

Performance of NiO/MgFe₂O₄ composite cathode for a molten carbonate fuel cell

H. Okawa^{a,*}, J.-H. Lee^a, T. Hotta^a, S. Ohara^a, S. Takahashi^a,
T. Shibahashi^b, Y. Yamamasu^b

^a Material Research and Development Laboratory, Japan Fine Ceramics Center, 2-4-1 Mutsumo, Atsuta-ku, Nagoya 456-8587, Japan

^b Ishikawajima-Harima Heavy Indus. Co., 5292, Aioi, Aioi-shi, Hyogo-ken 678-0041, Japan

Received 24 September 2003; accepted 19 November 2003

Abstract

To improve the stability of the cathode in a molten carbonate (Li/Na) electrolyte an attempt has been made to fabricate a new cathode structure in which NiO grains are coated with an outer layer such as MgFe₂O₄. This is considered to offer a new cathode material for molten carbonate fuel cells.

Metal (Ni) and ceramics (MgFe₂O₄) composite particles, which consisted of a filament-shaped Ni grain coated with fine ceramic particles have been successfully prepared by a mechanical coating technique using a Theta Composer. The solubility of nickel from the NiO/MgFe₂O₄ composite cathode is about one-fourth of that of NiO. A single cell with a NiO/MgFe₂O₄ composite cathode displays a high performance and a good stability.

© 2004 Elsevier B.V. All rights reserved.

Keywords: NiO/MgFe₂O₄; Composite particle; Mechanical coating; Molten carbonate fuel cell

1. Introduction

The molten carbonate fuel cell (MCFC) is an attractive power generation system because of its high electric efficiency and low pollution. For practical application, however, it is essential to improve the performance and stability of its components, namely electrodes, electrolyte and inter-connector. The short-circuiting of cells due to the dissolution and deposition of cathode (NiO) in molten carbonate is a major problem that has to be solved if MCFCs are to provide long-term operation, i.e., for over 40,000 h. To improve the stability of the cathode in molten carbonate, new cathode materials such as LiFeO₂ and LiCoO₂, have been developed [1–5]. The studies found that LiFeO₂ and LiCoO₂ were the promising candidates because they were more stable than NiO in molten carbonate. Nevertheless, the application of LiFeO₂ and LiCoO₂ as cathode materials have been limited to the fabrication of small electrodes because large ceramic sheets too brittle to be handled. In the author's earlier work, this problem was solved by designing an NiO cathode that was covered with LiCoO₂ in a molten

carbonate [6,7]. In addition, a solubility of LiFeO₂ was lower than that of LiCoO₂ and the addition of Mg improved the conductivity of LiFeO₂. Therefore, an attempt has been made to develop a new cathode structure, in which NiO grains are coated with outer layer such as MgFe₂O₄. In this paper, we discuss the solubility and cell performance of the NiO/MgFe₂O₄ cathode in more detail.

2. Experimental

2.1. Preparation of Ni/MgFe₂O₄ composite powder

Nickel powder (Inco, carbonyl-nickel type 255, particle size: about 3 μm) and fine MgFe₂O₄ powder (particle size: about 0.5 μm) obtained by a solid-state reaction were used as starting materials. Nickel particles coated with fine MgFe₂O₄ particles (MgFe₂O₄/Ni composite particle) were prepared by a mechanical coating technique using a new vessel type mixer known as a Theta Composer (Tokujin Corp., Type THC-B1) [8], as shown in Fig. 1. The mass ratio of MgFe₂O₄ to Ni was set at 3 mass%. The microstructure of the composite particle was examined by means of a scanning electron microscope (SEM, Hitachi, S-800)

* Corresponding author. Tel.: +81-52-871-3500; fax: +81-52-871-3599.
E-mail address: okawa@jfcc.or.jp (H. Okawa).

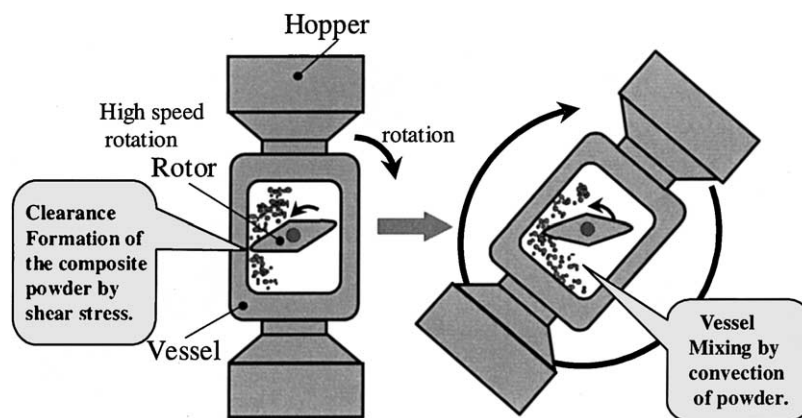


Fig. 1. Schematic diagram of a new vessel type mixer, the Theta Composer.

with an energy dispersive X-ray analysis (EDAX, Philips, PV9900).

2.2. Preparation of Ni/MgFe₂O₄ composite cathode and evaluation of composite cathode

An Ni/MgFe₂O₄ composite cathode was prepared by the tape-casting method. The composite powder was mixed in water with a binder, a dispersing agent and a deformer to obtain a slurry for tape casting with a doctor blade. The composite cathode tape was sintered at 850 °C in a 5% H₂–Ar atmosphere.

To evaluate the solubility of the composite cathode in molten carbonate, samples were excised from the sintered tape. Each sample was immersed in a (Li_{0.52}Na_{0.48})₂CO₃ melt at 650 °C in a 10% CO₂–7% O₂–83% N₂ atmosphere at 1.2 MPa. The sample was oxidized in situ during the solubility test. The concentration of nickel in the molten carbonate after the test was analyzed by inductively coupled plasma atomic emission spectrometry (Nippon Jarrell-Ash Corp. Ltd.). The saturated concentration of nickel was regarded as the solubility. More details of the measurement of solubility are described elsewhere [5,6].

The composite cathode tape was cut to obtain a cathode sheet with an area of 100 cm² for evaluating the single-cell performance using the composite cathode. The operating conditions are shown in Table 1. The single cell was oper-

ated at 650 °C and 0.1 MPa. The load current density was fixed at 150 mA cm⁻². The gas compositions of the anode and the cathode were 64% H₂–16% CO₂–20% H₂O and 30% CO₂–70% air, respectively.

3. Results and discussion

3.1. Morphology of Ni/MgFe₂O₄ composite particles and composite cathode microstructure

Scanning electron micrographs of the Ni particles and MgFe₂O₄ fine particles as starting materials are shown in Fig. 2. The Ni particles have some projections ('spikes', see Fig. 2(a)), and are weakly inter-connected to make a filament-shape like a chain. The size of the particles was about 3 μm. The MgFe₂O₄ particles have a square-shape (Fig. 2(b)) and a size of about 5 μm, as measured by the X-ray sedimentation method (Micromeritics, Sedigraph5100).

Scanning electron micrographs of Ni particles coated with MgFe₂O₄ particles prepared by the mechanical coating technique are presented in Fig. 3(a) and (b). Elemental analysis of Fe and Ni in the latter particles is given in Fig. 3(c) and 3(d), respectively. It is clear from these micrographs that fine MgFe₂O₄ particles are fixed on to the surface of the Ni particles without changing the filament-shaped structure. Moreover, Fe element analysis suggests that the fine MgFe₂O₄ particles are homogeneously dispersed of the surface Ni particles. It is concluded that mechanical forces such as shear and compression at the clearance between the rotor and the vessel are instantaneously exerted on to the surface of the filament-shaped Ni as well as on the fine MgFe₂O₄ particles during operation in the Theta Composer.

The microstructure of the Ni/MgFe₂O₄ composite cathode is presented in Fig. 4. The composite cathode is found to have a homogenous porous structure. The average pore-size and the average porosity (determined by mercury-porosimetry) is about 5 μm and 70%, respectively.

Table 1
Operating conditions of single-cell performance test

Cathode	NiO coated with MgFe ₂ O ₄ , $S = 100 \text{ cm}^2$ NiO–MgO (current cathode), $S = 100 \text{ cm}^2$
Anode	Ni–Al, Cr, $S = 100 \text{ cm}^2$
Electrolyte	(Li _{0.4} Na _{0.6}) ₂ CO ₃
Pressure	0.1 Mpa
Temperature	650 °C
Cathode gas	CO ₂ /air = 30/70%, $U_{\text{ox}} = 70\%$
Anode gas	H ₂ /CO ₂ /H ₂ O = 64/16/20%, $U_{\text{f}} = 75\%$
Current density	150 mA cm ⁻²
Operating time	NiO coated with MgFe ₂ O ₄ : about 5000 h NiO–MgO (current cathode): about 4000 h

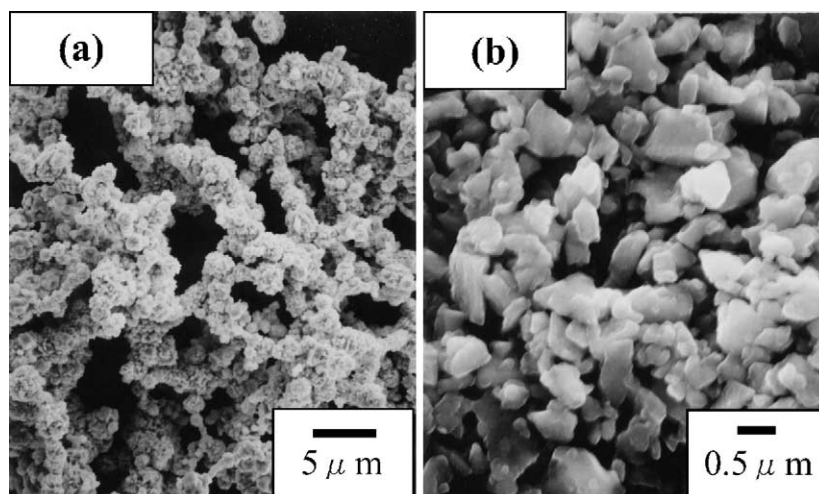


Fig. 2. Scanning electron micrographs of the starting materials: (a) filament-shaped Ni particles; (b) fine MgFe₂O₄ particles.

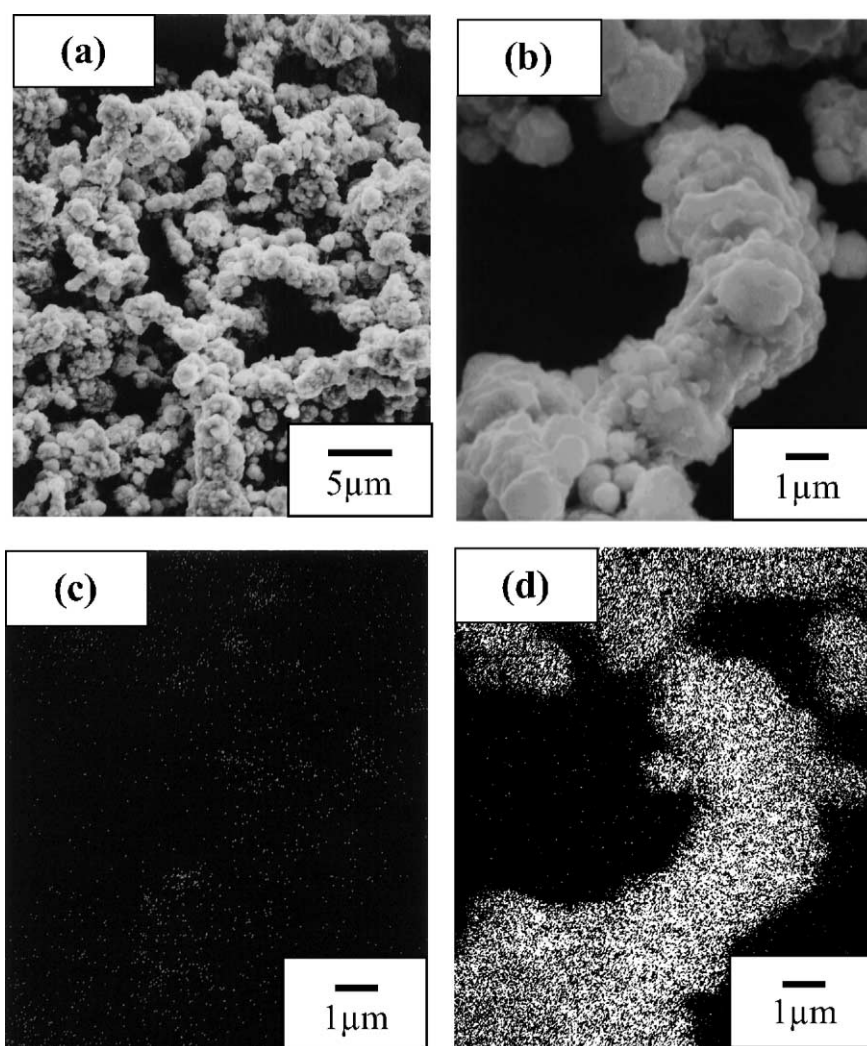


Fig. 3. Scanning electron micrographs of Ni-coated with MgFe₂O₄ particles prepared by mechanical coating method: (a) low magnification; (b) high magnification; (c) Fe element analysis; (d) Ni element analysis.

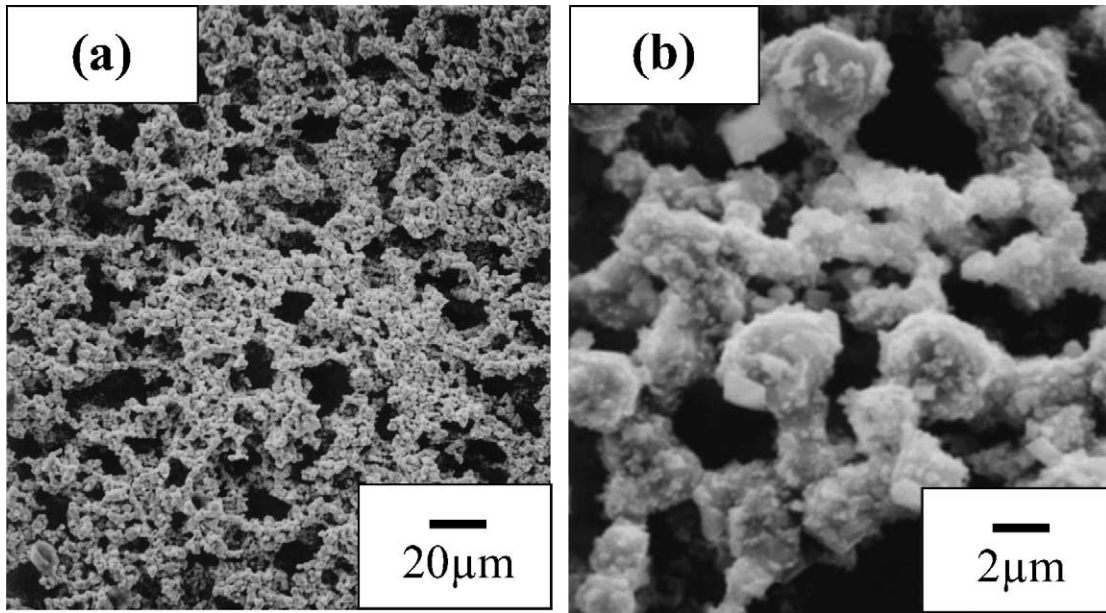


Fig. 4. Scanning electron micrographs of Ni/MgFe₂O₄ composite cathode: (a) low magnification; (b) high magnification.

3.2. Solubility and performance of NiO/MgFe₂O₄ composite cathode

The cathode samples were oxidized in situ during the first stage of the solubility test. The concentration of nickel dissolved from the composite cathode (NiO/MgFe₂O₄) and from a conventional cathode (NiO) in molten carbonate at high pressure are given in Fig. 5. The amount of Ni in the molten carbonate increases with time and reaches a constant value after 500 h, which is considered to be the Ni solubility of the NiO/MgFe₂O₄ composite cathode or NiO cathode. As shown in Fig. 5, the Ni solubility of the NiO/MgFe₂O₄ composite cathode with 3 mass% MgFe₂O₄ is about one-fourth of that of the NiO cathode.

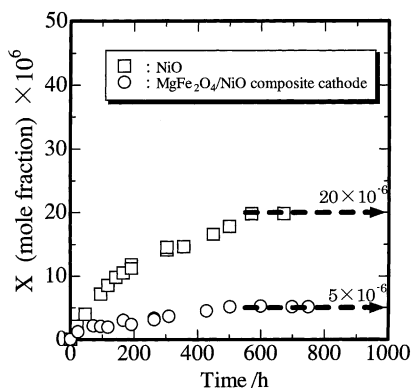


Fig. 5. Amount of nickel dissolved from a composite cathode and a conventional cathode into (Li_{0.52}Na_{0.48})₂CO₃ melt at 650 °C in 10%CO₂–7%O₂–83%N₂ at 1.2 MPa.

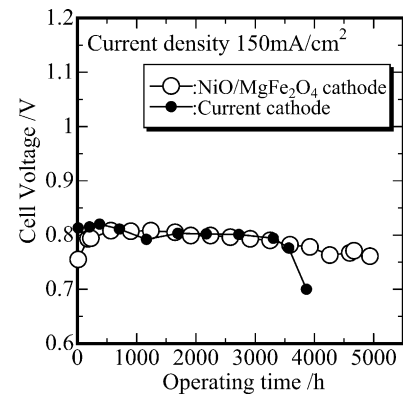


Fig. 6. Performance of single cell with NiO/MgFe₂O₄ composite cathode.

3.3. Performance of a single cell with NiO/MgFe₂O₄ composite cathode

A single cell with a conventional cathode (MgCO₃-added NiO) and another with a NiO/MgFe₂O₄ composite cathode were tested at 150 mA cm⁻² for about 4000 and 5000 h, respectively. The results are given in Fig. 6. The cell voltage of the conventional cathode decreases from 0.82 to 0.70 V from 500 to about 4000 h while that of the NiO/MgFe₂O₄ composite cathode maintains a cell voltage of 0.81–0.77 V from 500 to about 5000 h. These results show that the single cell with a NiO/MgFe₂O₄ composite cathode has a high performance and a good stability.

4. Conclusions

Metal (Ni) and ceramic (MgFe₂O₄) composite particles, which consist of a filament-shape Ni grain coated with fine

ceramic particles, have been prepared successfully by a mechanical coating technique using a Theta Composer. The solubility of nickel from the NiO/MgFe₂O₄ composite cathode is about one-fourth of that from a conventional NiO cathode. A single cell with a NiO/MgFe₂O₄ composite cathode exhibits high performance and good stability. Therefore, the NiO/MgFe₂O₄ composite cathode fabricated in this study is a promising candidate for molten carbonate fuel cells.

Acknowledgements

This work was conducted by the MCFC Research Association, which was commissioned to do the work by NEDO (New Energy and Industrial Technology Development Organization) under the guidance of METI (Ministry of Economy, Trade and Industry).

References

- [1] L. Plomp, E.F. Sitters, C. Vessies, F.C. Eckes, J. Electrochem. Soc. 138 (1991) 629–630.
- [2] C. Lagergren, A. Lundbland, B. Bergman, J. Electrochem. Soc. 141 (1994) 2959–2966.
- [3] K. Ota, Y. Takaishi, S. Shibata, H. Yoshitake, N. Kamiya, J. Electrochem. Soc. 142 (1995) 3322–3326.
- [4] L. Giorgi, M. Carewska, S. Scaccia, E.F. Zarzana, *Denki Kagaku* 64 (1996) 482–485.
- [5] T. Fukui, H. Okawa, T. Tunooka, *J. Power Sources* 71 (1998) 239–243.
- [6] T. Fukui, H. Okawa, T. Hotta, M. Naito, *J. Power Sources* 86 (2000) 340–346.
- [7] T. Fukui, H. Okawa, T. Hotta, M. Naito, T. Yokoyama, *J. Am. Ceram. Soc.* 84 (2001) 233–235.
- [8] T. Hotta, T. Fukui, H. Okawa, S. Ohara, M. Naito, S. Asahi, S. Endoh, K. Nogi, *J. Power Technol. Jpn.* 38 (2001) 408–413.