An evaluation of a stabilized NiO cathode for the reduction of NiO dissolution in molten carbonate fuel cells

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Abstract

A stabilized NiO cathode was proposed and evaluated for the reduction of NiO dissolution in molten carbonate fuel cells. The NiO cathode was stabilized by the addition of alkaline earth oxide to the cathode. The solubilities of NiO and stabilized NiO in alkali metal carbonate ($62Li_2CO_3$–$38K_2CO_3$) were measured as a function of temperature, pCO_2 and pO_2. The MgO content in the stabilized NiO cathode was optimized with respect to its solubility. Half-cell and single-cell tests were also performed to evaluate the electrochemical performance of stabilized NiO cathode. In a long-run operation of single cell tests with a 10% MgO-stabilized cathode, a significant reduction of Ni precipitation was obtained.

Keywords: Molten carbonate fuel cells; Cathodes; Nickel oxide

1. Introduction

The dissolution of lithiated NiO cathodes has been a problem in molten carbonate fuel cells (MCFCs) and may result in being the major life-limiting factor. It is well-known that lithiated NiO dissolves slowly in the electrolyte, eventually depositing sufficient bridged grains of metallic nickel across the cell to cause short-circuiting and to degrade cell performance [1]. To solve the NiO dissolution problem, several possible approaches have been studied [2–4]. One of them is to optimize the melt composition in order to lower the solubility of NiO in the electrolyte [5–12]. For example, the addition of alkaline earth carbonate to the electrolyte has been extensively studied. However, this approach has not been successful in extending the anode–cathode shorting time during a cell operation. This failure was attributed to the segregation of added ionic species from the bulk electrolyte due to the differences in ion mobility [13].

In this study, a stabilized NiO cathode is proposed and evaluated in order to reduce the dissolution rate without suffering any deterioration of the electrochemical activity during the cell operation. NiO is stabilized by the addition of alkaline earth oxide. When stabilized NiO is used as the cathode material, alkaline earth oxide contained in the stabilized NiO will be dissolved into the electrolyte under the cell operation

conditions. The dissolution of alkaline earth oxide increases the basicity of the electrolyte, and then the solubility of NiO decreases. In this case, the segregation of ionic species may not be important. To evaluate a stabilized cathode material, the solubilities of unstabilized NiO cathode and stabilized NiO in the eutectic carbonate melt were measured and compared. The content of alkaline earth oxide in the stabilized NiO was optimized with respect to the solubility of MgO. Half-cell and single-cell tests were also performed to examine the electrochemical performance of a stabilized NiO cathode. Post-test analyses by electron probe microanalysis (EPMA), atomic absorption spectrophotometer (AAS) or inductively coupled plasma (ICP) and scanning electron microscopy (SEM) were carried out to compare the Ni content in the matrix after 500 h of continuous operation.

2. Experimental

The solubility of NiO and stabilized NiO in the melt of $62Li_2CO_3$–$38K_2CO_3$ eutectic mixture was measured. The reagent grade NiO, Li_2CO_3, K_2CO_3 and alkaline earth oxides (MgO, CaO, SrO, BaO) were used as raw materials. NiO or well-mixed NiO with alkaline earth oxide were pelletized to a thickness of 1.2 mm and a diameter of 13 mm by means of a hydraulic press. After pelletizing, it was sintered at 850 °C for 5 h. An alumina crucible containing 30 g of the pre-dried
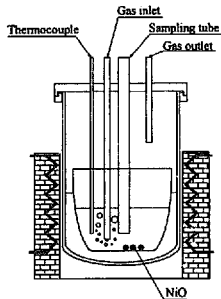
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Fig. 1. Diagram of the experimental apparatus for solubility measurements.

Fig. 2. Schematic diagram of the half-cell apparatus for electrochemical characteristics tests.

eutectic carbonate mixture ($62Li_2CO_3$–$38K_2CO_3$) and the sintered pellet were placed in a covered quartz container. The cover of container had been adapted to accommodate thermocouple, gas inlet/outlet and sampling port. Fig. 1 shows the schematic diagram of the experimental apparatus for solubility measurements. The crucible was heated to 650 °C in a electric furnace and then a CO_2–N_2 gas mixture was introduced in the carbonate melt. The gaseous atmosphere was mainly N_2–CO_2 mixture, in which the pCO_2 varied from 0.2 to 1 atm. To investigate the effect of pO_2, O_2 was added to the CO_2–N_2 gas mixture. The temperature varied from 550 to 750 °C. In order to analyze the solubility of NiO, the carbonate melt was sampled periodically. The collected sample was dissolved in a HNO_3 solution and the concentration of nickel was measured by inductively coupled plasma/mass spectroscopy (ICP/MS) (Perkin-Elmer, Model elan 5000). After the each solubility test, the pellet was analyzed by energy dispersive spectroscopy (EDS) (Philips, Model 530) to determine the Mg/Ni ratio.

The conductivity test was performed to evaluate the electrical resistance of the stabilized NiO as the cathode material. Conductivity was measured by standard a.c. four-probe method between 25 and 650 °C.

Oxygen reduction tests by linear sweep voltammetry using a half-cell apparatus were performed to evaluate the catalytic property of the stabilized NiO. The experimental apparatus is shown in Fig. 2. An alumina crucible contained a half-cell system. A large gold foil was used as the counter electrode and the reference electrode was made of a gold wire encased in a holed alumina tube that was positioned just above the bottom of the alumina crucible. A gold flag (2 cm²) working electrode was used to set the standard for the oxygen reduction current. The oxygen reduction current of the working electrode consisting of stabilized NiO was compared with that of NiO. The linear sweep voltammetry was carried out using a potentiostat (EG&G Princeton Applied Research, Model 273) and a PC equipped with data acquisition software.

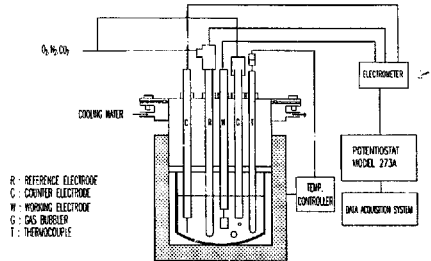Single-cell tests were performed to evaluate the suppression effect of stabilized NiO cathode on NiO dissolution under real MCFC conditions. The active area of the cell was 25 cm². All components including the stabilized NiO cathode were prepared by the tape-casting method. Green sheets of the electrode were sintered in reducing atmosphere according to the pre-determined sintering schedule. The cathode, which was sintered as reduced Ni or stabilized Ni, would be oxidized in situ and lithiated during the pre-treatment step of the single cell. The physical properties of the components used in the single-cell tests are listed in Table 1. A humidified H_2–CO_2 (80/20) anode gas and air–CO_2 (70/30) cathode gas were used as the reactant gases. The cell components and operation conditions of the cell are summarized in Table 2. The cell performance (open-circuit potential (OCV), current–voltage characteristics, and IR loss) was measured versus operating time. After 500 h of continuous operation under a load of 150 mA/cm², the cross sections of matrix fracture were taken for the analysis of the Ni deposit distribution in the matrix by EPMA (JEOL, JXA-8600) and SEM (Philips, Model 530). In order to determine the total amount of Ni deposit in the matrix, matrix samples were first dissolved in perchloric acid, and then analyzed by AAS (Perkin-Elmer, Model 5000) or ICP/MS.

Table 1
Physical properties of cell components

Component/property	Pore size (μm)	Porosity	Thickness (mm)
Matrix	0.3–0.4	50–55	0.6–0.8
Cathode	8–9	70–80	0.6–0.7
Anode	3–4	50–55	0.7–0.8

Table 2
The cell components and operating condition of the 25 cm² cell

Anode	Ni + 10%Cr
Matrix	LiAlO₂
Cathode	NiO, MgO + NiO
Electrolyte	$62Li_2CO_3$–$38K_2CO_3$
Fuel	H_2–CO_2 (80/20, humidified)
Oxidant	Air–O_2 (70/30)
Temperature	650 °C

3. Results and discussion

3.1. Solubility tests

Fig. 3 shows the typical result obtained from the solubility test of unstabilized NiO cathode at 650 °C under a pCO_2 of 0.9 atm. The concentrations were expressed in mole fraction (mol ppm). The nickel concentration in the melt increased rapidly and reached an equilibrium after 45 h. In this particular experiment, the solubility taken from an equilibrated state was 15.2 ppm (mole). This value is in good agreement with other investigations [5], but is less than the results obtained by Ota et al. [6].

Fig. 4 shows the results of the solubility tests of stabilized NiO when small amounts of MgO were added to the NiO cathode. Experimental conditions were kept at 650 °C under a pCO_2 of 0.9 atm. The solubility of stabilized NiO decreased from 15.2 to 5.5 ppm and increased again with increasing the MgO content. From this result, it is shown that the solubility of NiO in eutectic carbonate melt can be suppressed by the addition of MgO to the NiO cathode. The change in basicity of the electrolyte due to the dissolution of MgO into the electrolyte may be considered to be a key factor to the reduction of NiO solubility, as observed in previous studies, where
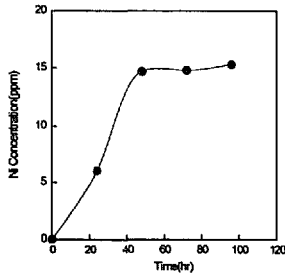

Fig. 5. Dissolved Mg concentration in the $62Li_2CO_3$–$38K_2CO_3$ melt vs. MgO concentration in the stabilized NiO.

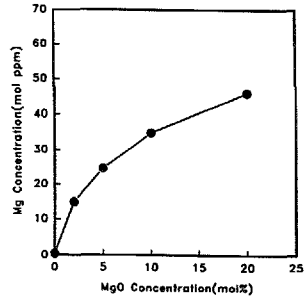Fig. 3. Time vs. Ni concentration in the $62Li_2CO_3$–$38K_2CO_3$ melt, p_{CO2} = 0.9 atm, and T = 650 °C.
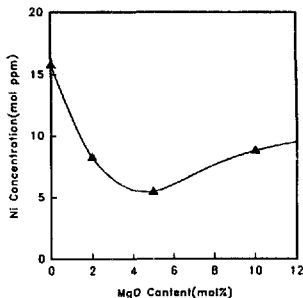
Fig. 4. Solubility of the stabilized NiO in the $62Li_2CO_3$–$38K_2CO_3$ vs. MgO concentration.
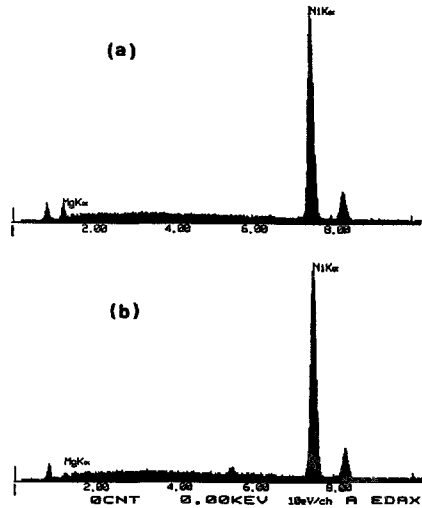

Fig. 6. EDS analysis of the 5% MgO-stabilized NiO: (a) before the experiment, and (b) after the experiment.

the NiO solubility can be reduced by the addition of basic alkaline earth oxides (carbonates) to the electrolyte [7–12]. Fig. 5 shows the equilibrium concentration of Mg ions dissolved in the electrolyte as a function of the added MgO content in the stabilized NiO cathode. The concentration of Mg in the electrolyte increased with increasing MgO content. As shown in the Fig. 6, EDS analysis also indicates that the concentration MgO/NiO ratio in the surface of stabilized NiO decreased from 0.052 to 0.030 due to the preferential dissolution of MgO.

Fig. 7 shows the effect of addition of other alkaline earth oxides. The solubility dependence of stabilized NiO cathode on the alkaline earth oxide content is similar to that of the
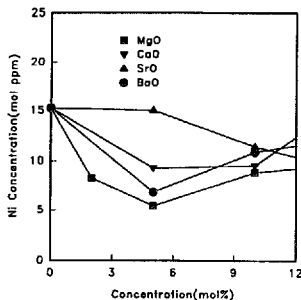
Fig. 7. Effect of additives on the solubility of the stabilized NiO in the 62Li$_2$CO$_3$–38K$_2$CO$_3$ melt.

Fig. 9. Effect of temperature on the solubility of 5% MgO-stabilized NiO in the 62Li$_2$CO$_3$–38K$_2$CO$_3$ melt.

Fig. 8. Effect of pCO$_2$ on the solubility of 5% MgO-stabilized NiO in the 62Li$_2$CO$_3$–38K$_2$CO$_3$ melt.
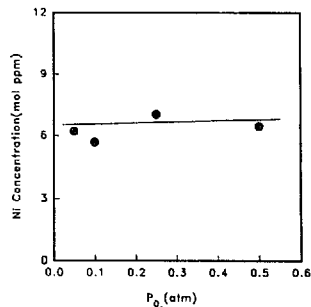
Fig. 10. Effect of pO$_2$ on the solubility of 5% MgO-stabilized NiO in the 62Li$_2$CO$_3$–38K$_2$CO$_3$ melt.

MgO-stabilized NiO cathode, but the degree of solubility reduction is lower than that of the MgO-stabilized NiO cathode. However, the reason why MgO was the most effective in suppressing the NiO dissolution has yet to be elucidated.

The dependence of pCO$_2$ on the solubility of stabilized NiO cathode was also investigated. The result is shown in Fig. 8, where the solubility of stabilized NiO in the carbonate melt increased linearly with increasing pCO$_2$. It is well-known that the dependence of NiO dissolution on the pCO$_2$ depends upon the mechanism of NiO dissolution. When an acidic dissolution mechanism predominates at higher pCO$_2$'s, which are usually the MCFC operating conditions, then the NiO solubility is found to increase linearly with pCO$_2$. In this respect, it may be concluded that the stabilized NiO is dissolved by an acidic dissolution mechanism.

Under conditions of acidic dissolution, the solubility of NiO was also found to decrease with increasing temperature, while it was not affected by pO$_2$ [14–18]. To check the hypothesis that the solubility of stabilized NiO cathode is influenced by acidic dissolution conditions, the effect of temperature and pO$_2$ on the solubility of 5% MgO-stabilized NiO were also studied. The results are given in Figs. 9 and 10.
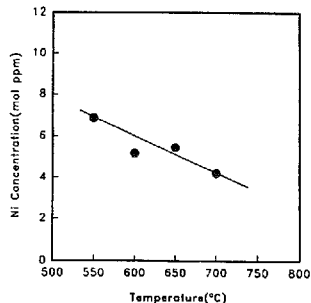
3.2. Conductivity tests

One of the cathode requirements is that the cathode is electrically conductive. Loss of conductivity due to the addition of MgO was checked. Fig. 11 shows the conductivities of lithiated NiO and stabilized NiO as a function of temperature. The conductivity increased with increasing temperature because lithiated NiO is a semiconductor. Conductivity of the lithiated NiO at 650 °C was 38 S/cm, which is in good agreement with data found in the open literature [19]. The conductivity of 10% MgO-stabilized NiO decreased to 22 S/cm. However, the loss of conductivity due to the addition of 10% MgO results only in about 0.23 mV decrement of cell performance at the 150 mA/cm^2 load of a 25 cm^2 cell. This means that the conductivity of the stabilized NiO cathode is more than adequate for cell operation.

3.3. Half-cell tests

Fig. 12 shows the results of linear sweep voltammetery of NiO and stabilized NiO. The scan rate varied from 0.01 to 0.2 V/s. During the initial period, the current density
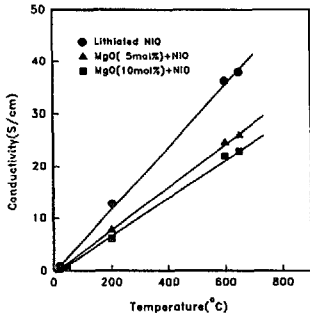
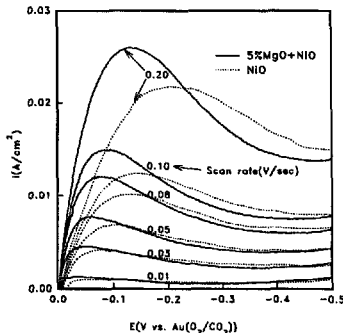Fig. 11. NiO and stabilized NiO conductivities vs. temperature.

Fig. 12. Results of linear sweep voltammetry for oxygen reduction on NiO and 5% MgO-stabilized NiO at 650 °C.

increased with increasing applied potential, but if the applied potential is higher than a certain value it decreased with increasing applied potential because of the diffusion limitation of reactant [20–24]. As observed in Fig. 12, the peak current density of the stabilized NiO is even higher than that of the NiO at the same potential and scan rate. From this result, we can infer that the catalytic activity of the stabilized NiO cathode for oxygen reduction should be comparable with that of the NiO cathode.

3.4. Single-cell tests

Fig. 13 shows typical current–voltage characteristics for an NiO cathode and two stabilized NiO cathodes in a 25 cm^2 cell. The single cells were operated at a constant load of 150 mA/cm^2 using a humidified fuel and a dry air at 40% utilization. It is seen from Fig. 13 that the OCVs are all 1.05 V which are a somewhat lower than the theoretical value of 1.07 V for this particular experimental condition. Under the load of 150 mA/cm^2, however, a 5% MgO-stabilized NiO cathode gave the best performance. This result is somewhat surpris-
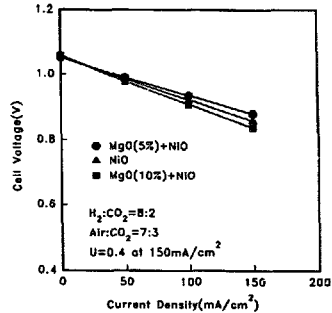

Fig. 13. Single-cell performances of an NiO cathode and stabilized NiO cathodes.

ing, considering the potential loss of cell performance due to the slight loss of conductivity as well as of catalytic activity by the addition of MgO to the NiO cathode. Although the reason why a 5% MgO-stabilized cathode gives a better performance than an unstabilized cathode has yet to be elucidated; it may be explained by the change in the microstructure of the stabilized cathode during the sintering process.

It is well-known that metal oxide functions as a sintering inhibitor of metallic nickel electrodes. Addition of MgO to the metallic nickel not only resulted in an increase in porosity from 75 to 80% after sintering but also increased the difficulty in obtaining a mechanically stable cathode, causing a problem in the cell assembly. A better performance with a 5% MgO-stabilized cathode may be attributed to the increase in porosity; the slightly worse performance with the 10% MgO-stabilized cathode may be associated with the poor strength of the sintered cathode. When the MgO content in the stabilized cathode reached 10%, its mechanical strength was very low.

Fig. 14 shows the distribution of the Ni deposit in the cross section of the matrix obtained by EPMA analyses after 500
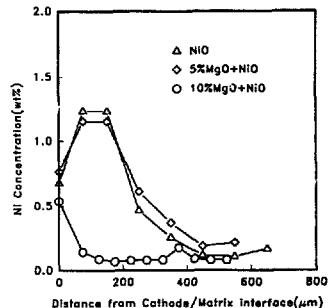

Fig. 14. Distribution of the Ni deposit in the cross section of the matrix after 500 h operation.
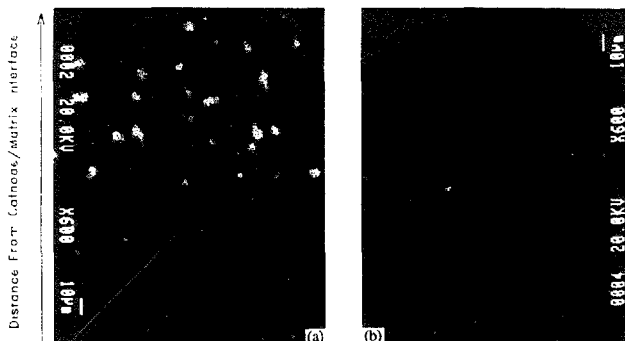
Fig. 15. EPMA map of nickel particles in the cross section of the matrix after 500 h operation: (a) NiO cathode, and (b) 10% MgO-stabilized NiO cathode.

h cell operation. The nickel content in the unstabilized NiO cathode was 1.2 wt.% in the vicinity of the cathode–matrix interface; then it decreased. The distribution of the Ni deposit in a 5% MgO-stabilized NiO cathode was similar to that of the unstabilized NiO cathode. However, a significant reduction of the Ni deposit in all positions of matrix was observed for 10% MgO-stabilized NiO cathode. It may be concluded from this result that the NiO dissolution in the single-cell operation can be suppressed by the modification of NiO with a 10% MgO addition. In batch solubility tests, a 5% MgO addition was optimal in reducing the NiO solubility. In the single-cell tests, the suppression effect appeared with 10% MgO addition. EPMA dot map of the cross section of matrix after 500 h cell operation is given in Fig. 15. In the case of the NiO cathode, Ni particles of 5–10 μm diameter were distributed in the matrix. However, an Ni deposit was not observed in the 10% MgO-stabilized cathode. This result is quite consistent with the EPMA results given in Fig. 14. This result also could be confirmed from AAS analyses of the Ni amount in the matrix. After cell operation, matrix samples were collected from cell assembly and then it was dissolved in perchloric acid. The solution of the matrix dissolved was analyzed by AAS for the determination of total Ni content, see Table 3. The amount of Ni deposit in the matrix was 2.0 wt.% in the case of unstabilized NiO cathode, while it was 0.5 wt.% for the 10% MgO-stabilized cathode.

4. Conclusions

A stabilized NiO cathode was proposed and evaluated for the reduction of NiO dissolution in MCFCs. The main results of this evaluation are:

1. The solubility of NiO in the electrolyte can be reduced by the addition of alkaline earth oxide to the NiO cathode. In a batch solubility test, a 5% MgO addition is optimal in reducing the NiO solubility.

Table 3
Total Ni amount in the matrix after 500 h of continuous operation

Cathode	Ni amount in matrix (wt.%)
NiO	2.0
5% MgO + NiO	2.0
10% MgO + NiO	0.5

2. Based on laboratory tests (conductivity test, half-cell and single-cell tests) it is concluded that a stabilized NiO cathode does not suffer any deterioration of the electrochemical activity during a cell operation.

3. A single-cell test with a 10% MgO-stabilized cathode showed a significant reduction of Ni precipitation in the matrix after a long-run operation. However, a 10% MgO addition to the NiO cathode resulted in a poor mechanical strength of the sintered cathode.

References

[1] A.J. Appleby and F.R. Foulkes, *Fuel Cell Handbook*, Van Nostrand Reinhold, New York, 1989, p. 570.
[2] L. Plomp, J.N.J. Veldhuis, E.F. Silters and S.B. van der Molun, *J. Power Sources, 39* (1992) 369–373.
[3] E.T. Ong and R.A. Donado, *Program and Abstr., 1988 Fuel Cell Seminar, Long Beach, CA, USA, 1989*, pp. 390–393.
[4] G. Schaumberg, K. Ledjeff and L. Stockert, *Program and Abstr., 1992 Fuel Cell Seminar, Tuscon, AZ, USA, 1992*, pp. 117–120.
[5] J.D. Doyon, T. Gilbert and G. Davies, *J. Electrochem. Soc., 134* (1987) 3035–3038.
[6] K. Ota, S. Mitsushima, K. Kato and N. Kamiya, in J.R. Selman et al. (eds.), *Proc. 2nd Symp. Molten Carbonate Fuel Cell Technology, Seattle, WA, USA, 1990*, The Electrochemical Society, Pennington, NJ, USA, 1990, pp. 318–337.
[7] R.D. Pierce, J.L. Smithand R.B. Poeppel, in J.R. Selman et al. (eds.), *Proc. Symp. Molten Carbonate Fuel Cell Technology, Montreal, Que., Canada, 1982*, The Electrochemical Society, Pennington, NJ, USA, 1984, pp. 147–174.

[8] P. Pigeaud, C-Y. Yuh and H. Maru, *Seminar Program and Abstr., 1988 Fuel Cell, Long Beach, CA, USA, 1988*, pp. 193–197.

[9] K. Tanimoto, Y. Miyazaki, M. Yanagida, S. Tanabe, K. Kojima, N. Ohtori, H. Okuyama and T. Kodama, *J. Power Sources, 39* (1992) 285–297.

[10] H. Ohzu, T. Ogawa, Y. Akasaka, M. Yamamoto and K. Murata, *Seminar Program and Abstr., 1988 Fuel Cell, Long Beach, CA, USA, 1988*, pp. 291–295.

[11] P.A. Shores, J.R. Selman and E.T. Ong, in W.J. Huber (ed.), *Proc. 1st Annual Fuel Cells Contractors Review Meet., Morgantown, WV, USA, 1989*, pp. 161–182.

[12] T. Ogawa, H. Oozu, K. Murata and T. Shirogami, *Denki Kagaku, 58* (1990) 336–340.

[13] H.R. Kunz and L.J. Begoli, in J.R. Selman et al. (eds.), *Proc. 2nd Symp. Molten Carbonate Fuel Cell Technology, Seattle, WA, USA, 1990*, The Electrochemical Society, Pennington, NJ, USA, 1990, pp.157–168.

[14] Y. Qu, G. Zhao and D.A. Shore, in J.R. Selman et al. (eds.), *Proc. 2nd Symp. Molten Carbonate Fuel Cell Technology, Seattle, WA, USA, 1990*, The Electrochemical Society, Pennington, NJ, USA, 1990, pp. 338–356.

[15] C.L. Baumgartner, *J. Electrochem. Soc., 131* (1984) 1850–1851.

[16] T.D. Kaun, in M. Blander et al. (eds.), *Proc. 4th Int. Symp. Molten Salts, San Francisco, CA, USA, 1983*, The Electrochemical Society, Pennington, NJ, USA, 1984, pp. 480–498.

[17] M.L. Orefield and D.A. Shore, *J. Electrochem. Soc., 135* (1988) 1662–1668.

[18] M.L. Orefield and D.A. Shore, *J. Electrochem. Soc., 136* (1989) 2862–2866.

[19] A.J. Nosnan, C. Crevecoeur, *Phys. Rev., 144* (1966) 763–770.

[20] I. Uchida, T. Nishina, Y. Mugikara and K. Itaga, *J. Electranal. Chem., 206* (1986) 229–239.

[21] I. Uchida, T. Nishina, Y. Mugikura and K. Itaya, *J. Electroanal. Chem., 206* (1986) 241–252.

[22] B.B. Dave, R.E. White, S. Srinivasan and A.J. Appleby, *J. Electrochem. Soc., 140* (1993) 2139–2145.

[23] B.B. Dave, R.E. White, S. Srinivasan and A.J. Appleby, *J. Electrochem. Soc., 138* (1991) 673–678.

[24] B.B. Dave, R.E. White, S. Srinivasan and A.J. Appleby, *J. Electrochem. Soc., 138* (1991) 2675–2683.