

FABRICATION AND CHARACTERISTICS OF POROUS Ni AND NiO(Li) CATHODES FOR MCFC

Hyeoung-Ho Park[†], Chun-Il Jang*, Hyung-Shik Shin** and Kyu-Taek Lee

Dept. of Metallurgical Eng., Chonbuk Nat'l Univ., Chonju 560-756, Korea

*L.G., Semi-conductor, Co., Ltd., Chongju 360-480, Korea

**Dept. of Chemical Eng., Chonbuk Nat'l Univ., Chonju 560-756, Korea

(Received 9 March 1995 • accepted 1 November 1995)

Abstract—*In-situ* Ni and *ex-situ* NiO(Li) cathodes were fabricated by cold pressing using Ni powder and Li₂CO₃ (in case of *ex-situ* cathode) with paraffin wax as a binder. The effects of compaction pressure, amount of binder, and sintering temperature on porosity, the average size of pore, Li⁺ cation fraction, and the fracture strength were investigated in this study. The optimum compaction pressure was 100 kg/cm² to prevent the brittleness and stress concentration caused by high compaction pressure. Also, 10 wt% of binder yielded best results and the strength decreased dramatically and revealed nonuniform pore and pore distribution beyond 10 wt%. To obtain reasonably high electric conductivity in *ex-situ* cathode, the sintering temperature was chosen to be below 950°C to maintain the cation fraction of Li⁺ is in the range of 0.02-0.06. In terms of the Ni-dissolution rate, *ex-situ* cathode was more efficient than *in-situ* cathode in the long-term operation except the initial 24hr period.

Key words: In-situ Cathode, Ex-situ Cathode, Cation Fraction, Electric Conductivity, Ni-dissolution Rate

INTRODUCTION

A fuel cell is an electrochemical device which continuously converts the chemical energy of a fuel and an oxidant to electrical energy by a process involving an essentially invariant electrode-electrolyte system. Since fuel cells convert energy from a primary source directly into electricity without the intermediate of thermal energy, their conversion efficiency is not subject to the Carnot limitation [Appleby and Foulkes, 1989; Appleby, 1986]. The molten carbonate fuel cell (MCFC) is one of the most promising devices due to use a variety of fuels including reformed naphtha or natural gas [Baker, 1984; Selman and Maru, 1983]. A typical fuel cell assembly consists of a porous and stabilized Ni anode and a porous Ni or NiO cathode separated by molten alkali carbonate electrolyte (62 mol% Li₂CO₃ : 38 mol% K₂CO₃) contained within the interstices of a porous LiAlO₂ compact.

The cathode is prepared by the *in-situ* oxidation of presintered porous Ni plaque during the cell operation. Although the Ni plaque goes through preliminary quality control examination, the large volume expansion accompanying in-cell Ni oxidation leads to dramatic morphological changes within the structure [Charles and Kenneth, 1985]. These changes are, to a large extent, uncontrollable in the present process. In addition, stresses generated within the cathode during oxidation due to its confinement within the cell hardware increase the probability of cathode fracture. Nowadays, *ex-situ* methods, fabricating the porous NiO cathode prior to fuel cell assembly, have been studied in order to avoid the problems occurred in *in-situ* method [Charles and Kenneth, 1985; Nguyen, 1988]. Since the performance of MCFC is affected by the conductivity of cathode, it is necessary to consider the factors governing conductivity. Some reported that the electric conductivity of cathode was enhanced by adding the Li⁺ ion when

fabricating the cathode [Nguyen, 1988; Veldhuis et al., 1990; Arons, 1980].

The major problems in MCFC technology are the corrosion of the separator plate, which is an essential component in cell stack, and dissolution of the cathode. Especially, in the MCFC, the cathode gradually dissolves in the carbonate melt resulting in a degradation of cathode performance. There is also a risk that dissolved Ni will precipitate in the matrix on the anode side and cause the short circuit of the cell. The dissolution of the cathode is one of the life-limiting factors in MCFC systems. In this respect, the stability and behavior of the cathode play a vital role.

Therefore, we examined the porosity, the average size of pore, Li⁺ cation fraction, and the fracture strength according to the compaction pressure, amount of binder, and sintering temperature on *in-situ* Ni cathode and *ex-situ* NiO(Li) cathode. Also, the dissolution of Ni on the *in-situ* and *ex-situ* cathode under MCFC operation condition were investigated.

EXPERIMENTAL PROCEDURE

In-situ Ni and *ex-situ* NiO(Li) cathodes were fabricated using; 65-95 wt% of Ni powder (purity : 99.8%, average size : 3-7 μm, Nilaco Co.); 5-30 wt% of paraffin wax as a binder; 0-5 wt% of commercial Li₂CO₃. Ni powder, paraffin wax, and Li₂CO₃ (in case of *ex-situ*) were blended by a ball milling in acetone, dried, and briefly comminuted to yield a free flowing powder mixture. A disk type cathode (diameter : 10 mm, thickness : 0.8 mm) was prepared by a compressor under various pressures at room temperature. Sintering of *in-situ* Ni and *ex-situ* NiO(Li) cathodes was then performed in the alumina tube furnace according to the heat treatment cycle shown in Fig. 1.

To determine the Ni-dissolution rate on *in-* and *ex-situ* cathodes, the test have been carried out with the following conditions;

[†]To whom all correspondences should be addressed.

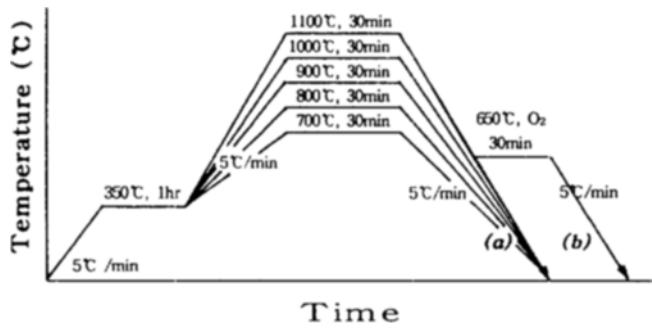


Fig. 1. Heat treatment cycles for *in-situ* (a) and *ex-situ* (b) cathodes.

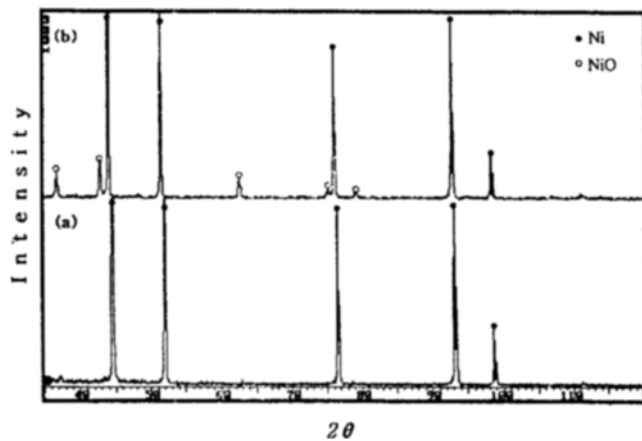


Fig. 2. X-ray diffraction patterns of sintered cathodes.

(a) *in-situ* cathode fabricated by the heat treatment cycle in Fig. 1(a), (b) *ex-situ* cathode fabricated by the heat treatment cycle in Fig. 1(b).

1) MCFC cathode condition, oxidant gas composition was 70 vol% air and 30 vol% CO₂, 2) using the electrolyte composition was the mixture of 62 mol% Li₂CO₃ and 38 mol% K₂CO₃, which were mixed by a ball milling during 2hr, 3) the operating temperature was 650°C. The strength of the fabricated cathodes was evaluated using the Marshall's equation through the ball-on-three-ball method [Ban et al., 1992; Marshall, 1980]. The analyses of surface layer, phase transformation, and morphology were performed by XPS (X-ray Photoelectron Spectroscopy, VSW ESCA System), XRD (X-ray Diffractometer, RIGAKU D/max-III type), and SEM (Scanning Electron Microscopy, HITACHI X-650), respectively. The concentration of Li⁺ ion and the dissolution of Ni were determined by ICP (Induction Coupled Plasma).

RESULTS AND DISCUSSION

1. XRD and XPS

Fig. 2 shows the result of the X-ray diffraction patterns of *in-situ* [Fig. 2(a)] and *ex-situ* [Fig. 2(b)] cathodes fabricated by the heat treatment cycle in Fig. 1. In Fig. 2(a), no other phase was observed but Ni phase, which indicates that the sintering of Ni has been carried out perfectly. However, even though Ni was still the major phase, both Ni and NiO phases coexisted in the case of *ex-situ* cathode [Fig. 2(b)]. This is because the process used for the fabrication of *ex-situ* cathode is to form NiO phase just at the surface in order to prevent the sharp decrease of

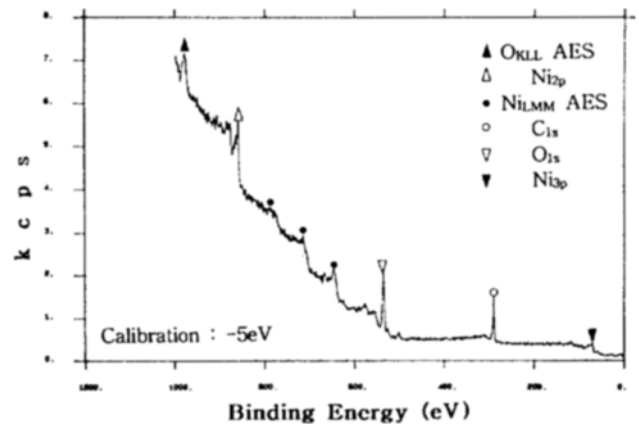


Fig. 3. XPS spectrum of *ex-situ* cathode.

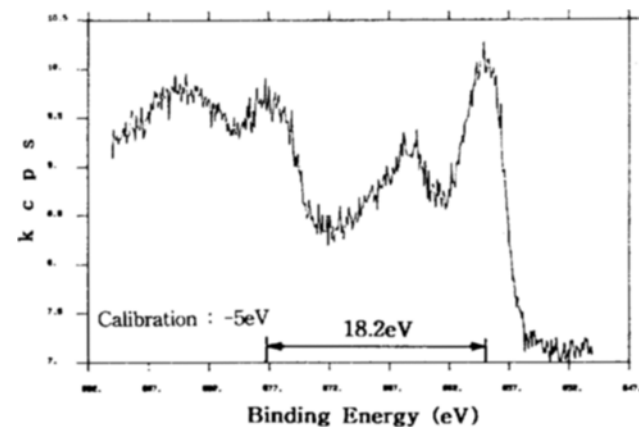


Fig. 4. XPS spectrum of *ex-situ* cathode.

strength generated when the whole cathode is oxidized to NiO.

Fig. 3 is the result of the XPS analysis to determine if NiO resulted from the X-ray diffraction pattern of *ex-situ* cathode is the phase formed at the surface. It shows that the surface of *ex-situ* cathode composed of both Ni and O. Also Fig. 4 reveals that the Ni peak in Fig. 3 is the one from NiO on the ground that the chemical shift of binding energies between Ni_{2p} peaks is 18.2 eV (853.3 eV-872.5 eV), which is typical of Ni²⁺ ion [Wagner et al., 1978].

It is believed, thus, from the results of the XRD and XPS, we had a perfect Ni cathode in case of *in-situ* and NiO at the surface with Ni inside in case of *ex-situ* cathode.

2. Effect of Compaction Pressure

Fig. 5 shows the relationship between strength and porosity with compaction pressure of *in-* and *ex-situ* cathodes fabricated at the condition of 10 wt% binder and 700°C sintering temperature. The strength increased sharply with increasing the compaction pressure to 100 kg/cm², culminated in the range of 100-200 kg/cm² compaction pressure and then appeared to decrease beyond 200 kg/cm². It is noteworthy that the strengths of 120 MPa and 80 MPa at 50 kg/cm² in cases of *in-* and *ex-situ* cathodes, respectively, are relatively high. It seems because the increase of green density affects the strength greatly. The increase of the strength between 50 kg/cm² and 100 kg/cm² should be partly due to the increase of the particle density and also due to the increase of dislocation density at higher pressure. Since the dislocation

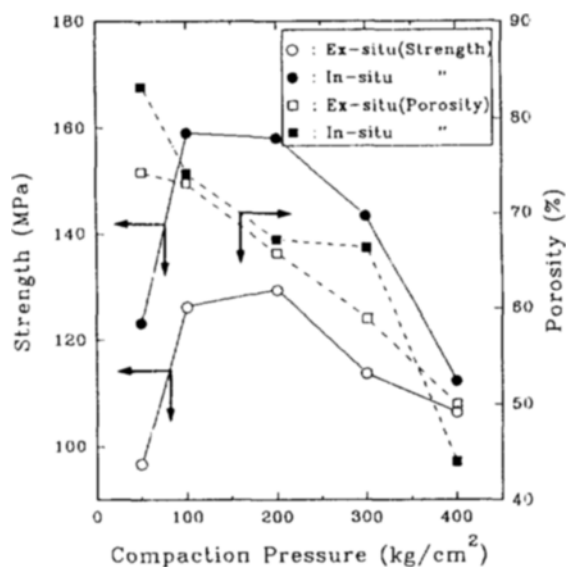


Fig. 5. The change of the strength and porosity according to the compaction pressure for the cathode specimen fabricated with 10 wt% binder at 700°C.

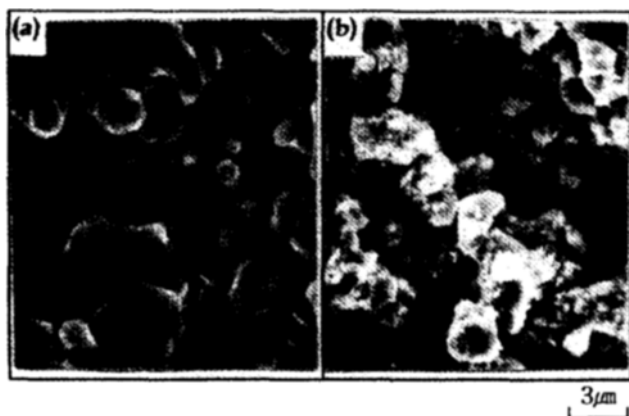


Fig. 6. SEM micrographs of *in-situ* cathode(a) and *ex-situ* cathode(b) with 10 wt% binder under 100 kg/cm² compaction pressure.

density saturates through cold working in the range of 100 kg/cm² to 200 kg/cm², the slope of strength curve became smooth. Beyond 200 kg/cm², on the other hand, the strength sharply dropped because of the brittleness of the specimen due to high dislocation density and stress concentration.

The strength value of *in-situ* cathode is higher than that of *ex-situ* cathode. It can be explained by the volume expansion associated with oxidation of nickel and stress accumulation inside the specimen in fabricating *ex-situ* cathode. However, porosity decreased with increasing the compaction pressure. In view of porosity and strength, optimal compaction pressure showing the best porosity of 75% with maintaining the highest strength in both *in-* and *ex-situ* cathodes is concluded to be 100 kg/cm². Fig. 6 shows the SEM morphology of *in-* and *ex-situ* cathodes fabricated under the optimal compaction pressure (100 kg/cm²). The average pore size of *in-* and *ex-situ* cathodes are 5 µm and 4 µm, respectively.

3. Effect of Binder

Fig. 7 shows the effect of binder quantity on strength and po-

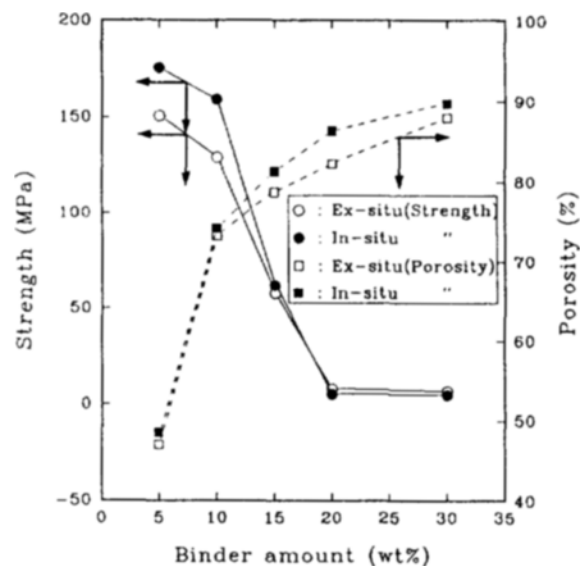
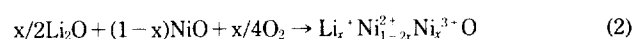


Fig. 7. The change of the strength and porosity according to the amount of binder at 700°C under 100 kg/cm² compaction pressure.

rosity of the *in-* and *ex-situ* cathodes fabricated at sintering temperature of 700°C under 100 kg/cm² compaction pressure. Generally, as the amount of binder increases, the porosity increases while the strength decreases. It is because the binder decomposes at the sintering temperature giving a higher porosity and the increase of porosity results in the decrease of strength. When 5 wt% to 10 wt% of binder was added, the porosity increased greatly. In case of over 10 wt% of binder addition, the porosity increase smoothed out because an excessive binder oozed out of the die failing in an increase of porosity. In addition to that, the generation of nonuniform pores was experimentally observed so that it was impossible to obtain cathodes with a high enough strength for MCFC. Thus, comparing strength and porosity with the amount of binder, it is thought that the optimal amount of binder is 10 wt% showing small, uniform pores, and uniform distribution.

4. The Concentration of Li⁺ in *ex-situ* NiO(Li) Cathode According to the Sintering Temperature

Since the performance of MCFC is affected by the conductivity of cathode, it is necessary to consider the factors governing conductivity. As it is known, Li₂CO₃ in electrolyte decomposes to Li₂O as Eq. (1) and then reacts with both NiO in cathode and O₂ in cathode gas according to Eq. (2). NiO is a p-type impurity semiconductor material [Adler, 1968; Goodenough, 1971]. Its conductivity can be enhanced by doping with lithium from Li₂CO₃ in the molten electrolyte since the incorporation of lithium into NiO provides more electron holes by replacing Ni²⁺ with Ni³⁺ [Adler, 1968; Goodenough, 1971].



Consequently, the electric conductivity of NiO increases significantly due to the exchange of electron holes between Ni²⁺ and Ni³⁺ ions. Thus, the electrical performance of the cell was considerably improved by enhancing the conductivity of cathode through adding Li₂CO₃ in fabrication of the cathode [Nguyen, 1988; Vel-

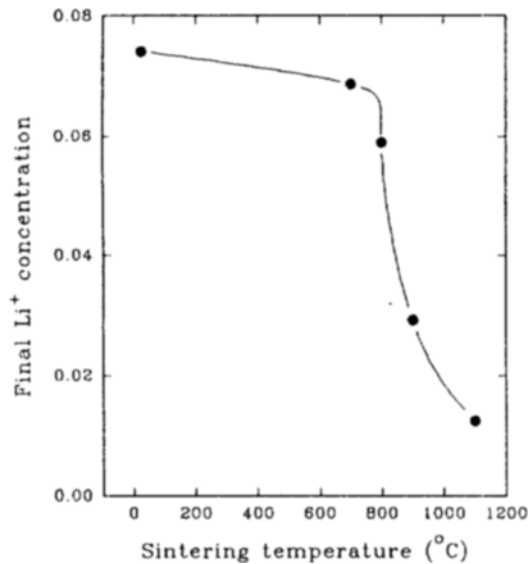


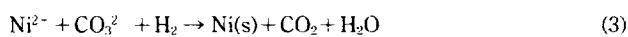
Fig. 8. Final Li⁺ concentration in *ex-situ* cathode as a function of sintering temperature.

dhuis et al., 1990; Arons et al., 1980]. In the fuel cell cathode environment, the adequate cation fraction of Li⁺ in NiO is known to be in the range of 0.02-0.06 [Nguyen, 1988; Arons, 1980; Selman and Marianowski, 1982]. For example, the conductivity of NiO at 700°C increased from about 0.03 (Ωcm)⁻¹ to about 47 (Ωcm)⁻¹ when doped with 0.034 cation fraction [Nguyen, 1988].

Fig. 8 shows the result of ICP analysis for the change of Li⁺ concentration inside *ex-situ* cathode as a function of the sintering temperature. Cation fraction of Li⁺ at 700°C was about 0.069. Beyond that temperature, it sharply dropped presumably because Li₂CO₃ decomposes into Li₂O and CO₂ more rapidly at higher temperature. Thus, to obtain reasonably high electric conductivity for this purpose, the sintering temperature was chosen to be below 950°C to maintain adequate cation fraction [Nguyen, 1988; Arons, 1980].

5. The Ni-dissolution Rate on *in-* and *ex-situ* Cathodes under the MCFC Operation Condition

The instability of cathode during cell operation is now considered as one of the major technical difficulties facing MCFC development. Especially, the dissolved Ni ions diffuse due to a concentration gradient: from the cathode toward the anode. At some location between the two electrodes and under the influence of reducing conditions caused by the anode gas, the dissolved Ni precipitates as Ni metal according to Eq. (3).



The precipitation of Ni creates a sink for the Ni ions, which facilitates further NiO dissolution. Thus, the dissolution of NiO can be a major life-limiting factor for the MCFC.

NiO is an amphoteric oxide and can dissolve as a base or an acid [Shores, 1983]. In a relatively acidic melt, NiO dissolves by the so-called acid mechanism;



In a basic melt, NiO reacts with oxide ions to produce one of two forms of nickelate ions;

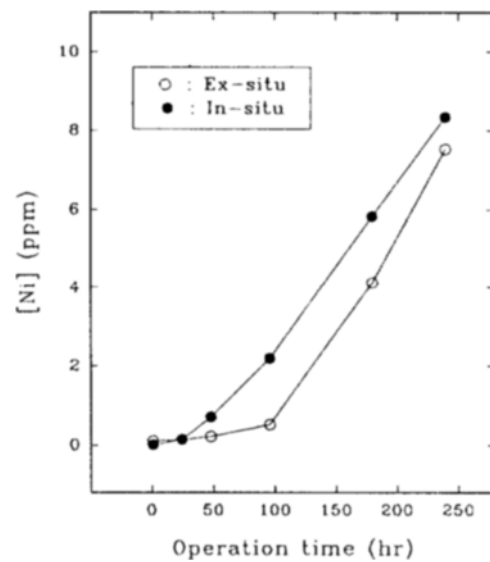


Fig. 9. The amount of Ni(ppm) in the electrolyte according to the operation time.

or



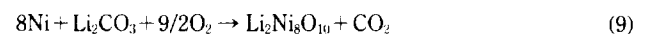
In the MCFC cathode environment, the melt is relatively acidic and the acidic dissolution is important [Nguyen, 1988].

Fig. 9 shows the result of the Ni-dissolution rate under the MCFC cathode condition which was analyzed by determining the Ni-concentration in electrolyte as a function of operating time. As the operating time increases, the amount of Ni-dissolution on *ex-situ* cathode was slightly higher than that of *in-situ* cathode until the first 24hr operating time. This reason is that, typically, the dissolution of Ni on cathode proceeded via the steps from Eq. (7) to Eq. (8). However, in case of *in-situ* cathode, it does not form sufficient NiO phase to dissolve Ni



ions during the initial operation period (24hr). Thus, the amount of Ni-dissolution in *ex-situ* cathode, which formed the NiO phase prior to dissolution test, gets higher during the initial operation period.

As the operation time increases over 24hr, such a phenomenon reversed. It seems that, in case of *in-situ* cathode, Ni-dissolution proceeds not only from NiO phase but also from the corrosion product, Li₂Ni₈O₁₀, which was formed by the reaction between Ni and electrolyte according to the Eq. (9).



Thus, from the above results, *ex-situ* cathode is more efficient than *in-situ* cathode in terms of Ni-dissolution during the long-term cell operation.

CONCLUSION

In order to fabricate the *in-situ* Ni and *ex-situ* NiO(Li) cathodes by cold pressing using paraffin wax as a binder, the effects of compaction pressure, amount of binder and sintering temperature

on cathode characteristics were investigated and following experimental results were obtained.

1. The strength of *in-situ* and *ex-situ* cathodes increased as compaction pressure increased until 200 kg/cm², but rather decreased beyond 200 kg/cm² due to the brittleness and stress concentration caused by a high compaction pressure. On the other hand, the porosity decreased with compaction pressure. Thus the optimum compaction pressure was 100 kg/cm².

2. The strength of *in-situ* and *ex-situ* cathodes decreased with binder amount, while the porosity increased. 10 wt% of binder yielded best results and the strength decreased dramatically and revealed nonuniform pore and pore distribution beyond 10 wt %.

3. The dopant concentration of Li⁺ in case of *ex-situ* cathode decreased with increase of sintering temperature. To obtain reasonably high electric conductivity, the sintering temperature was chosen to be below 950°C to maintain the cation fraction of Li⁺ in the range of 0.02-0.06.

4. *Ex-situ* cathode is more efficient than *in-situ* cathode in terms of Ni-dissolution during the long-term cell operation, though the amount of Ni-dissolution on *ex-situ* cathode was slightly higher than that of *in-situ* cathode during the initial 24hr operation.

REFERENCES

- Adler, D., in Seitz, F., Turnbull, D. and Ehrenreich, H. (eds.), "Solid State Physics", Academic Press, New York, **21**, 1 (1968).
- Appleby, A. J. and Foulkes, F. R., "Fuel Cell Handbook", Van Nostrand Reinhold, New York (1989).
- Appleby, A. J., "Fuel Cells; Trends in Research and Application", Electric Power Research Institute, Palo Alto, CA, U.S.A., 161 (1986).
- Arons, R. M., "Fabrication of Prelithiated Porous Cathodes for Molten Carbonate Fuel Cells", Ext. Abs. 158th Electrochem. Soc. Meeting, The Electrochem. Soc. Princeton, NJ, **80(2)**, 383 (1980).
- Baker, B. S., "Molten Carbonate Fuel Cell Technology, The Past Decade", 84-13, Proc. Symp. Molten Carbonate Fuel Cell Technology, ed. Selman, J. R. and Claar, T. D., Electrochem. Soc., Penning NJ (1984).
- Ban, S., Hasegawa, J. and Anusavice, K. J., "Effect of Loading Conditions on Bi-axial Flexure Strength of Dental Cements", *Dent. Mater.*, **8**, 100 (1992).
- Charles, E. B. and Kenneth, P. Z., "Fabrication and Characterization of Porous Lithium-Doped Nickel Oxide Cathodes for Use in Molten Carbonate Fuel Cells", *Ceram. Bull.*, **64**, 593 (1985).
- Goodenough, J. B., in Reiss, H. (ed.), "Progress in Solid State Chemistry", Pergamon Press, New York, **5**, 271 (1971).
- Marshall, D. B., "An Improved Biaxial Flexure Test for Ceramics", *Am. Ceram. Soc. Bull.*, **59**, 551 (1980).
- Nguyen, Q. M., "Technological Status of Nickel Oxide Cathodes in Molten Carbonate Fuel Cells", *J. of Power Source*, **24**, 1 (1988).
- Selman, J. R. and Marianowski, L. G. in Lovering, D. G. (ed), "Molten Salt Technology", Plenum Press, New York (1982).
- Selman, J. R. and Maru, H. C., "Physical Chemistry and Electrochemistry of Alkali Carbonate Melts", Advances in Molten Salt Chemistry, Vol. 4, ed. Mamantov, G., Braunstein, J. and Mamantov, C. B., 159 (1983).
- Shores, D. A., "High Temperature Corrosion", Nation Association of Corrosion Engineers, Houston, TX, 493 (1983).
- Veldhuis, J. B. J., Molen, S. B., Makkus, R. C. and Broers, G. H. J., "NiO Cathode Dissolution and Long Term MCFC Operation", *Ber. Bunsenges. Phys. Chem.*, **94**, 947 (1990).
- Wagner, C. D., Riggs, W. N., Davis, L. E., Moulder, J. F. and Muileberg, G. E., "Handbook of X-ray Photoelectron Spectroscopy", Perkin-Elementer, Minnesota (1978).