

Behaviour of Ni, NiO and $\text{Li}_x\text{Ni}_{1-x}\text{O}$ in molten alkali carbonates

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Ni, NiO and $\text{Li}_x\text{Ni}_{1-x}\text{O}$ are the cathodic materials commonly used in molten carbonate fuel cells (MCFCs). *Since the instability of the cathode is recognized as a major hindrance to MCFC development*, in this report the behaviour of these nickel species in molten alkali carbonates is reviewed, analyzing step by step the processes of lithiation, dissolution and sinterization at cell operating temperatures. © 2000 Kluwer Academic Publishers

1. Introduction

The molten carbonate fuel cells (MCFCs) are under development worldwide as the next generation of fuel cells. In Japan, two 100 kW class MCFCs have been developed and tested since 1993 [1]. A typical MCFC assembly consists of a porous nickel anode and a porous lithium-doped nickel oxide cathode. These are separated by an electrolyte structure, constituted of a mixture of molten alkali metal carbonates (typically in the eutectic composition 62 mol% Li_2CO_3 -38 mol% K_2CO_3) retained by capillarity into the interstices of an array of chemically inert inorganic crystallites, commonly LiAlO_2 [2]. MCFC cathode material must possess a good electronic conductivity and must be stable in the molten carbonates.

Pure, stoichiometric nickel oxide is an insulating compound. When some lithium is built into the lattice, nickel oxide becomes a p-type semiconductor [3], whose bulk transport properties fulfil the requirements of a MCFC cathode. However, the structural degradation and dissolution of $\text{Li}_x\text{Ni}_{1-x}\text{O}$ cathodes in the molten carbonates is now recognized as a major hindrance for long-time pressurized operation of a MCFC. $\text{Li}_x\text{Ni}_{1-x}\text{O}$ has been found to dissolve into the molten carbonate; the nickel species dissolved in the melt are reduced to metallic Ni by H_2 in the fuel gas and bridges the anode and the cathode [4, 5]. The bridges short circuit and degrade cell performance and shorten cell life. Ni metal precipitates have been found in the electrolyte of the cell after 10,000 h of operation [6] and the life of $\text{Li}_x\text{Ni}_{1-x}\text{O}$ cathode is thought to be far less than 40,000 h, which is the desired lifetime of a fuel cell. In spite of this, at the present lithium doped nickel oxide is the material worldwide used as MCFC cathode.

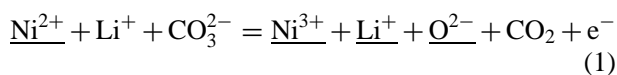
There are three ways of obtaining lithium doped nickel oxide cathode for MCFCs. In cell oxidation and lithiation of a porous metallic nickel plaque (*in situ* formation) is the method commonly used [6]. Another way is in cell lithiation of a porous nickel oxide plaque. Finally, the electrode can be in cell assembled as a porous $\text{Li}_x\text{Ni}_{1-x}\text{O}$ plaque (*ex situ* formation) [7].

In this report a critical overview of the behaviour of Ni, NiO and $\text{Li}_x\text{Ni}_{1-x}\text{O}$ in molten alkali carbonates is presented, by analyzing in a separate way the processes of lithiation, dissolution and sintering of the materials.

2. Lithiation

Metallic nickel plaque is oxidized and lithiated during the start up of the cell in the temperature range 400–650°C. The *in situ* oxidation of the nickel plaque causes the original microstructure to break into clusters of much smaller particles with no interconnections, leading to a cathode that is structurally weak. Moreover, a 30–40% volume expansion takes place during the oxidation process of nickel [7]. Lithiation of NiO gives rise to electrode dilatation too, both by solid state reaction with Li_2CO_3 [8] and by reaction in molten Li/K carbonates [9].

As Kunz *et al.* [10], the lithiation of NiO in molten carbonate can be described as an electrochemical reaction:



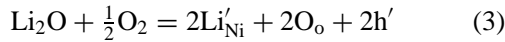
where underlining of symbols is used to indicate the solid state. Replacing the ion activities with the respective ionic fractions, and assuming equal concentrations of Ni^{3+} and Li^+ in the solid, the equilibrium potential of relation (1) is the following:

$$E = E_0 + \frac{RT}{F} \ln(x^2 P_{\text{CO}_2}) / [(1 - 2x)\{\text{Li}^+\}] \quad (2)$$

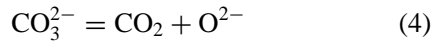
where x is lithium atomic fraction in $\text{Li}_x\text{Ni}_{1-x}\text{O}$, P_{CO_2} is CO_2 partial pressure and $\{\text{Li}^+\}$ is lithium cationic fraction in the melt. The anionic fraction of O^{2-} in the solid and CO_3^{2-} in the melt are close to unity. As the relation (2), lithium atomic fraction x increases with increasing Li concentration in the melt and with decreasing carbon dioxide partial pressure.

As Tomczyk *et al.* [11], the lithiation of NiO in the molten carbonates takes place in the following way.

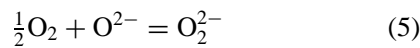
$\text{Li}_x\text{Ni}_{1-x}\text{O}$ solid solution is formed according to the mechanism:



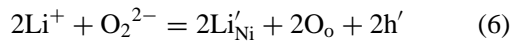
where Li'_{Ni} denotes a lithium ion which has replaced a nickel ion in the Ni sublattice and O_o is an excess oxygen ion on a regular oxygen site. Positive holes h' formed according to mechanism (3) are represented by Ni^{3+} ions in the lattice. The number of Ni^{3+} ions is equal to the number of incorporated Li^+ ions. Since molten carbonates decompose according to the reaction:



and molecular oxygen is consumed in the reaction of peroxide (O_2^{2-}) formation:



the relation (3) can be rewritten as:



Taking $[\text{O}_o] = 1$ and $[\text{Li}'_{\text{Ni}}] \equiv x = [\text{h}']$, the concentration x of Li^+ in *in-situ* lithiated NiO can be expressed as:

$$x = K_o K_r P_{\text{O}_2}^{1/8} P_{\text{CO}_2}^{-1} \quad (7)$$

where K_o and K_r are the equilibrium constants of the reactions (4) and (5), respectively. An interesting method to evaluate time-dependence of lithiation process is to follow the open-circuit potential (OCP) of a nickel foil in molten Li/K carbonates. The increase in the potential value up to 100s corresponds to a region, as Nishina *et al.* [12], where a NiO layer was formed and the lithiation process had not yet taken place. Afterwards, a stable potential was observed, attributable to lithiation process. The presence of a potential arrest in the OCP decay confirms that the lithiation is not a simple incorporation of Li^+ ions but an electrochemical process involving the oxidation of Ni(II) to Ni(III) in the NiO lattice. The potential will change drastically if the oxidation of Ni(II) to Ni(III), i.e. the lithiation process, is finished. The period of stable potential, related to lithiation rate, was as longer as higher was partial pressure of carbon dioxide [13, 14]. The presence of lithiated compounds was confirmed by atomic absorption [12] and X-ray diffraction analyses [15] performed following the OCP treatment. The process of lithiation will cease when Li^+ content inside the oxide phase reaches a certain level. It was previously noted that 1–4 at% Li is in equilibrium with melts [16, 17], but these works did not consider the distribution of Li^+ into NiO. More recent works found that at 650–700°C (MCFC operation temperatures) the lithiation was not homogeneous, but Li concentration decreased going from external to internal layers of NiO crystals, owing to the slow diffusion rate of lithium ions into NiO lattice at these temperatures.

TABLE I Lithium content in successive layers of *in-situ* (Ref. [19]) and *ex-situ* (Ref. [11]) lithiated NiO at 700°C

Layer/ <i>in-situ</i> (molten Li/Na CO ₃)	Thickness/ μm	Lithium atomic fraction
1	10	0.207
2	14	0.054
3	11	0.016
4	11	0.007
Layer/ <i>ex-situ</i> (solid state Li ₂ CO ₃)		
outer	—	0.157
inner	—	0.042

Table I shows that non-homogeneous lithiation was obtained at 700°C both by solid state reaction of Ni and Li_2CO_3 [18, 19] and by reaction of molten Li/Na carbonates and NiO [11]. Data on the effective resistance R_{eff} of NiO electrodes confirmed the non-homogeneous lithiation of nickel oxide in molten carbonate at 700°C [20]. R_{eff} of *ex-situ* lithiated electrodes with 2 at% Li was lower than for *in-situ* lithiated electrodes, because of a different distribution of Li (responsible for the electrical conductivity of NiO [3, 21]) within their volume. In the first case, the interior of the electrode and its surface layer are both electrically conductive, acquiring some Li content during fabrication and, additionally, from the melt during the experiments. In the second case, the interior consists of pure NiO, and Li is present only in the surface layer of the oxide, which probably results in a skin effect of current flow and, in consequence, in a comparatively higher effective ohmic resistance of this electrode.

Post-test analyses of *ex situ* $\text{Li}_x\text{Ni}_{1-x}\text{O}$ cathodes with x higher than the equilibrium concentration of Li immersed in molten carbonates, showed that lithium content was less than the initial composition [22]. Fig. 1 from Ref. 22 shows the change of x in $\text{Li}_x\text{Ni}_{1-x}\text{O}$ with cell operating times. This behaviour means that the dissolution rate of lithium ions in molten carbonates

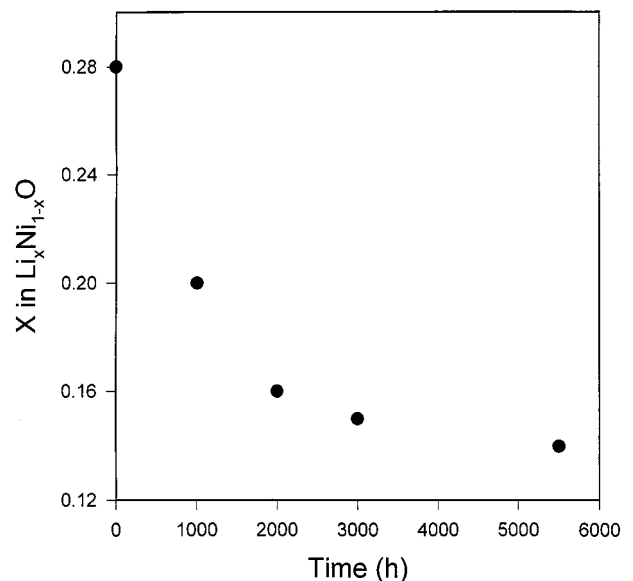


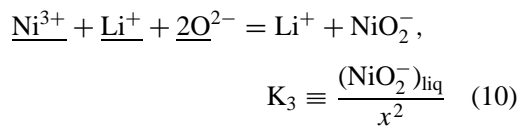
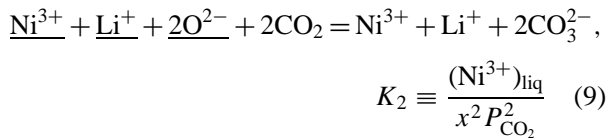
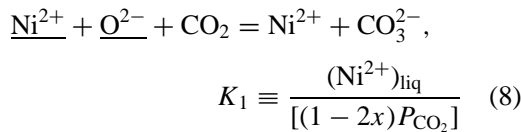
Figure 1 Dependence of x in $\text{Li}_x\text{Ni}_{1-x}\text{O}$ on cell operating time (from Ref. [22]).

is higher than that of nickel species. $\text{Li}_x\text{Ni}_{1-x}\text{O}$ dissolution in the molten carbonates will be the argument of the next paragraph.

3. Dissolution

Nickel oxide solubility in the molten alkali carbonates was studied in many works [23–27]. Under current MCFC operating conditions, the CO_2 partial pressure is such that NiO cathode solubility is found to occur under acidic dissolution conditions. For a given gas atmosphere, it was shown that NiO solubility can be reduced both by the addition of small amount of basic alkaline earth oxides to the acidic electrolyte [28] and by using a lithium-rich melt [29].

Being lithium content on the surface of NiO high, owing to non-homogeneous lithiation, a more accurate analysis of the dissolution process takes into account $\text{Li}_x\text{Ni}_{1-x}\text{O}$, instead NiO. To confirm the $\text{Li}_x\text{Ni}_{1-x}\text{O}$ dissolution, Mugikura *et al.* found that part of deposited Ni in the matrix cell exists as lithiated NiO [30]. Lithiated NiO can dissolve as simple Ni^{2+} and Ni^{3+} ions as well as NiO_2^{2-} and NiO_2^- . It is assumed that NiO_2^{2-} is negligible because NiO, being essentially a basic oxide, should not form such a complex except in very alkaline melts. As proposed by Kunz *et al.* [10], the dissolution reactions, and their equilibrium constants, are:



The total equilibrium concentration of dissolved nickel is:

$$[\text{Ni}]_{\text{eq}} = K_1(1-2x)P_{\text{CO}_2} + K_2x^2P_{\text{CO}_2}^2 + K_3x^2 \quad (11)$$

Table II shows K values and the dependence of equilibrium constants K_i on CO_2 partial pressure. In acidic conditions total dissolved nickel increases with lithium content of NiO. Fig. 2 shows total Ni dissolved (as the sum of Ni^{2+} , Ni^{3+} and NiO_2^-) vs lithium content in $\text{Li}_x\text{Ni}_{1-x}\text{O}$ for different values of P_{CO_2} . Fig. 3

TABLE II Equilibrium constants and exponential P_{CO_2} dependence at 650°C of $\text{Li}_x\text{Ni}_{1-x}\text{O}$ dissolution reactions, as Ref. [10]

Reaction	Equilibrium constant K (mg/cm ³)	Exponential P_{CO_2} dependence
(8)	0.0097	1
(9)	18	2
(10)	0.47	0

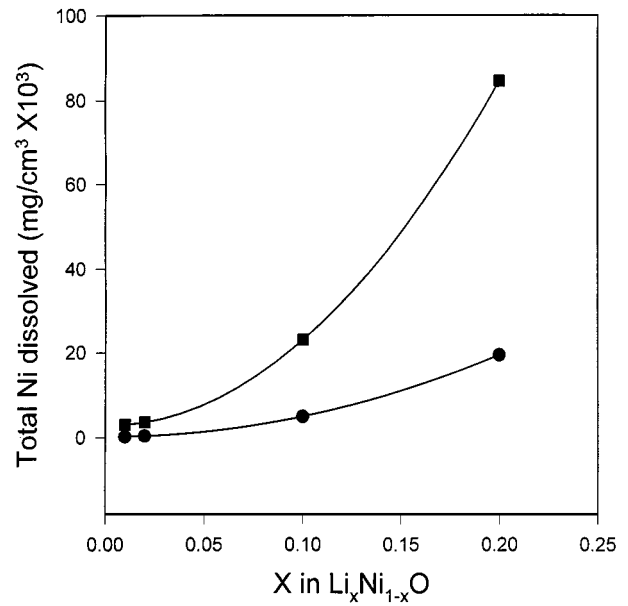


Figure 2 Total dissolved nickel, calculated from the relation (11), vs lithium content in $\text{Li}_x\text{Ni}_{1-x}\text{O}$. (●) $P_{\text{CO}_2} = 0.03$ atm; (■) $P_{\text{CO}_2} = 0.3$ atm.

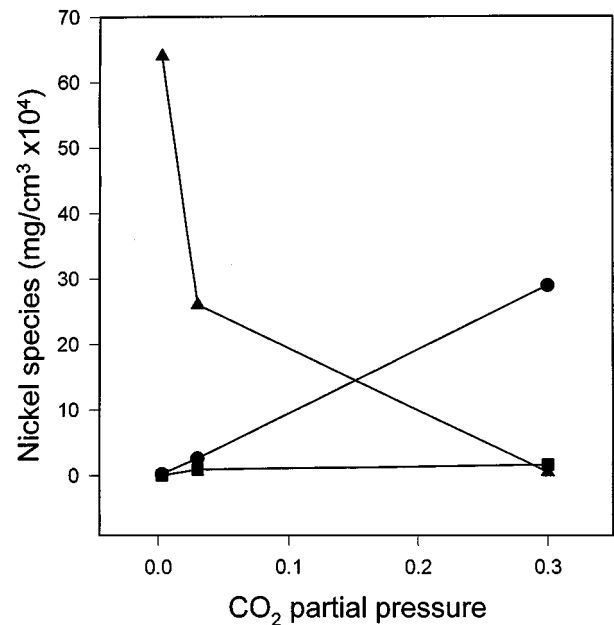


Figure 3 Concentration of nickel species vs P_{CO_2} , calculated using the values of x and P_{CO_2} of Ref. [9], and K_i values of Ref. [10]. (●) Ni^{2+} ; (■) Ni^{3+} ; (▲) NiO_2^- .

shows the concentration of nickel species dissolved in the molten carbonates vs P_{CO_2} , calculated putting in the relationships (8–10) the values of x and P_{CO_2} of Ref. [9] and the equilibrium constant values of Ref. [10]. The amount of NiO_2^- ions decreases with increasing P_{CO_2} : NiO_2^- solubility does not depend on P_{CO_2} , but its concentration increases with x , which, in its turn, decreases with P_{CO_2} (*in situ* lithiation). The amount of Ni^{2+} and Ni^{3+} , instead, increases with P_{CO_2} , as the solubility of these species increases with CO_2 partial pressure.

After dissolution, in MCFC nickel species can diffuse from the cathode toward the anode or reprecipitate

within the cathode. In the first case, at some location between the two electrodes and under the influence of reducing conditions by the anode gas, the dissolved nickel precipitates as nickel metal. The precipitation of nickel creates a sink for the nickel ions, which facilitates further NiO dissolution, resulting in a short-circuit phenomenon. In the second case, which we will consider in the next paragraph, a sintering process of the electrode takes place.

4. Sintering

Since the fuel cell uses molten alkali carbonates, the cathode materials tend to deform and deteriorate over time. There is concern that the thickness of lithiated nickel oxide cathodes may also be reduced over time. Work at GE indicated that the structure of *ex situ* fabricated cathodes tends to transform to that of *in situ* cathodes with time in the fuel cell [31]. Maru *et al.* reported an extensive coarsening of the material as a result of a dissolution/precipitation process [32]. Morphological changes, as the break of $\text{Li}_x\text{Ni}_{1-x}\text{O}$ particle agglomerates and disappearance of intragranular voids following cell operation was also reported [33]. Minh performed tests to clarify this phenomenon by varying the cathode thickness, compressive stress and manufacturing method, but could not obtain definitive results [2]. Muray *et al.* reported that, when the CO_2 partial pressure is low, rapid deformation of nickel oxide cathode in molten Li/K carbonates occurred [9], as shown in Fig. 4.

Out of cell sintering of $\text{Li}_x\text{Ni}_{1-x}\text{O}$ plaques in the presence of molten Li_2CO_3 was previously reported [34]. Fig. 5 shows the diameter change of $\text{Li}_x\text{Ni}_{1-x}\text{O}$ plaque following lithiation time at 700°C (solid Li_2CO_3) and 750°C (molten Li_2CO_3). While at 700°C lithiation process results in plaque dilatation, at

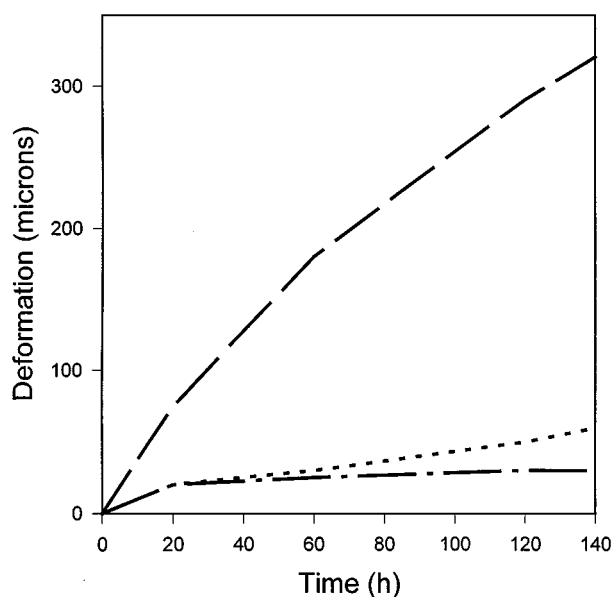


Figure 4 Deformation of nickel oxide cathode in molten Li/K carbonates with time at different CO_2 partial pressures, as Ref. [9]. (dashed-dotted line) $P_{\text{CO}_2} = 0.3$ atm; (dotted line) $P_{\text{CO}_2} = 0.03$ atm; (dashed line) $P_{\text{CO}_2} = 0.003$ atm.

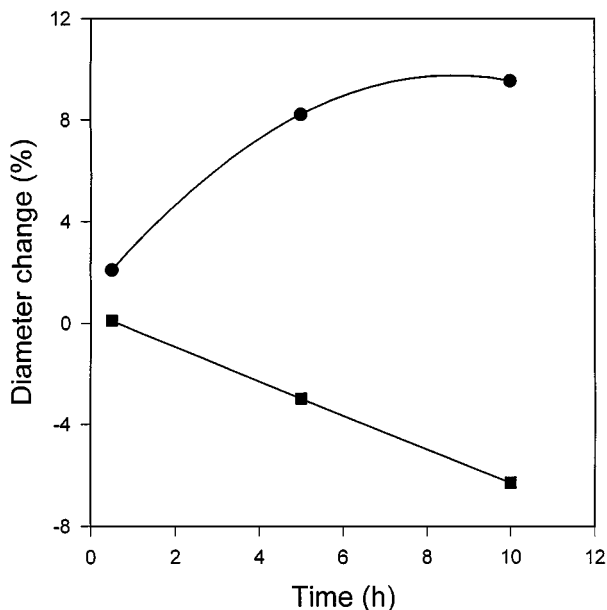


Figure 5 Diameter change of $\text{Li}_x\text{Ni}_{1-x}\text{O}$ plaque with lithiation time at (●) 700°C (solid Li_2CO_3) and (■) 750°C (molten Li_2CO_3), as Ref. [34].

750°C the presence of molten lithium carbonate gives rise to shrinkage of the specimen by reactive liquid phase sintering. Moreover, the presence of $\text{Li}_x\text{Ni}_{1-x}\text{O}$ in the hexagonal phase (nickel in NiO_2^- form) seems to be a basic requirement to sinterization process in molten lithium carbonate [35].

On the basis of the results reported in Figs 3 and 4 it can be inferred that, when the CO_2 partial pressure is low, the amount of NiO_2^- ions in molten carbonates is high and their reprecipitation promotes mass transportation between lithium nickel oxide particles. Likely liquid phase sintering of LiAlO_2 in molten carbonate [36], sintering by dissolution/reprecipitation process involving NiO_2^- ions takes place. When the CO_2 partial pressure in the gas is high, the amount of Ni^{2+} ions in molten carbonate is high too. However, as Equation 5, O^{2-} ions react with CO_2 to form CO_3^{2-} , resulting in a lower concentration of O^{2-} ions. This limits the reprecipitation reaction of Ni^{2+} and O^{2-} ions.

As shown in Table III, Hatoh *et al.* [22] found a retarding effect on the nickel deposition by using $\text{Li}_x\text{Ni}_{1-x}\text{O}$ with high lithium contents, i.e. with high amount of NiO_2^- . This behaviour seems to confirm the sintering

TABLE III The amount of deposited Ni in the electrolyte after cell operation for $\text{Li}_x\text{Ni}_{1-x}\text{O}$ with different lithium contents, as Ref. [22]

Nominal lithium atomic fraction	Electrolyte composition	Cell operation time (h)	Deposited Ni amount (mg/cm^2)
0.02	Alkali carbonates (Li/K = 62/38)	4570	8.3
0.02	5 mol% BaCO_3 in alkali carbonates	4490	5.2
0.28	Alkali carbonates	3640	3.8
0.28	5 mol% BaCO_3 in alkali carbonates	3810	1.5
0.42	5 mol% BaCO_3 in alkali carbonates	4560	1.3

process by dissolution/precipitation of NiO_2^- ions. As NiO_2^- does not migrate toward the anode but reprecipitates in the cathode, the amount of nickel deposited in the electrolyte decreases. Moreover, the sintering process gives rise to $\text{Li}_x\text{Ni}_{1-x}\text{O}$ surface area decay and, as a consequence, to the decrease of the molten carbonate/ $\text{Li}_x\text{Ni}_{1-x}\text{O}$ interface and lithium nickel oxide dissolution. Cathode sintering decreases the micro- porosity of the electrode, resulting in a slightly decrease of cell performance with operation time. But, as cell shorting is delayed, cell lifetime increases.

5. Conclusions

The dissolution and the sintering processes of lithium nickel oxide in molten carbonates strongly depend on Li concentration in $\text{Li}_x\text{Ni}_{1-x}\text{O}$ and on CO_2 partial pressure. In acidic conditions, total amount of dissolved Ni species increases with x and P_{CO_2} . Sintering process takes place in the presence of an appreciable amount of NiO_2^- (high x) or of Ni^{2+} (low x) and O^{2-} (low P_{CO_2}).

References

1. T. WATANABE, T. ABE, Y. IZAKI, Y. MUGIKURA and E. KODA, in Program and Abstracts, Fuel Cell Seminar, San Diego, CA, 1994, p. 446.
2. N. Q. MINH, *J. Power Source* **24** (1988) 1.
3. S. VAN HOUTEN, *J. Phys. Chem. Solids* **17** (1960) 7.
4. C. E. BAUMGARTNER, *J. Amer. Ceram. Soc.* **69** (1986) 162.
5. H. R. KUNZ and J. W. PANDOLFO, *J. Electrochem. Soc.* **139** (1992) 1549.
6. R. D. PIERCE, J. L. SMITH and R. B. POEPEL, in "Proceedings of the Symposium on Molten Carbonate Fuel Cell Technology," edited by J. R. Selman and T. D. Claar (The Electrochemical Society, Inc., Pennington, NJ, 1984) p. 147.
7. C. E. BAUMGARTNER and K. P. ZARNOCH, *Am. Ceram. Soc. Bull.* **64** (1985) 593.
8. E. ANTOLINI, M. LEONINI, V. MASSAROTTI, A. MARINI, V. BERBENNI and D. CAPSONI, *Solid State Ionics* **39** (1990) 251.
9. M. MURAI, K. TAKIZAWA, K. SOEJIMA and H. SOTOUCHI, *J. Electrochem. Soc.* **143** (1996) 2481.
10. W. M. VOGEL, L. J. BREGOLI, H. R. KUNZ and S. W. SMITH, in "Proceedings of the Symposium on Molten Carbonate Fuel Cell Technology," edited by J. R. Selman and T. D. Claar (The Electrochemical Society, Inc., Pennington, NJ, 1984) p. 443.
11. P. TOMCZYK, G. MORDASKI and J. OBLAKOWSKI, *J. Electroanal. Chem.* **353** (1993) 177.
12. T. NISHINA, K. TAKIZAWA and I. UCHIDA, *ibid.* **263** (1989) 87.
13. B. MALINOWSKA, M. CASSIR, F. DELCORO and J. DEVYNCK, *ibid.* **389** (1995) 21.
14. B. MALINOWSKA, M. CASSIR and J. DEVYNCK, *ibid.* **417** (1996) 135.
15. M. CASSIR, B. MALINOWSKA, C. CANEVET, L. SPORTOUCH and J. DEVYNCK, *J. Power Source* **61** (1996) 149.
16. J. R. SELMAN and H. C. MARU, in "Advances in Molten Salt Chemistry, Vol. 4," Edited by G. Mamantov and J. Braunstein (Plenum Press, New York, 1983) p. 308.
17. J. R. SELMAN and L. G. MARIANOWSKI, in "Molten Salt Technology," edited by D. G. Lovering (Plenum Press, New York, 1982) p. 323.
18. E. ANTOLINI, A. MARINI, V. BERBENNI, V. MASSAROTTI, D. CAPSONI and R. RICCARDI, *Solid State Ionics* **57** (1992) 217.
19. E. ANTOLINI, *J. Mater. Sci. Lett.* **12** (1993) 1947.
20. L. K. BIENIASZ and P. TOMCZYK, *J. Electroanal. Chem.* **353** (1993) 195.
21. R. J. MOORE and J. WHITE, *J. Mater. Sci.* **9** (1974) 1393.
22. K. HATOH, J. NIKURA, E. YASUMOTO and T. GAMO, *Denki Kagaku* **64** (1996) 825.
23. T. D. KAUN, in "4th International Symposium on Molten Salts," edited by M. Blander, D. S. Newman, G. Mamantov, M. L. Saboungi and K. Johnson (The Electrochemical Society, Pennington, NJ, 1984) p. 489.
24. C. E. BAUMGARTNER, *J. Electrochem. Soc.* **131** (1984) 1850.
25. K. OTA, T. SHINSHO and N. KAMIYA, *Denki Kagaku* **55** (1987) 323.
26. M. L. ORFIELD and D. A. SHORES, *J. Electrochem. Soc.* **135** (1988) 1662.
27. *Idem.*, *ibid.* **136** (1989) 2862.
28. J. D. DOYON, T. GILBERT, G. DAVIES and L. PAETSCH, *ibid.* **134** (1987) 3035.
29. K. OTA, S. MITSUSHIMA, S. KATO, S. ASANO, H. YOSHITAKE and N. KAMIYA, *ibid.* **139** (1992) 667.
30. Y. MUGIKURA, T. ABE, S. YOSHIOKA and H. URUSHIBATA, *ibid.* **142** (1995) 2972.
31. General Electric Company, Development of molten carbonate fuel cell power plant, Final Report, DOE/ET/17019-20, March 1985.
32. A. PIGEAUD, H. C. MARU, L. PAETSCH, J. D. DOYON and R. BERNARD, in "Proceedings of the Symposium on Porous Electrodes: Theory and Practice," edited by H. C. Maru, T. Katan and M. G. Klein (The Electrochemical Society, Inc., Pennington, NJ, 1984) p. 234.
33. E. ANTOLINI, *J. Power Source* **40** (1992) 265.
34. E. ANTOLINI and M. GIORDANI, *Mater. Lett.* **12** (1991) 117.
35. E. ANTOLINI, *Mater. Chem. Phys.* **52** (1998) 152.
36. K. NAKAGAWA, H. OHZU, Y. AKASAKA and N. TOMIMATSU, *Denki Kagaku* **65** (1997) 231.

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