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Synthesis of metal and ceramic composite particles for fuel cell electrodes

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Abstract

Metal and ceramic (CoO/Ni and $MgFe_2O_4$/Ni) composite particles for molten carbonate fuel cell (MCFC) cathodes were prepared from filament shaped Ni particles by a mechanical coating technique using a new vessel type mixer named the Theta composer. The morphology of the composite particles consisted of a Ni grain coated with fine ceramic particles without changing the filament structure. Moreover, a CoO/NiO composite cathode and a $MgFe_2O_4$/NiO composite cathode were successfully fabricated from the composite particles by a doctor blade tape casting method. The composite cathode had good porous structure with high porosity. It suggests that the composite cathode can be applied as practical large area cathodes. Ni solubility of the CoO/NiO composite cathode and $MgFe_2O_4$/NiO composite cathode into a $(Li_{0.52}Na_{0.48})_2CO_3$ melt at 650 °C in 10%CO_2–7%O_2–83%N_2 at 1.2 MPa were about half and one-quarter of that of NiO, respectively. Therefore, the composite cathode is a promising candidate for a new cathode of MCFCs because of its high stability in molten carbonate and good porous structure.

Keywords: Chemical properties; Composite particle; Fuel cells; Mechanical coating; NiO

1. Introduction

Molten carbonate fuel cell (MCFC) is one of attractive power generation systems because of its high electric efficiency and low pollution. However, it is important for its practical use to improve the performance and stability of its components, such as electrodes, electrolyte and inter-connector. Durability of the component materials, especially the cathode material, in molten carbonate is a problem for long-term operation.

Nickel oxide (NiO) is widely used as cathode material for MCFCs because the large sized NiO cathode with an area of 1 m^2 can be fabricated from Ni powder (Inco255) by using a tape casting technique. However, the NiO cathode fabricated from Ni powder has not yet satisfied a long-term stability over 40,000 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 molten carbonate, new cathode materials, such as $LiCoO_2$ and $LiFeO_2$, have been developed.[1–6] Such studies showed that $LiCoO_2$ and $LiFeO_2$ are promising candidates for a MCFC cathode material because they are more than NiO stable in molten carbonate. However, application of $LiCoO_2$ or $LiFeO_2$ for a new cathode material is still limited for fabrication of a large electrode because ceramic sheets with large size are too brittle to be handled. Therefore, for the practical use of $LiCoO_2$ or $LiFeO_2$, we have proposed a new cathode structure that consisted of NiO grains (core) covered with stable outer layer, which contained $LiCoO_2$.[7,8] In our proposal, metal and ceramic composite particles play an important part as the starting material for the new cathode structure. A composite cathode, which had the new cathode structure, was formed from the composite particles by the usual tape casting method.

It is important for practical use of the composite cathodes that fine ceramic particles, which form the stable outer layer, coat the Ni particle surface homogeneously without changing the structure of filament shape because high porosity of a MCFC cathode is caused by this filament shape. Moreover, in the near future, the composite particles need to be produced commercially for practical levels of MCFC manufacture. Therefore, we have

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already developed a new vessel type mixer, named Theta composer,[9] for commercial powder production.

The aim of this study is to determine the feasibility of fabricating composite cathodes from the metal and ceramic composite particles, which prepared by the new vessel type mixer for MCFC electrode. The morphology of the composite particles is observed, and the structure and solubility of the composite cathodes fabricated from the composite particles are investigated. Their relationship will be also discussed in this work.

2. Experimental

2.1. Preparation of metal and ceramic composite particles

Filament shape Ni powder (Inco255, particle size: about 3 μm), fine CoO powder (UM Cobalt & Energy Products, particle size: about 0.3 μm), and fine $MgFe_2O_4$ powder obtained by solid-state reaction were used as starting materials. Ni particles coated with fine CoO particles (CoO/Ni composite particle) and Ni particles coated with fine $MgFe_2O_4$ particles ($MgFe_2O_4$/Ni composite particle) were prepared by a mechanical coating technique using a new vessel type mixer.[9] The mixture of Ni powder and fine powder (Ni or $MgFe_2O_4$) was treated by Theta composer (TOKUJU Corp. Type THC-B1), as shown in Fig. 1, to obtain the composite particles. Theta composer consists of the elliptical rotor and vessel with two hoppers. The rotor rotates for mechanical treatment of the powders. Ni particles and fine particles were mixed by high-speed rotation of the rotor when both powders drop from the upper hopper to the under hopper. Then the fine particles were fixed onto the surface of Ni particle by mechanical force such as shear and compression at the clearance between rotor and vessel. Moreover, after all the powders dropped from the upper hopper to the under hopper, the vessel with hoppers rotated one half rotation, and at that time under hopper changes to upper hopper. Then the mechanical treatment started again as shown in Fig. 1. Rotation speed of the rotor for mechanical treatment was set at 2000 rpm. The mechanical treatment was repeated 300 times.

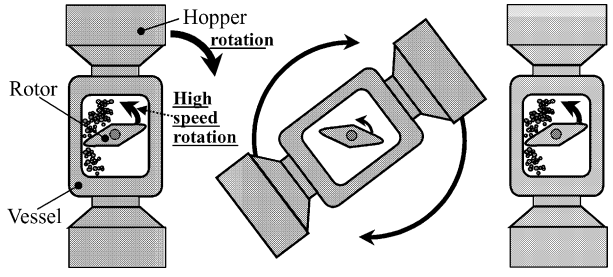

Fig. 1. Schematic diagram of a new vessel type mixer named Theta composer.

The mass ratios of CoO and $MgFe_2O_4$ to Ni was set at 5 and 3 mass%, respectively. 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, PV9900).

2.2. Evaluation of composite cathodes fabricated by tape casting method

Some organic additives, such as binder, deflocculant and plasticizer were mixed with the composite particles to obtain the slurries for the tape casting. The cathode tapes were prepared from the slurries by the doctor blade tape casting method. The tapes were sintered at 950 °C in 5% H_2–argon atmosphere and were further oxidized at 850 °C in air to obtain the CoO/NiO and $MgFe_2O_4$/NiO composite cathodes. A normal NiO cathode was also fabricated from Ni powder (Inco 255) by the above-mentioned method. Their average pore size and porosity were measured by mercury-porosimetry (SHIMADZU, 9420) in the pressure range up to 345 kPa and Archimedes method, respectively.

To evaluate the solubility of the composite cathodes, the samples were cut from the composite cathodes and sintered at 950 °C in 5% H_2–argon atmosphere. The samples were immersed into $(Li_{0.52}Na_{0.48})_2CO_3$ melt at 650 °C in 10%CO_2–7%O_2–83%N_2 at 1.2 MPa. The composite cathodes were in situ oxidized into molten carbonate during the solubility test. Ni concentration dissolved into molten carbonate was analyzed by ICP-AES (Nippon Jarrell-Ash Corp. Ltd.). The saturation concentration of Ni was regarded as the solubility of the composite cathodes. More details of the measurement of the solubility are described elsewhere.[6,7]

3. Results and discussion

3.1. Morphology of the metal and ceramic composite particles

Fig. 2 shows SEM photographs of the filament shape Ni particles as a starting material. It is clear in Fig. 2, that the Ni particles have some projections like a spike [Fig. 2(b)], and the particles weakly connect each other to make filament shape like a chain [Fig. 2(a)]. The size of the particles is about 3 μm. MCFC cathode showed high porosity of about 70% due to this filament shape of Ni particles. Therefore, when fine particles coat on the Ni particles, it is important not to damage the filament shape of the particles. Fig. 3 shows SEM photographs of the fine particles, which is coated on Ni particles. Fine CoO particles are almost spherical and their size is observed to be about 0.3 μm [Fig. 3(a)]. On the other hand, fine $MgFe_2O_4$ particles show square

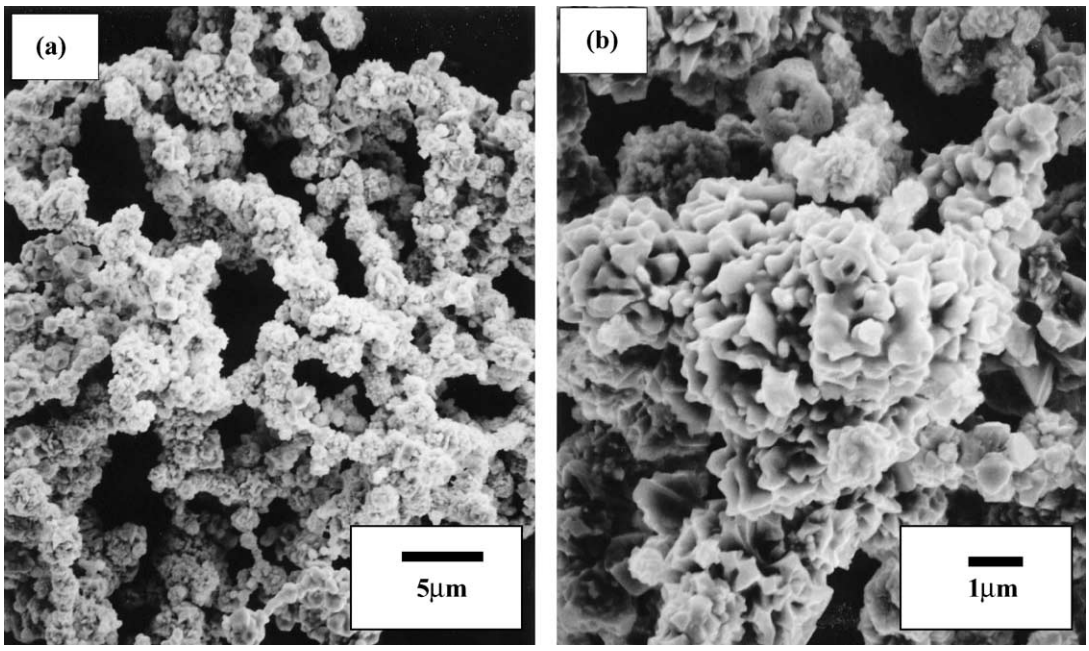

Fig. 2. SEM photographs of filament shape Ni particles: (a) low magnification image, (b) high magnification image.

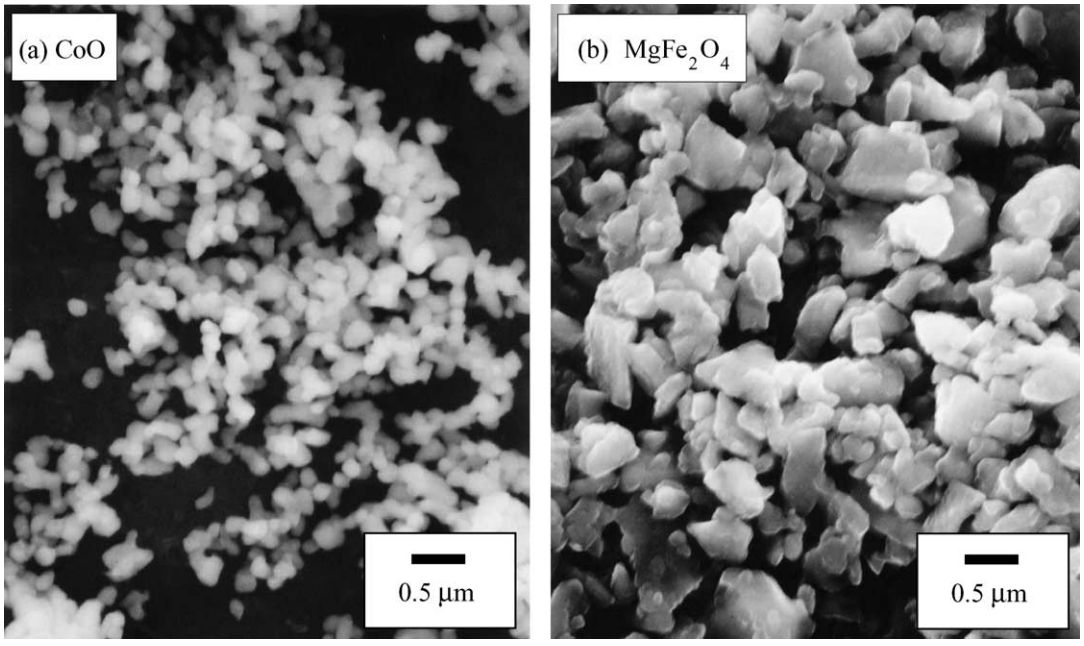

Fig. 3. SEM photographs of (a) fine CoO particles and (b) fine $MgFe_2O_4$ particles as starting materials.

shape, and the size of the particles was about 0.5 μm measured by X-ray sedimentation method (Micromeritics, Sedigraph 5100).

Fig. 4 shows SEM photographs of CoO/Ni composite particles prepared by mechanical treatment using Theta composer. Fig. 4(a) and (b) are low and high magnification image, respectively. It is confirmed from Fig. 4(b) that fine CoO particles fix almost homogeneously onto the surface of Ni particles. Also, some of the projections on the Ni particles are crushed by the mechanical treatment. However, it is clear from Fig. 4(a) that the composite particles keep the filament shape without changing the structure. So, it is confirmed that CoO/Ni composite particles can be successfully prepared from the filament shape Ni particles by the mechanical method. In general, the filament structure of the particle is easily deformed and cut by the mechanical effect such as grinding. However, from this result, the composite

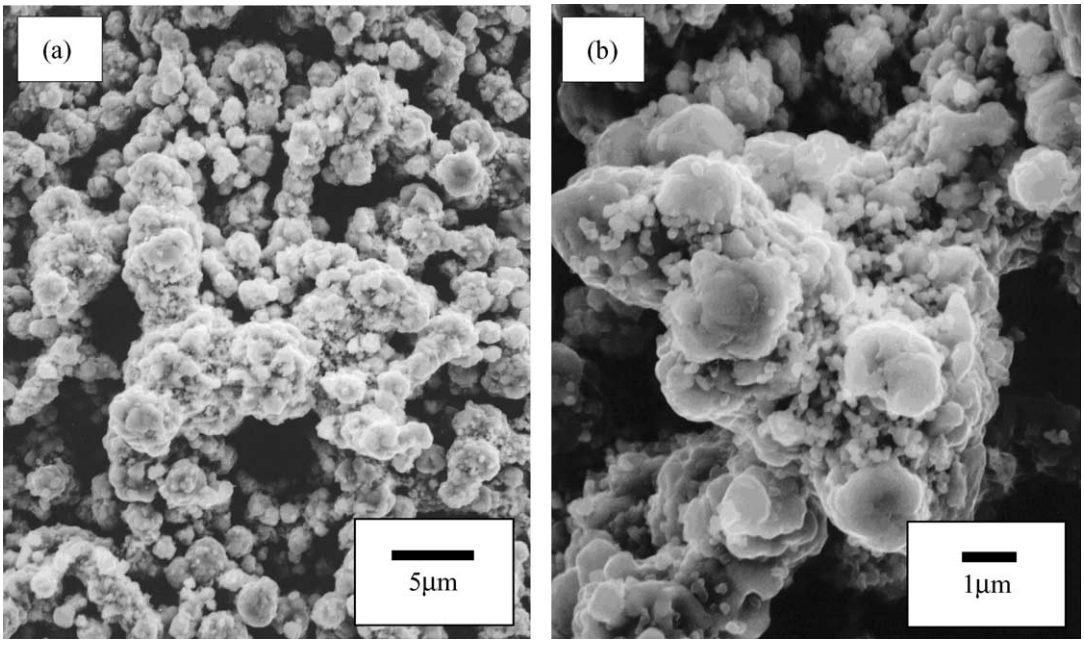

Fig. 4. SEM photographs of CoO/Ni composite particles prepared by mechanical coating method using Theta composer: (a) low magnification and (b) high magnification.

particles coated with fine CoO particles are successfully prepared by the mechanical method and keep the filament structure. It is considered that mechanical forces such as shear and compression at the clearance between rotor and vessel are instantaneously exerted onto the surface of filament shape Ni as well as fine CoO particles during operation in the Theta Composer.

SEM photographs of $MgFe_2O_4$/Ni composite particles prepared by mechanical treatment are shown in Fig. 5(a) and (b). Fig. 5(c) and (d) also show Fe and Ni elemental analysis of Fig. 5(b), respectively. It is confirmed from Fig. 5(b) that fine $MgFe_2O_4$ particles fix onto the surface of Ni particles. Moreover, Fe elemental analysis suggests that fine $MgFe_2O_4$ particles are homogeneously dispersed on the surface of Ni particles. Also, it is clear form Fig. 5(a) that the $MgFe_2O_4$/Ni composite particles as well as CoO/Ni particles keep the filament shape without changing the structure substantially.

3.2. Porous structure of the composite cathode

Table 1 shows average pore size and porosity of CoO/NiO composite cathode, which was fabricated from the composite particles by the usual tape casting method. Average pore size and porosity of NiO cathode are also shown in Table 1. It is clear from Table 1 that the composite cathode has a highly porous structure and its porosity is almost the same as that of a normal NiO cathode. It is considered that the high porosity of the composite cathodes is caused by the filament shape of the composite particle. It suggests that the composite particles really keep the same structure as Ni starting particles. However, the average pore size of the composite cathode decreases in comparison with that of NiO cathode. It is thought that this decrease is influenced by damage to the surface projection structure of a Ni particle.

Table 1

	Average pore size (μm)	Porosity (%)
CoO/NiO composite cathode	6.0	66
NiO cathode	8.0	70

3.3. Solubility of composite cathodes

The composite cathodes sintered at 950 °C in 5% H_2–argon atmosphere were immersed into $(Li_{0.52}Na_{0.48})_2CO_3$ melt at 650 °C in 10%CO_2–7%O_2–83%N_2 at 1.2 MPa. The composite cathodes are in situ oxidized during the first stage of the solubility test. Ni dissolution of the composite cathodes (CoO/NiO and $MgFe_2O_4$/NiO) and NiO cathode in high pressure (1.2 MPa) is shown in Fig. 6. The Ni dissolution of the cathodes increases against time and reaches the constant value after 600 h. These dissolution values are regarded as Ni solubility of the composite cathodes or NiO cathode. As shown in Fig. 6, Ni solubility of the CoO/NiO composite cathode with 5 mass% CoO appears about half of that of NiO. It is supposed that the CoO/NiO composite cathode has a new structure that consisted of

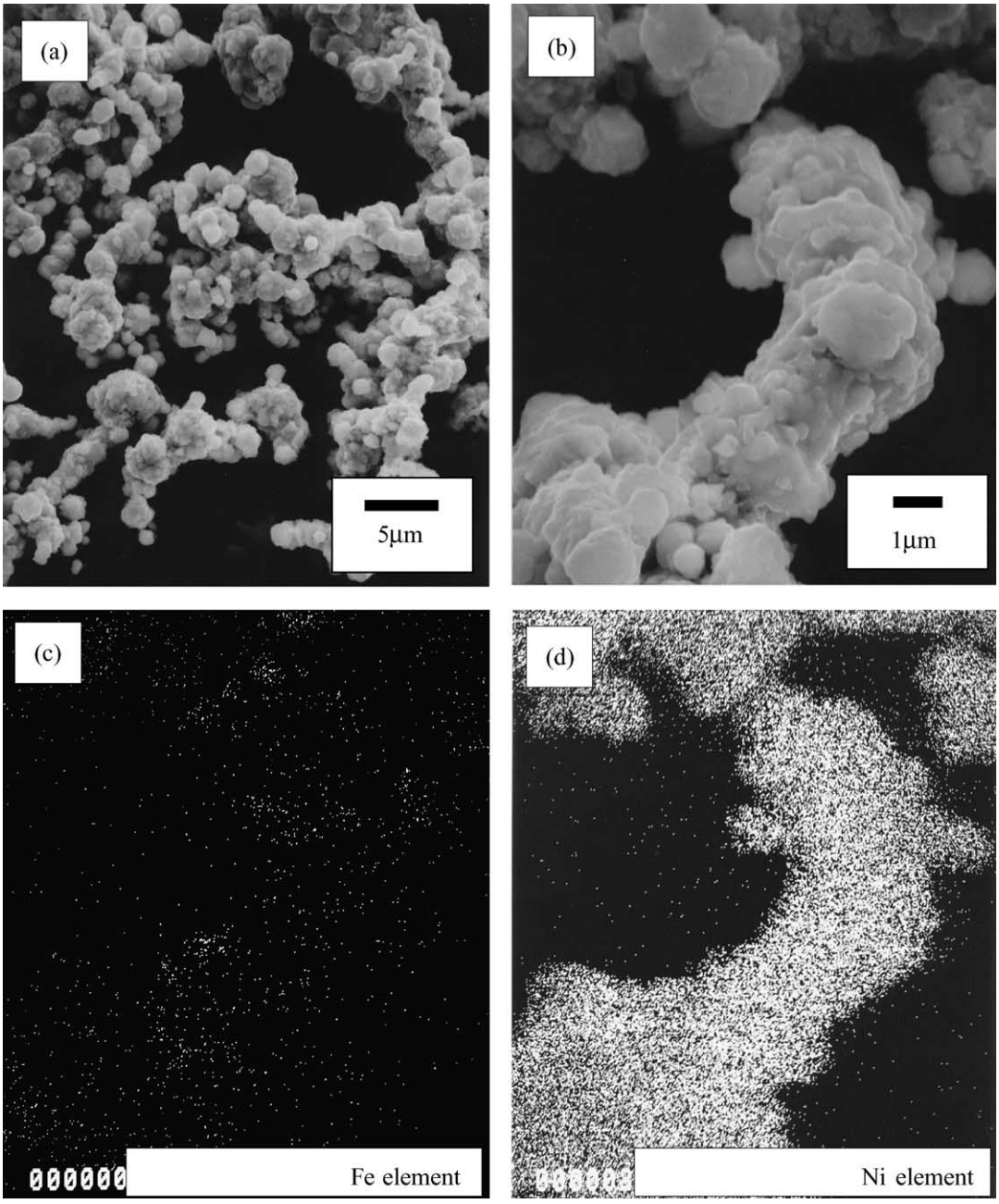

Fig. 5. SEM photographs of $MgFe_2O_4$/Ni composite particles prepared by mechanical coating method using Theta composer: (a) low magnification, (b) high magnification, (c) Fe elemental analysis and (d) Ni elemental analysis.

the NiO grains (core) covered with stable outer Li(Co,Ni) oxide layer as already reported by the authors.[8] Therefore, it is considered that the Li(Co,Ni) oxide layer prevented the dissolution of Ni from NiO core. Moreover, solubility of the $MgFe_2O_4$/NiO composite cathode with 3 mass% $MgFe_2O_4$ apparently shows about one-quarter of that of NiO. In the $MgFe_2O_4$/NiO composite cathode, the stability of the cathode is improved 4 and 2-times higher than that of NiO and CoO/NiO cathode, respectively. Generally, solubility of $LiFeO_2$ was lower than that of LiCoO2.[1,2] Therefore, it suggests that a higher stability outer layer containing $LiFeO_2$ is formed on the surface of NiO grains in the $MgFe_2O_4$/NiO composite cathode.

Consequently, the composite cathode had highly porous structure and high stability in a molten carbonate at 1.2 MPa. However, for application in a MCFC stack, it is really necessary that a cell with this composite cathode operates with the same performance as a cell with normal NiO. In the near future, we will report the performance results for the composite cathodes.

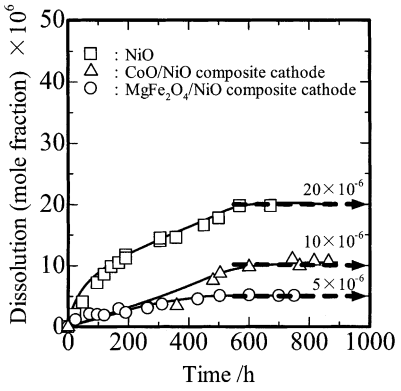

Fig. 6. Dissolution of the composite cathodes into $(Li_{0.52}K_{0.48})_2CO_3$ melt at 650 °C in 10%CO_2–7%O_2–83%N_2 at 1.2 MPa. □: Ni dissolution of normal NiO cathode, △: Ni dissolution of the CoO/NiO composite cathode and ○: Ni dissolution of the $MgFe_2O_4$/NiO composite cathode.

4. Conclusion

Metal and ceramic (CoO/Ni and $MgFe_2O_4$/Ni) composite particles, which consisted of a filament shape Ni grain coated with fine ceramic particles, were successfully prepared by the mechanical coating technique using Theta composer. They formed the composite structure without changing the filament structure of the starting Ni particles. Moreover, the composite cathodes were also successfully fabricated from the composite particles by the tape casting technique. The composite cathode had a good porous structure with high porosity. Also, Ni solubility of the CoO/NiO composite cathode and $MgFe_2O_4$/Ni composite cathode into a $(Li_{0.52}Na_{0.48})_2CO_3$ melt at 650 °C in 10%CO_2–7%O_2–83%N_2 at 1.2 MPa appeared to be about half and one-quarter of that of NiO, respectively. Therefore, the composite cathode fabricated in this work is a promising candidate for a new cathode of MCFCs because of its high stability in molten carbonate and high possibility for fabricating the large sized composite cathode.

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