Performance and Morphology of a New Cathode Made from CoO/Ni Composite Particles for MCFCs

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CoO/Ni composite particle was prepared from filament shape Ni particle as a cathode material for Molten Carbonate Fuel Cells (MCFCs) by a mechanical coating technique. The composite particle had the morphology consisted of a Ni grain coated with fine CoO particles without changing the filament structure. Moreover, the composite cathode was successfully fabricated from the CoO/Ni composite particles by a doctor blade tape casting method. The composite cathode had homogenous porous structure with good connections of grains. It suggests that a large sized composite cathode can be fabricated by the usual tape casting technique. Also, Ni solubility of the composite cathode into $(\text{Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3$ melt at 650°C in 30% CO_2 -70% air atmosphere was about half of that of NiO. The cathode activity and IR of the composite cathode was almost the same as that of the usual NiO cathode. As a result, it is concluded that the composite cathode can be used as a new cathode for MCFCs which achieves its high stability in the carbonate melt and the large sized composite cathode.

Key Words : MCFCs, Cathode, LiCoO_2 , Composite Particle, Morphology

1 Introduction

Nickel oxide (NiO) is widely used as cathode material for MCFCs because the large sized NiO cathode with an area of 1 m² can be fabricated from Ni powder by using a tape casting technique. However, the NiO cathode fabricated from Ni powder has not yet satisfied a long-term stability over 10,000 h of operation because the short circuit of cells due to the dissolution of NiO and deposition of Ni in the carbonate melt. To improve the stability of cathode in the carbonate melt, new cathode materials, such as LiCoO_2 and LiFeO_2 , have been developed.¹⁻⁴⁾ The authors have examined LiCoO_2 as an alternative cathode material for MCFCs.⁴⁾ Our previous studies showed that LiCoO_2 is one of the promising candidates for MCFCs because it is more stable in a carbonate melt than NiO. However, application of LiCoO_2 for new cathode material is still limited for fabrication of the large electrode because the large size of ceramics sheet of LiCoO_2 is too brittle to be handled, and because Co is more expensive than Ni. Therefore, for the practical use of LiCoO_2 , we have proposed a new cathode structure that consisted of the NiO grains (core) covered with Li (Co,Ni) oxide grains prepared from CoO-coated Ni composite particles.^{5, 6)}

In general, the large sized NiO cathode with an area of 1 m² have been fabricated by the usual tape casting method using filament shape Ni powder (INCO255). Electrochemical property of the cathode in MCFCs operation highly depends on the morphology of the cathode. High porosity, homogeneous pore size distribution

and controlled pore size are required for preparation of high performance cathode. The use of the filament shape Ni powder is easy to control the above-mentioned morphology of the cathode for MCFCs. Therefore, in order to fabricate the new practical cathode coated with the Li (Co, Ni) oxide layer, it is important to coat fine CoO particles onto the surface of the filament shape Ni particle without changing its filament structure. Moreover, it is necessary for a large sized tape of cathode to be prepared by the usual tape casting method using the composite particles.

The aim of this study is to make clear the activity and solubility in the carbonate melt of the new cathode made from CoO-coated Ni composite particles and find the possibility of the application for the cathode in MCFCs. Moreover, the feasibility of fabricating the large size tape is also discussed.

2 Experiment

2.1 Preparation of CoO-coated Ni particle

Filament shape Ni powder (INCO255, particle size: about 3 μm) and fine CoO powder (UM Cobalt & Energy Products, particle size: about 0.3 μm) were used as starting materials. Ni particle coated with fine CoO particles (CoO/Ni composite particle) was prepared by a mechanical method. The mixture of CoO and Ni powders were treated for 15 min by the Theta Composer (TOKUJU Corp.) as shown in Fig. 1. Theta composer consists of the elliptical rotor and vessel. The rotor and vessel rotate in the opposite direction for mechanical

Fig. 1 Schematic diagram of Theta composer.

treatment of the powders. Rotation speed of the rotor and vessel for mechanical treatment was set at 2000 and 50 rpm, respectively. Then the fine CoO particles can be fixed onto the surface of a Ni particle by the mechanical coating technique using the Theta Composer. In this experiment, mechanical force such as shear and compression is continuously exerted onto particles.⁷⁾ The mass ratios of CoO to Ni was set at 5 mass%. The microstructure of the composite particle was observed by a scanning electron microscopy (SEM, Hitachi, S-800) with an energy dispersive analysis of X-ray (EDAX, Philips, PV 9900).

2. 2 Fabrication of new cathode by tape casting method

Figure 2 shows the flow sheet for fabrication of a new cathode and evaluation of its morphology, solubility and cathode performance. Some organic additives, such as binder, deflocculant and plasticizer were mixed with the CoO/Ni composite particles to obtain the slurry for the tape casting. The ethanol was used as solvent. MgCO_3 was also added to improve the conductivity of the new cathode material.^{2, 8)} The cathode tapes were prepared from the slurry by the doctor blade tape casting method. The tape was sintered at 950°C in 5% H_2 -argon atmosphere to obtain the composite Ni and Co metal tape. The composite metal tape was further sintered at 850°C in air to obtain the composite cathode. The composite metal tape and the composite cathode were analyzed by SEM-EDAX. Moreover, their pore size distribution and porosity were measured by mercury-porosimetry (SHIMADZU, 9420) in the pressure range up to 345 kPa.

2. 3 Evaluation of the solubility and electrochemical activity of the composite cathode

To evaluate the solubility of the new cathode, the samples were cut from the composite Ni and Co metal tape sintered at 950°C in 5% H_2 -argon atmosphere (see Fig. 2). The samples were immersed into $(\text{Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3$ melt at 650°C in 30% CO_2 -70% air atmosphere. The composite metal tape was *in-situ* oxidized into the carbonate melt during the solubility test to form the composite cathode. Co and/or Ni concentration dissolved into a carbonate melt was analyzed by ICP-AES (Nippon Jarrell-Ash Corp. Ltd.). The saturation concentration of Co or Ni was regarded as the solubility. More details of the meas-

Fig. 2 Fabrication process of the composite cathode and its evaluation methods.

Fig. 3 Schematic diagram of a half cell for measuring the performance of the composite cathode.

urement of the solubility are described elsewhere.^{4, 5)}

The composite Ni and Co metal tape was cut to obtain a cathode sheet with area of 10 cm^2 for evaluating the performance of the composite cathode (see Fig. 2). The performance (polarization: activity as the cathode overpotential and IR) of the composite cathode was evaluated by the current interruption method at 150 mA/cm^2 by using a half cell as shown in Fig. 3 which consisted of the cathode sheet area of 10 cm^2 and $(\text{Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3$ electrolyte with LiAlO_2 . Au plate and wire were used as the counter electrode and reference electrode, respectively. The 30% CO_2 -70% air was adapted as a cathode gas.

Fig. 4 SEM photographs of starting materials: (a) filament shape Ni particles, (b) fine CoO particles as starting materials.

Fig. 5 SEM photographs of CoO/Ni composite particles prepared by mechanical coating method using Theta composer: (a) low magnification, (b) high magnification.

3 Results and Discussions

3.1 Morphology of the composite particles using filament shape Ni particles

Figure 4 shows SEM photographs of the filament shape Ni particles and fine CoO particles. Figure 5 shows the CoO/Ni composite particles prepared by the mechanical coating technique. It is clear from these figures that the fine CoO particles fix onto the surface of Ni particles without changing the structure of the filament shape Ni. It confirms that CoO/Ni composite particles are successfully prepared from the filament shape particles by the mechanical method using Theta Composer. In general, the filament structure of the particle is easy to be deformed by the mechanical effect such as grinding force. However, the composite particle coated with fine CoO particles is successfully prepared by the mechanical method and keeps its filament structure. It is considered that mechanical forces such as shear and compression under the grinding force are repeatedly ex-

erted onto the surface of filament shape Ni as well as fine CoO particles during operation in the Theta Composer.

3.2 Morphology of the composite cathode

The morphology of the composite Ni and Co metal tape sintered at 950°C in 5% H₂-argon atmosphere is shown in Fig. 6. The composite cathode further sintered at 850°C in air is also shown in Fig. 7. Both figures show the SEM photographs of the composite metal tape and that of the cathode, respectively. It is clear from both figures that the composite metal tape and the composite cathode have the homogeneous porous structure. Moreover, it is confirmed that the composite cathode further sintered at 850°C in air shows the good connection between grains. As a result of mercury-porosimetry measurement, the average pore size and the average porosity of the composite metal tape were 6.5 μm and 74%, respectively. Also, the average pore size and the average porosity of the composite cathode were 6 μm and 60%,

Fig. 6 SEM photograph of the composite Ni and Co metal tape.

Fig. 7 SEM photograph of the composite.

respectively. It means that the oxidation of the metal tape caused a bit reduction of the both values. However, the high porosity structure of the composite cathode was achieved by the doctor blade tape casting method using CoO/Ni composite particles. Therefore, it suggests that a large sized new cathode can be fabricated from the filament shape Ni particles by the usual tape casting technique.

3. 3 Solubility of composite cathode

The composite metal tape with 5 mass% CoO sintered at 950°C in 5% H₂-argon atmosphere was immersed into (Li_{0.62}K_{0.38})₂CO₃ melt at 650°C in 30% CO₂-70% air atmosphere. The composite metal tape is oxidized at first stage of the solubility test to make the composite cathode. Ni and Co dissolution of the composite cathode are shown in Fig. 8. The data of Ni dissolution of NiO as an usual cathode material reported in our previous paper⁵⁾ was also shown in Fig. 8. The Ni and Co dissolution of the composite cathode increases against time and reaches the constant value after 150 h and 50 h, respectively.

Fig. 8 Dissolution of the composite cathode into (Li_{0.62}K_{0.38})₂CO₃ melt at 650°C in 30% CO₂-70% air atmosphere. ○: Ni dissolution of the composite cathode, □: Co dissolution of the composite cathode and - - -: Ni dissolution of NiO.⁵⁾

Fig. 9 Cathode activity (η) and IR of the composite cathode. cathode gas: 30% CO₂ + 70% air (1 atm), temperature: 650°C, current density: 150 mA/cm², cathode activity (η) and IR vs. Au/CO₂/O₂ = 2/1.

These dissolution values are regarded as Ni and Co solubility of the composite cathode, respectively. The Ni solubility of NiO in Fig. 8 also agreed to the result of Ota *et al.*⁹⁾. It is confirmed from Fig. 8 that Ni solubility of the composite cathode with 5 mass% CoO apparently decreases about half of that of NiO. Co solubility of the composite cathode also indicated the lower value of 1×10^{-6} mol-ppm. It is supposed that the new cathode material has Li (Co, Ni) oxide on the surface of NiO grains which improved the stability into the carbonate melt in the composite cathode material, as already reported by the authors⁶⁾. Therefore, It is considered that the Li (Co, Ni) oxide layer prevented the dissolution of Ni from NiO core.

3. 4 Performance of composite cathode

Figure 9 shows the cathode performance such as the polarization (activity as the cathode overpotential and IR)

of the composite cathode measured by the current interruption method. The composite metal tape, which is set in a half cell (see Fig. 3), is *in-situ* oxidized to form the composite cathode during the first stage of the performance test. The cathode overpotential (η) and IR loss due to the resistance of the cathode (IR) of the composite cathode show 110 mV and 12 mV, respectively. Total polarization (122 mV) of the composite cathode is almost the same as that of the usual NiO cathode.¹⁰⁾ It is concluded that the composite cathode proposed in this paper has the feasibility of a new cathode for MCFCs which achieves its high stability in the carbonate melt and the large sized composite cathode.

4 Conclusion

1. CoO/Ni composite particles, which consisted of a filament shape Ni grain coated with fine CoO particles, can be successfully prepared by the mechanical coating technique. They formed the composite structure without changing the filament structure of Ni particles.
2. The composite cathode was also successfully fabricated from the CoO/Ni composite particles by the tape casting technique. The composite cathode had high homogenous and porous structure with high porosity, and the better connections of grains similar to usual NiO cathode.
3. Ni solubility of the composite cathode into $(\text{Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3$ melt at 650°C in 30% CO_2 -70% air atmosphere was about half of that of NiO.
4. The cathode activity and IR of the composite cathode achieved almost the same values as those of the usual NiO cathode.
5. The composite cathode is one of the promising candi-

dates for a new cathode of MCFCs because its high stability in the carbonate melt and high possibility for fabricating the large sized composite cathode.

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References

- 1) L. Plomp, E.F. Sitters, C. Vessies, and F.C. Eckes, *J. Electrochem. Soc.*, **138**, 629 (1991).
- 2) L. Giorgi, M. Carewska, S. Scaccia E. Simonetti, and F. Zarzana, *Denki Kagaku* (presently *Electrochemistry*), **64**, 482 (1996).
- 3) C. Lagergren, A. Lundblad, and B. Bergman, *J. Electrochem. Soc.*, **141** [11], 2959 (1994).
- 4) T. Fukui, H. Okawa, and T. Tunooka, *J. Power Sources*, **71**, 239 (1998).
- 5) T. Fukui, H. Okawa, T. Hota, and M. Naito, *J. Power Sources*, **86**, 340 (2000).
- 6) T. Fukui, H. Okawa, T. Hota, M. Naito, and T. Yokoyama, *J. Am. Ceram. Soc.*, **84** [1], 233-35 (2001).
- 7) M. Naito, T. Hotta, T. Tanimoto, S. Endoh and K. Nogi, *Kagaku Kogaku Ronbunshu*, **26** [1], 62 (2000).
- 8) H. Okawa, T. Fukui K. Kodera, and T. Tsunooka, Proceeding of 63rd Denikagakuikai, 3D02, 107 (1996).
- 9) K. Ota, S. Mitsushima, S. Asano, H. Yoshitake, and N. Kamiya, *J. Electrochem. Soc.*, **139**, 667 (1992).
- 10) J. R. Selman, Proceeding of 2nd International Fuel Cell Conference, Japan, Kobe, 103 (1996).