly when the rare-earth oxide dissolves in molten carbonate as shown in Eqs. (8) and (9). In the case of alkali-earth carbonate additive, the production of the oxide ion has to go through the dissociation equilibrium of the carbonate ion as shown in Eqs. (5) and (10). Thus, the rare-earth oxide additive is much effective than the alkali-earth carbonate additive for the acid–base equilibrium of molten carbonate. Based on the NiO solubility data in molten carbonate [14], the basicity effect of oxide ion would be almost 5 times larger than that of carbonate ion. Assuming that the parameter which was shown in our previous report [14] indicated the parameter of carbonate ion ($f_{dis}(CO_3{}^{2-})$). The parameter ($f_{dis}(O^{2-})$) concerned with the oxide ion can be expressed as the following equation:

$$f_{dis}(O^2) = 5f_{dis}(CO_3{}^2) = 5\frac{1}{N_c}\sum_{i_c}^{N_c}\frac{Z_c^2}{r_c} \qquad (11)$$

where N_c was the amount of cation, Z_c was the cation valence, and r_c was the radius of cation that Shannon et al. [25] was reported. The ionic radii increase with the increase of coordination number, and it is useful to acquire the ionic radii of molten carbonates. There are various sizes of ions.
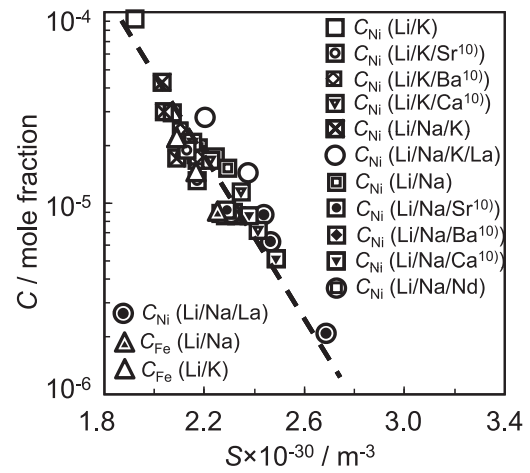

Fig. 8. Relationships between parameter of S and solubility of C in molten carbonate with and without additives under $p_{CO_2}/p_{O_2} = 0.7/0.3$ atm at 923 K.

The new parameter ε'_α of acid–base equilibrium on molten carbonates is expressed as the following equation:

$$\varepsilon'_\alpha = f_{dis}(CO_3{}^2) + f_{dis}(O^2) \qquad (12)$$

The parameter of the activity of solid was considered where the Coulomb force between the cation and anion of material sample (G) was defined as follows:

$$G = \frac{1}{N_{F_{a-c}}}\sum\frac{Z_aZ_c}{(r_a + r_c)^2} \qquad (13)$$

where $N_{F_{a-c}}$ was amount of pairs between cation and anion on a material sample, Z_a was the anion valence, and r_a was the radius of anion that Shannon et al. [25] was reported. Originally, metal solubility in molten carbonates determined by effects of solid solution and acid–base equilibrium of molten carbonates. These effects are not independent on each other. According to above facts, the synergic effect of ε'_α and G would be larger than additive effects of them to establish the total parameter (S) of metal solubility in molten carbonates. Therefore, the parameter S was defined as the following equation:

$$S = \varepsilon'_\alpha \times G \qquad (13')$$

Fig. 8 shows the relationship between the S and the solubility of metal under $p_{CO_2}/p_{O_2} = 0.7/0.3$ atm at 923 K. Other results [9–11] were also plotted in Fig. 8. The solubility of the 4 types metal oxides such as NiO, $LiFeO_2$, $LaNiO_3$, and Nd_2NiO_4, in 34 melt compositions which mainly consisted Li/Na, Li/K, and Li/Na/K carbonate with and without additives showed a linear relation with the S under $p_{CO_2}/p_{O_2} = 0.7/0.3$ atm at 923 K. According to this relationship, the metal solubility in the alkaline metal carbonate with the additive will be predicted. Therefore, the S seems to be useful index to predict the metal solubility in molten carbonate.

4. Conclusions

In order to improve the performance of MCFCs, we have investigated solubilities of $LaNiO_3$ and Nd_2NiO_4 as new materials for MCFCs. The La_2O_3 additive to molten carbonate significantly decreased the solubility of NiO in molten carbonates by controlling the acid–base equilibrium of molten carbonate and the activity of Ni in solid. Solubilities of $LaNiO_3$ and Nd_2NiO_4 were also smaller than that of NiO in molten carbonate as the same reason as that of NiO in molten carbonates with saturated amount of La_2O_3.

We also considered effects of solid and melt composition to propose the parameter for the prediction of solubility of metal ion. In

order to refine the parameter related to the acid–base equilibrium of molten carbonate, the parameter (ε'_α) was added to the terms due to the effect of O^{2-} ion in the melt. On the other hands, in order to evaluate the parameter concerned with the activity of solid, the parameter (G) was also configured by the Coulomb force between the cation and anion of material sample. By multiplying the ε'_α and G, the overview parameter (S) was obtained. Compared with the measured solubility of metal in molten carbonate, Solubilities of the 4 types metal oxides in 34 melt compositions which mainly consisted Li/Na, Li/K, and Li/Na/K carbonate with and without additives show the linear relation with the S under p_{CO_2}/p_{O_2} = 0.7/0.3 atm at 923 K. According to this relationship, the metal solubility in the alkaline metal carbonate with the additive will be predicted.

References

[1] M. Bischoff, J. Power Sources 154 (2006) 461.
[2] K. Ota, S. Mitsushima, S. Kato, S. Asano, H. Yoshitake, N. Kamiya, J. Electrochem. Soc. 139 (1992) 667–671.
[3] C. Lagergren, A. Lundblad, B. Bergman, J. Electrochem. Soc. 141 (1994) 2959–2966.
[4] L. Plomp, J. Veldhius, E. Sitters, S. Van der Molen, J. Power Sources 39 (1994) 369–373.
[5] L. Giorgi, M. Carewska, M. Patriarca, S. Scaccia, E. Simonetti, A. Di Bartolomeo, J. Power Sources 49 (1994) 227–243.
[6] C. Yuh, R. Johnsen, M. Farooque, H. Maru, J. Power Sources 56 (1995) 1–10.
[7] H.-J. Choia, S.-K. Ihma, T.-H. Limb, S.-A. Hong, J. Power Sources 61 (1996) 239–245.
[8] N. Motohira, T. Sensou, K. Yamauchi, K. Ogawa, X. Liu, N. Kamiya, K. Ota, J. Mol. Liq. 83 (1999) 95–103.
[9] J.D. Doyon, T. Gibert, G. Davies, L. Paetsch, J. Electrochem. Soc. 134 (1987) 3035–3038.
[10] K. Tanimoto, Y. Mizusaki, M. Yanagida, T. Kojima, N. Ohtori, T. Kodama, Denki Kagaku 63 (1995) 316–318.
[11] M. Cassir, M. Olivry, V. Albin, B. Malinowska, J. Devynck, J. Electroanal. Chem. 452 (1998) 127–137.
[12] S. Mitsushima, K. Matsuzawa, N. Kamiya, K. Ota, Electrochim. Acta 47 (2002) 3823–3830.
[13] K. Matsuzawa, T. Mizusaki, S. Mitsushima, N. Kamiya, K. Ota, J. Power Sources 140 (2005) 258–263.
[14] K. Matsuzawa, G. Tatezawa, Y. Matsuda, S. Mitsushima, N. Kamiya, K. Ota, J. Electrochem. Soc. 152 (2005) A1116–A1120.
[15] K. Ota, Y. Matsuda, K. Matsuzawa, S. Mitsushima, N. Kamiya, J. Power Sources 160 (2006) 811–815.
[16] L. Daza, C. Rangel, J. Baranda, M. Casais, M. Martínez, J. Alonso, J. Power Sources 86 (2000) 329–333.
[17] M. Escudero, X. Nóvoa, T. Rodrigo, L. Daza, J. Power Sources 106 (2002) 196–205.
[18] P. Ganesan, H. Colon, B. Haran, B. Popov, J. Power Sources 115 (2003) 12–18.
[19] B. Huanga, G. Chena, F. Li, Q. Yu, K. Hu, Electrochim. Acta 49 (2004) 5055–5068.
[20] S. Mitsushima, N. Takahashi, N. Kamiya, K. Ota, Electrochemistry 73 (2005) 651–656.
[21] A. Norman, M. Morris, J. Mater. Process. Technol. 92–93 (1999) 91–96.
[22] H. Wustenberg, JCPDS File 33-710, Hahn Inst. für Kristallogr., Technische Hochschule Aachen, Germany.
[23] U. Lehmann, H. Mueller-Buschbaum, JCPDS File 71-1941, B. Naturforsch, Anorg. Chem. Org. Chem. 35 (1980) 389.
[24] Y. Castrillejo, M.R. Bermejo, E. Barrado, A.M. Martinez, P. Diaz Arocas, J. Electroanal. Chem. 545 (2003) 141–157.
[25] R.D. Shannon, Acta Cryst. A32 (1976) 751–767.