용융탄산염 연료전지용 Ni-Al 합금 anode의 소결 및 creep 특성

오인환·, 한재일··, 윤성필·, 임태훈·, 남석우·, 하흥용·, 홍성안·
*연료전지연구센터, 한국과학기술연구원
**전기화학연구실, 삼성종합기술원

Sintering and Creep Characteristics of the Ni-Al Alloy Anode for Molten Carbonate Fuel Cells

In-Hwan Oh·, Jae-Il Han··, Sung Pil Yoon·, Tae Hoon Lim·,
Suk Woo Nam·, Heung Yong Ha·, and Seong-Ahn Hong·
*Fuel Cell Research Center, Korea Institute of Science and Technology,
39-1 Hawolkok-dong, Seongbuk-ku, Seoul 136-791, Korea
**Electrochemistry Lab., Samsung Advanced Institute of Technology,
Suwon 440-600, Korea

ABSTRACT

기존 Ni-10w/o Cr 연료극과 성능은 대등하면서 creep 저항성이 뛰어난 연료극을 제조하기 위하여 Ni-5w/o Al 합금 연료극의 제조 공정을 연구하였다. 소성 분위기에 따라 완전산화 방법과 부분산화 방법으로 나누어 제조된 전극들의 미세구조 변화를 관찰하였으며, 실험 결과 부분산화 방법으로 제조한 Ni-5w/o Al 합금 연료극이 가장 우수한 소결 및 creep 저항성을 나타내었다. 이는 연료극이 산화물 분산강화 구조를 갖기 때문으로 부분산화 방법으로 제조한 Ni-5w/o Al 합금 연료극을 장착한 단전지의 경우 기계적 안정성 및 전극 안정성이 향상되었다.

주요기술용어 : Anode(연료극), Ni-Al alloy(Ni-Al 합금), Sintering and creep(소결 및 크립), Molten carbonate fuel cell(MCFC: 용융탄산염 연료전지), Oxide-dispersed-strengthened(ODS) structure(산화물 분산 강화 구조)

1. Introduction

In order for MCFC to compete with traditional power sources on an economic basis, the operational life time of a commercial unit is required to approach 40,000 hours. To achieve such a life time several problems must be overcome. In the case of MCFC,

most of all, it is important to develop a stable anode because the cell is operated under the operation temperature of 650℃ and the loading pressure of a few kg/cm² [1]. The structural deformations by sintering and creep are not critical in the cathode side although MCFC cathodes start as Ni plaques. These Ni cathodes are converted directly into lithiated NiO by in situ oxidation during the cell operation. But MCFC anodes in the form of metal are subject to sintering and creep[2-4]. In this case, sintering is referred to densification between Ni powders and creep is referred to shrinkage of the anode thickness, resulting from a mechanical stress applied to the anode. Originally, creep is described as deformation and fracture of a bulk metal due to sliding of dislocation when thermal and mechanical stresses are applied to the metal at temperatures greater than approximately 0.4 of the absolute melting temperature[5]. In the porous materials, however, the creep mechanisms are slightly different from those of bulk materials because of existence of pores. The potential sintering and creep mechanisms in a porous material under high temperature and constant load are as follows[6]

(a) Diffusive Sintering : metal flow from the smooth curved bulk particle body to the highly curved neck region between two particles.

(b) Compressive Creep : particles are drawn closer together as the metal yields due to sliding of dislocation under the load.

(c) Particle Rearrangement : collapsing of the large pores as the particles rearrange due to particle sliding under the compressive load.

Consequently, the structural change of the porous anode by sintering is attributed to surface diffusion of the anode materials, whereas the structural change by creep is ascribed to sliding of particles in the macroscopic view and to sliding of dislocation at grain boundaries in the microscopic view. These sintering and creep occur simultaneously under high temperature and mechanical stress. As the performance decay of the cell is partially ascribed to the structural deformation of the anodes, the anode having a good structural stability must be prepared for a long-term operation.

Since sintering and creep problems of an anode were reported in the early 1980's, sintering and creep have been actively studied to obtain a stable anode under the operation conditions. To overcome the problems, Cr, Al, Mg, La, or Zr powders which could be easily oxidized were added to Ni [7-10], the oxides like α-Al_2O_3 or $LiAlO_2$ were directly added to Ni [11], Ni was deposited on Al_2O_3, $SrTiO_3$, or $LiAlO_2$ by an "electroless" plating method[2], and the alloy powders of Ni-Cr or Ni-Al were used as the anode material [12]. In these approaches, the oxide particles which are located in, on, or between the Ni powders act as an impediment to prevent the powders from sliding of dislocation at grain boundaries and as an inhibitor to decrease the surface diffusion among the powders. Especially, it was reported that Ni powders including 10 w/o Cr powders and the Ni-based alloy powders were suitable for preventing sintering and creep deformation. Marianowski and his co-workers[7] have demonstrated the effect of adding Cr, ZrO_2 and Al_2O_3 to Ni or Co plaque on the decrease in the anode surface area during the 1,000 hour test. These studies

suggested that the Ni-10 w/o Cr anode showed relatively lower decrease rates of the surface area. Also it was reported by Iacovangelo[2] that the formation of Cr_2O_3 which was produced on the surface of the anode by adding Cr to Ni plaque inhibited the decrease in the anode surface area and reduced the creep rate lower than 5-10%. But, when lithium carbonates is used in the cell as an electrolyte, lithiation of Cr_2O_3 can occur under the typical fuel atmosphere, resulting in the formation of mico-pores in the Ni-Cr anode [2,14]. These micro-pores may increase wetting ability of the anode, but, if the amount of the micro-pores exists so much that the pore size of the micro-pores becomes equal to or less than that of the matrix, the electrolyte in the matrix may be re-distributed through the variation of the capillary forces between the matrix and the anode.

These days Ni powders including 2-10 w/o Cr as a sintering and creep inhibitor are being widely used, but these technologies are sometimes confidential. Also, the detailed mechanism of sintering and creep and the effect of the micro-pore formation with respect to the cell operation have not been fully reported. Therefore, authors[15] have examined the anti-sintering and creep characteristics and the structural stability of Ni-10 w/o Cr anode. They have also analyzed the amount of the micro-pores newly formed in the anode during the cell operation and investigated the effect of the micro-pore formation in addition to the sintering and creep phenomena on the cell performance.

Although the mixture of Ni and 10 w/o Cr powders which has been widely used as an anode material shows a good creep resistance,

lithiation of Cr_2O_3 under the cell operation condition results in electrolyte redistribution by micropore formation and electrolyte loss. To solve this problem, Ni-Al alloy powders have been investigated as alternative materials against the conventional Ni-Cr powders. In this study, the fabrication process of a stable Ni-5 w/o Al alloy anode was examined as a function of sintering conditions based on full oxidation or partial oxidation followed by reduction. The creep test and single cell test along with the investigation of the physical properties were carried out.

2. Experimental

The raw materials for the anode were Ni-5 w/o Al alloy powders with a mean particle size of $5\mu m$ (Nippon Atomized, Japan). The slurry of Ni-Al alloy powders with binder, plasticizer, defoamer, solvent, and surfactant was tape-casted into green sheets. The sintering of the green sheets was carried out through full oxidation-reduction or partial oxidation-reduction. In the full oxidation-reduction process, the green sheets were sintered at the temperature range of 500~900 °C for 10 hours in air atmosphere where Ni and Al are oxidized into NiO and Al_2O_3, followed by reduction at 1100 °C for 3 hours under reduction atmosphere (H_2:Ar=20:80). The partial oxidation-reduction process consisted of the similar sintering sequences in the same temperature ranges but the partial pressure of oxygen was controlled in the ratio of $P_{H2O}/P_{H2}=100$ to make it sure that Ni was not excessively oxidized while Al was fully oxidized into tiny particles inside as well as on the surface of the Ni particles.

The physical properties of the alloy anode were examined by SEM (Hitachi, S-4200), EPMA (Hitachi, JXA-8600), and mercury porosimeter (Micromeritics, Autopore II 9220). Creep tests were performed under a pressure of 20kgf/cm² at 650 °C for 100 hours, where a gas composition of $H_2:CO_2:H_2O= 72:18:10$ was used to simulate a typical cell anode operation environment. Single cell test was also performed at 650 °C and atmospheric pressure for 1,000 hours using the 5cm x 5cm single cell[16]. The cell consisted of NiO cathode, Li_2CO_3/K_2CO_3 electrolyte, -$LiAlO_2$ matrix, and Ni-Al alloy anode, and Ni and SS AISI 316L were used for the anode and cathode current collectors, respectively. The load current density was fixed at the 150mA/cm² with 40% fuel utilization in measuring the cell performances. After the 1,000 hr cell operation, the post analysis of the anodes has been carried out to investigate the structural changes during the operation.

3. Results and Discussion

3.1 Microstructure changes with sintering conditions

Fig. 1 and Fig. 2 show the pore size distribution of Ni-Al anode as a function of sintering temperature and atmosphere. It was shown from Fig.1 that the pore size distribution for the anode sintered by the full oxidation-reduction process changed significantly with the oxidation temperature. At lower sintering temperature (500 °C) the anode had a single pore size distribution with a mean pore diameter (MPD) of 3.7μm. However, the anodes sintered over 700 °C started to contain micropores and moreover, the anodes sintered at 900 °C for 10 hours
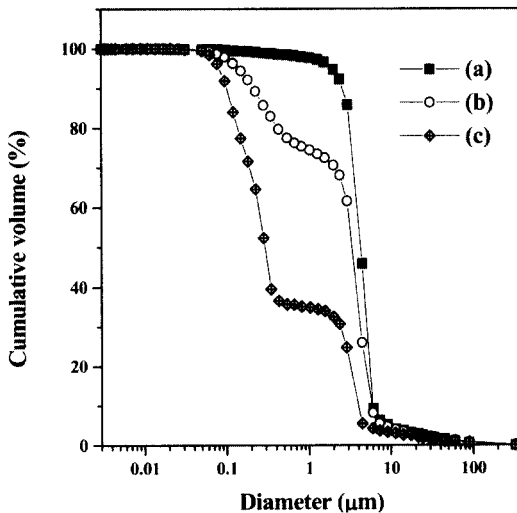

Fig. 1. Pore size distribution of Ni-5 w/o Al anode sintered by full oxidation at (a) 500℃, (b) 700℃ and (c) 900℃ for 10hours followed by reduction at 1,100℃ for 3 hours.
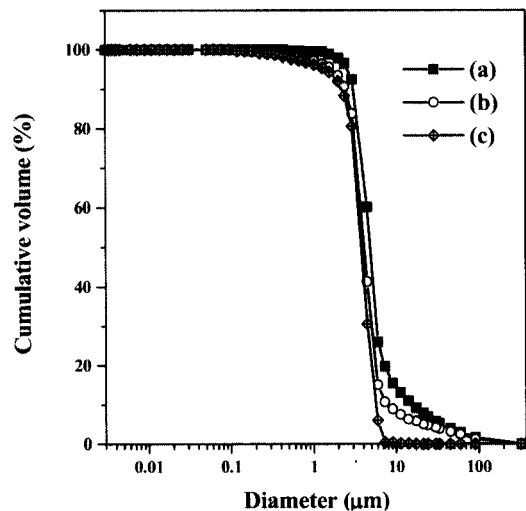
Fig. 2. Pore size distribution of Ni-5 w/o Al anode sintered by partial oxidation at (a) 500℃, (b) 700℃ and (c) 900℃ for 10 hours followed by reduction at 1,100℃ for 3 hours.

오인환 · 한재일 · 윤성필 · 임태훈 · 남석우 · 하홍용 · 홍성안

Fig. 3. EPMA line profile image of Ni-5 w/o Al anode sintered by full oxidation at 900℃ for 10hours followed by reduction at 1100℃ for 3 hours.

Fig. 4. EPMA line profile image of Ni-5 w/o Al anode sintered by partial oxidation at 900℃ for 10hours followed by reduction at 1100℃ for 3 hours.

had micropores ($<$ 1μm) of about 60%, resulting in the dual pore structure. The dual pore structure is resulted from the microstructure changes by excessive formation of NiO. When Ni is oxidized to NiO during the full oxidation procedure, volume expansion is accompanied due to a different density between Ni and NiO. Since this volume expansion is irreversible in the reductive atmosphere (H_2:Ar=20:80 at 1100 ℃ for 3 hours), the volume changes create micopores. Therefore, the changes in the pore size distribution with oxidation temperature are determined by the amount of Ni particles, which are severely oxidized.

In the sintering process involving partial oxidation and reduction, partial oxidation was performed first in a temperature range of 500~900 ℃ for 10 hours under the atmosphere in which P_{H2O}/P_{H2} ratio was controlled so that only Al was oxidized to Al_2O_3 while Ni was unchanged. Reduction was then followed under the reduction atmosphere

(H_2:Ar=20:80) at 1100 ℃ for 3 hours. Fig. 2 revealed that the pore size distribution remained in a mono pore structural pattern with a MPD of 3~5 μm independent of the oxidation temperature, although a slight change in the pore size distribution was observed, where a small portion of the large pores disappeared with a little formation of micropores as the oxidation temperature increased. This was because the Ni particles were not oxidized, but sintered a little bit due to the surface and bulk diffusion of the Ni phase under the partial oxidation condition. The extent of such sintering between the Ni particles was also minimized by the existence of Al_2O_3 on and in the Ni particles.

particles : The existence and distribution of Al_2O_3 were examined by the SEM and EPMA analyses. Fig. 3 and Fig. 4 show the EPMA line profile images of Ni-5 w/o Al anode prepared by full and partial oxidation followed by reduction, respectively. The upper profile in

the figures corresponds to the Ni phase and the lower one for the Al phase. Fig. 3 shows that under the full oxidation condition the majority of the anode surface consisted of the Ni phase with a small portion of the Al_2O_3 particles. When the Ni-Al alloy green sheet is sintered under the full oxidation condition, both Ni and Al phase are fully oxidized to NiO and Al_2O_3 respectively, with the rupture of the surface of the particle structure due to the volume expansion, resulting in the formation of micropores as explained earlier. When the oxidized particles are then sintered under the reduction condition, the easily reducible component, NiO, is readily converted to Ni, but during the reduction reaction the newly formed Ni particles merge together to form a continuous Ni phase at the surface of the particles, hiding the Al_2O_3 particles beneath the Ni film. Therefore, under the full oxidation condition, the total rupture of the Ni-Al alloy particles during the sintering

Fig. 6. Creep rates of Ni-5 w/o Al anode sintered by (1) partial oxidation-reduction and (2) full oxidation-reduction at the various oxidation temperatures: (a) 500℃, (b) 700℃, and 900℃.

process is inevitable.

However, it could be seen from the Al profile in Fig. 4 that for the anode which was oxidized under the partial oxidation condition many tiny Al_2O_3 particles were formed on the surface of the Ni particles, resulting in the oxide dispersed strengthened structure. Al_2O_3 partially existing on the surface can inhibit sintering between the Ni-based particles by slowing down surface diffusion of metal to the neck region and Al_2O_3 existing in the particle inhibits movement of dislocation and sliding of grain boundary.

3.2 Creep and single cell tests

Fig. 5 shows the creep rates of the various anodes under the condition of 20 kgf/cm² and 650℃. It is seen that the thickness shrinkage rate of Ni-5 w/o Al anode prepared by partial oxidation-reduction (1.2%) was very low

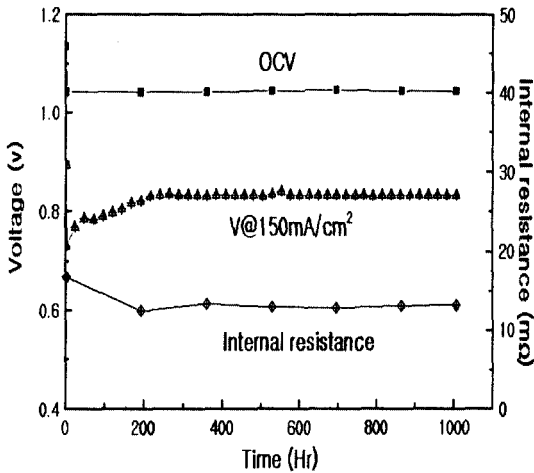Fig. 5. Creep rates of the various anodes under the condition of 20 kgf/cm² and 650℃.

Fig. 7. Evolution of the performance for the single
cell with Ni-Al anode prepared by the full
oxidation-reduction process.

compared with that of Ni-only anode (52%)
and Ni-10 w/o Cr anode (13%). The
conventional Ni-10 w/o Cr anode was
fabricated from the mixture of Ni and Cr
powders as raw materials and the Ni-Cr solid
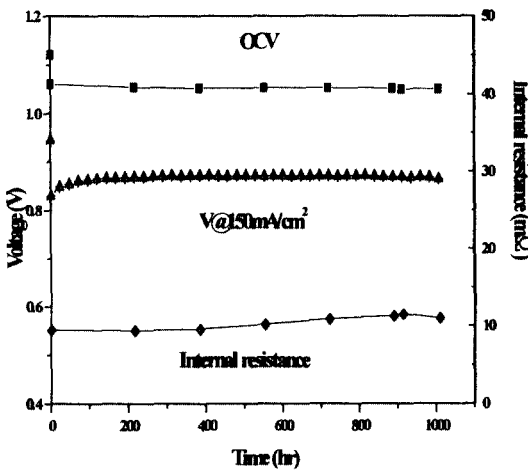solution is expected to form during the

Fig. 8. Evolution of the performance for the single
cell with Ni-Al anode prepared by the partial
oxidation-reduction process

sintering process under the reduction
condition[15]. In the case of the Ni-10 w/o Cr
anode, however, the formation of Cr_2O_3
results in a moderate creep resistance,
because the Cr_2O_3 particles exist only on the
Ni particles and there is little capability to
prohibit the creep phenomena occurring
inside the particles. The Ni-Al alloy anode
shows a superior creep resistance, because
the tiny Al_2O_3 particles exist not only on
the surface but also inside of the Ni
particles to form the oxide dispersed
strengthened structure and this is possible
by the adaptation of the two stage sintering
process; oxidation followed by reduction.

In Fig. 6 the creep rate is shown with
different sintering conditions. The higher
sintering temperature was, the smaller creep
rate was exhibited and the anodes prepared by
the partial oxidation-reduction process were
more stable than those produced from the full
oxidation-reduction process. It is noticeable
that the anode prepared by full
oxidation-reduction even shows a lower creep
rate than the conventional Ni-10 w/o Cr
anode. It is seen from Fig. 6 that the anode
prepared by partial oxidation-reduction at the
oxidation temperature of 900℃ exhibited the
best creep resistance among the samples and
experimental conditions tested in this study.
Therefore, it is expected that dispersion of
Al_2O_3 on and in the Ni-based particles
through partial oxidation without formation of
micropores will effectively restrict the
densification and sintering of the porous Ni-Al
alloy anode during the cell operation.

Fig. 7 and Fig. 8 show the single cell
performances during the 1,000 hour operation
for the anodes prepared by full and partial

oxidation followed by reduction The open circuit voltages(OCV) were 1.053 and 1.055V, and the potentials at the current density of 150mA/cm² were 0.84 and 0.87V, respectively, at the operation time of 1,000 hours. Therefore, it is seen that the anode sintered by partial oxidation-reduction showed a slightly better performance than the one sintered by full oxidation-reduction. The initial performance and the overall internal resistance were also better for the anode sintered by partial oxidation-reduction because of the stable structure. The performance decay during the period was not observed for the both cases. These performances of the single cells with Ni-5 w/o Al alloy anodes were seen to be almost equal to that of the single cell with the conventional Ni-10 w/o Cr anode. However, the long-term operation of the cell with Ni-5 w/o Al alloy anode beyond 1,000 hours is expected to be superior to that with the conventional Ni-Cr anode because of the higher creep resistance.

To examine the stability of the Ni-Al anodes during the operation, the pore size distributions of the both anodes before and after the single cell operation for 1,000 hours were measured and are shown in Fig. 9 and Fig. 10. In Fig. 9 where full oxidation-reduction has been applied, the structure change still proceeded during the cell operation because the anode was not fully ODS structure. Although the anode which have had a dual pore structure of about 0.2 and 3 μm before the operation remained the same structure after the operation, the portion of the micropore around 0.2 μm decreased from almost 60 % to 40 %, with a new formation of the micropores below 0.1μm. Also, the portion of
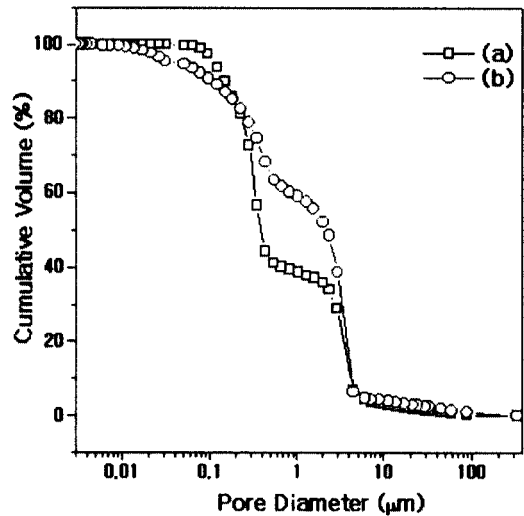

Fig. 9. Changes of pore size distribution between (a) before and (b) after the 1,000hours single cell operation with Ni-5 w/o Al anode prepared by the full oxidation- reduction process.

the macropores around 3μm is seen to increase more than one and half times after the operation. The new formation of micropores below 0.1μm was attributed to the phase change of Al_2O_3 to $LiAlO_2$ through the lithiation reaction of Al_2O_3 with Li+ ions in the electrolyte, and the increase in the portion of macropores around 3μm (hence the decrease in the portion of micropores around 0.2μm) was because the Ni particles were coarsened through the sintering between them during the cell operation. For the anode sintered by partial oxidation-reduction, as shown in Fig. 10, the pore size distributions before and after the cell operation were seen to be nearly similar each other although a slight change in the distributions was observed, which was resulted from the higher creep resistance and less deformation of the anode structure during the operation. Such a stable pore structure of the Ni-5 w/o Al alloy anode will not induce a
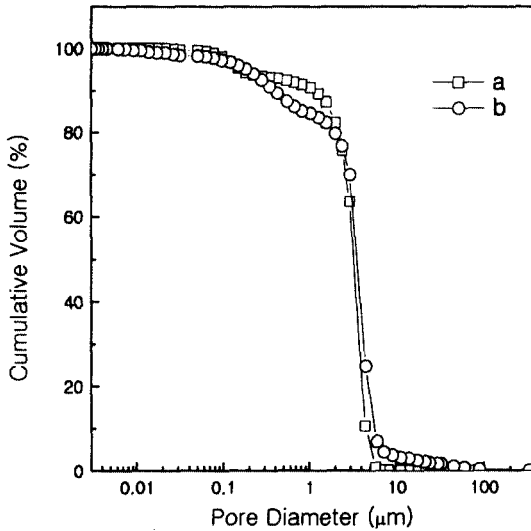
Fig. 10. Changes of pore size distribution between(a) before and(b) after the 1,000 hours single cell operation with Ni-5 w/o Al anode prepared by the partial oxidation-reduction process.

redistribution of the electrolyte between the matrix and the anode and, therefore, will enable the cell to last for a longer time.

4. Conclusions

Oxide dispersed strengthened Ni-5 w/o Al anode was successively fabricated through oxidation followed by reduction. However, it was seen that the microstructure of the alloy anode changed with the partial pressure of oxygen. In the case of full oxidation-reduction, it was found that high oxygen partial pressure and sintering temperature produced micropores due to excess oxidation of Ni particles, while for the partial oxidation-reduction process there was little formation of micropres, which resulted in the stable mechanical properties and electrode performance. It is seen, therefore, that the creep rate of the anode

sintered by partial oxidation-reduction, 1.2%, was better than the one by full oxidation-reduction, 1.6%. The creep rates of those anodes were very low compared with that of the conventional Ni-10 w/o Cr anode, 13%. The single cell operation using both anodes revealed that the cell with the anode sintered by partial oxidation-reduction was slightly better in the cell performance than the one by full oxidation-reduction, but in terms of the anode structure change during the cell operation the former changed little, while the latter significantly. Although the single cell performances for both anodes were almost equal to that of the single cell with the Ni-Cr anode, the long-term operation of the cell with the Ni-Al alloy anodes is expected to be superior to that with the Ni-Cr anode, with partial oxidation-reduction being preferable compared to full oxidation-reduction, because of the higher creep resistance and the little change in the pore size distribution during the cell operation.

References

1) C. Yuh, R. Johnsen, M. Farooque, and H.. Maru : "Status of Carbonate Fuel Cell Materials", Journal of Power Sources, Vol. 56, 1995, p. 1.

2) J. Larminie and A. Dicks : "Fuel Cell Systems Explained", John Wiley & Sons, Chichester, England, 2000, p. 152.

3) C. D. Iacovangelo : "Stability of Molten Carbonate Fuel Cell Nickel Anodes", J. Electrochem. Soc., Vol. 133, No. 11, 1986, p. 2410.

4) H. Okada,, Y. Iwase, M. Takeuchi and S. Nishimura : "Preparation of Aluminum

Diffusion Strengthened Nickel Anodes for Molten Carbonate Fuel Cell", Denki Kagaku, Vol. 60, 1992, p. 785.

5) H. E. Evans : "Mechanisms of Creep Fracture", Elsevier Applied Science Publishers, London and New York, 1984, p. 172.

6) E. T. Ong and E. H. Camara : "Molten Carbonate Fuel Cell Research and Development", Final Report by Institute of Gas Technology, Research Project No. 1085-10, EPRI, 1991.

7) L. G. Marianowski, R. A. Donado and H. C. Maru : "Carbonate Fuel Cell Anodes", U. S. Patent 4, 247, 604, 1981.

8) H. S. Chun, G. P. Park, J. H. Lim, K. Kim, J. K. Lee, K. H. Moon : "Pack Aluminization of Nickel Anode for Molten Carbonate Fuel Cells", Journal of Power Sources, Vol. 49, 1994, p. 245.

9) A. Suzuki, T. Ota, Y. Masuda, C. Shoji, K. Yuasa, and T. Matsuo : "The Improvement of Cell Components for a Long Life MCFC", Electrochemical Society Proceedings, Vol. 97, No. 4, 1997, p. 40.

10) K. Hoshino, T. Kohno : "Fabrication of Al Oxide Dispersed Ni-Cu Porous Sintered Alloy by Tape Casting and

Sintering Consisting of Oxidation and Reduction Process (Part 2), 粉体および"粉末冶金", Vol. 40, No. 4, 1993, p. 421.

11) L. Suski and J. Wyrwa : "The Addition of Aluminum Oxide to the Nickel Anodes of a Molten Carbonate Fuel Cell", J. Appl. Electrochem., Vol. 20, 1990, p. 625.

12) C. D. Iacovangelo : "Metal Plated Ceramic-A Novel Electrode Material," J. Electrochem. Soc., Vol. 133, No. 7, 1986, p. 1359.

13) P. Singh and M. Benedict : "Nickel Anode Electrode", U. S. Patent 4, 659, 379, 1987.

14) C. D. Iacovangelo and E. C. Jerabek : "Electrolyte Loss and Performance Decay of Molten Carbonate Fuel Cells", J. Electochem. Soc., Vol. 133, No. 2, 1986, p. 280.

15) I.-H. Oh, S. P. Yoon, T. H. Lim, S. W. Nam, S.-A. Hong, and H. C. Lim : "Effect of Structural Changes of the Ni-Cr Anode on the Molten Carbonate Fuel Cell Performance", Denki Kagaku, Vol. 64, 1996, p. 497.

16) 임태훈, 이갑수, 남석우, 오인환, 홍성안, 임회천 : "용융탄산염 연료전지의 운전 변수가 단위전지 성능에 미치는 영향", 화학공학, Vol. 32, No. 3, 1994, p. 498.