Phase changes of newly synthesized Co-coated Ni cathode in MCFC cathodic conditions

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A molten carbonate fuel cell (MCFC) is expected to provide high efficiency generation of electricity and an environmentally clean means of power generation [1, 2]. However, the durability of the MCFC experiences difficulties at over 40 000 hr of operation. One of the lifetime limiting problems of a MCFC is the slow dissolution of the state of the art cathode material NiO into the electrolyte [3]. Two main methods have been adopted to solve this problem. One method is to use an alternative electrolyte. More basic molten carbonate melts adopting Li/Na eutectic carbonates instead of Li/K eutectic carbonates have been used to decrease the Ni dissolution rate in the electrolyte [4]. The other method is to develop alternative cathode materials. Among cathode materials, $LiCoO_2$ seems to be one of the best candidates because of its higher stability in the molten carbonate, and the rate of dissolution is slower than that of the NiO cathode. However, application of $LiCoO_2$ as a new cathode material has problems in scaling up the electrode area and a relatively higher manufacturing cost than that of the NiO cathode. Therefore, recently many investigators have attempted to resolve the problem by developing new cathode materials in which NiO grains have been coated with a small amount of $LiCoO_2$ or CoO by various coating techniques to reduce their dissolution [5, 6].

In this study, we have tried to prepare a new candidate cathode material of Co_3O_4-coated Ni powders using the Pechini method [7] as a new coating technique. In addition, we report on the phase changes of the Co-coated Ni cathode in MCFC cathodic conditions.

The Co_3O_4-coated Ni powders were prepared by the following method. A stoichiometric amount of cobalt acetate (Aldrich, USA, purity of 98+%) and citric acid (CA) (Aldrich., USA, purity of 99.5+%) were dissolved in distilled water and thoroughly mixed with an aqueous solution of ethylene glycol (EG) (CA:EG:cobalt ions = 2:1:1). After that, the solution was adjusted by adding NH_4OH until pH 8 was achieved and Ni powder (filamentary nickel 255, Inco, USA) was immersed in the solution. The resultant solution was heated to 80 °C while being stirred until a gel precursor was produced. The gel precursor was calcined at 350 °C for 3 hr in air.

The Co-coated Ni cathode was made using a tape casting method utilizing synthesized powders. Binder (2.5 g, MC1500, Hanawa Co., Japan), plasticizer (1.38 g, Glycerol, Junsei Co., Japan), and defoamer (0.3 g, SN1540, San Nopco Ltd., Korea) were added into the solvent (H_2O) followed by ball milling for 24 hr. Then, synthesized powders (30 g) and dispersant (0.3 g, Cerasperse 5468, San Nopco Ltd., Korea) were added and ball-milled for 4 hr. After ball milling, the slurry was completely degassed using a ROTOVAP® evaporator, which was tape cast to get a Co-coated Ni cathode green sheet. The green sheet was dried slowly at room temperature for 24 hr. After drying, the cathode green sheet was given a heat treatment under a reducing atmosphere (H_2:N_2 = 30:70%) at 750 °C for 30 min. The phase changes of the Co-coated Ni cathode were investigated during immersion in molten $(Li_{0.62}K_{0.38})_2CO_3$ under CO_2:O_2 (67:33%) atmosphere at 650 °C.

Thermal behavior of the gel precursors was investigated by thermogravimetric analysis (TGA, SDT 2960). The phase changes and morphologies of the cathode material were characterized by X-ray diffraction (XRD, Rigaku Geigerflex DMAX-IIA, Cu-K_α radiation), Raman spectrometry (NR-1100, Innova 70 series Ar ion laser), and field emission scanning electron microscopy (FE-SEM, Hitachi 6300) with energy dispersive X-ray analysis (EDAX).

The removal of all volatile and decomposition of organic matters is completed below 350 °C in TGA. Therefore, an appropriate calcination temperature was determined to be 350 °C. Fig. 1 shows the XRD pattern of the Co_3O_4-coated Ni powders obtained after calcination treatment of the gel precursors at 350 °C for 3 hr. The major XRD peaks for Ni metal of (111) and (200) peaks (JCPDS 04-0850) appeared, and those for Co_3O_4 of (311) and (200) peaks (JCPDS 42-1467) were also observed. The NiO peaks did not appear because the oxidation rate of Ni is very slow, at least up to 400 °C [8]. In fact, chelated Co^{2+} is known to transform into the cubic Co_3O_4 during heating at about 300 °C in air. As a result, Co was coated on the surface of Ni powder so that it reacted with O_2 easily on the large surface area during heat treatment in air. From our lattice parameter analysis, it can be inferred that the Co_3O_4 has not formed a solid solution with Ni after calcination

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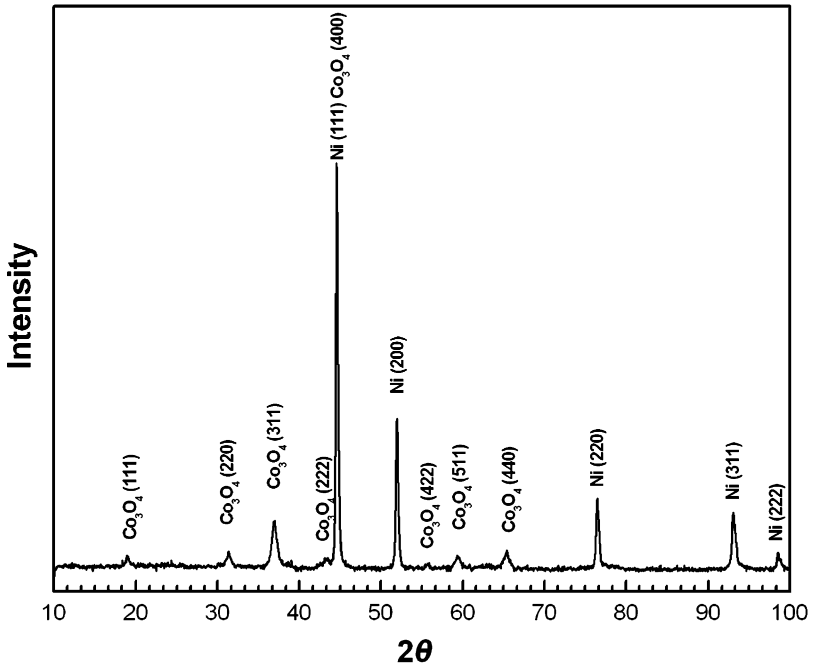

Figure 1 XRD pattern of the Co_3O_4-coated Ni powders obtained after calcination treatment of the gel precursor at 350 °C for 3 hr.

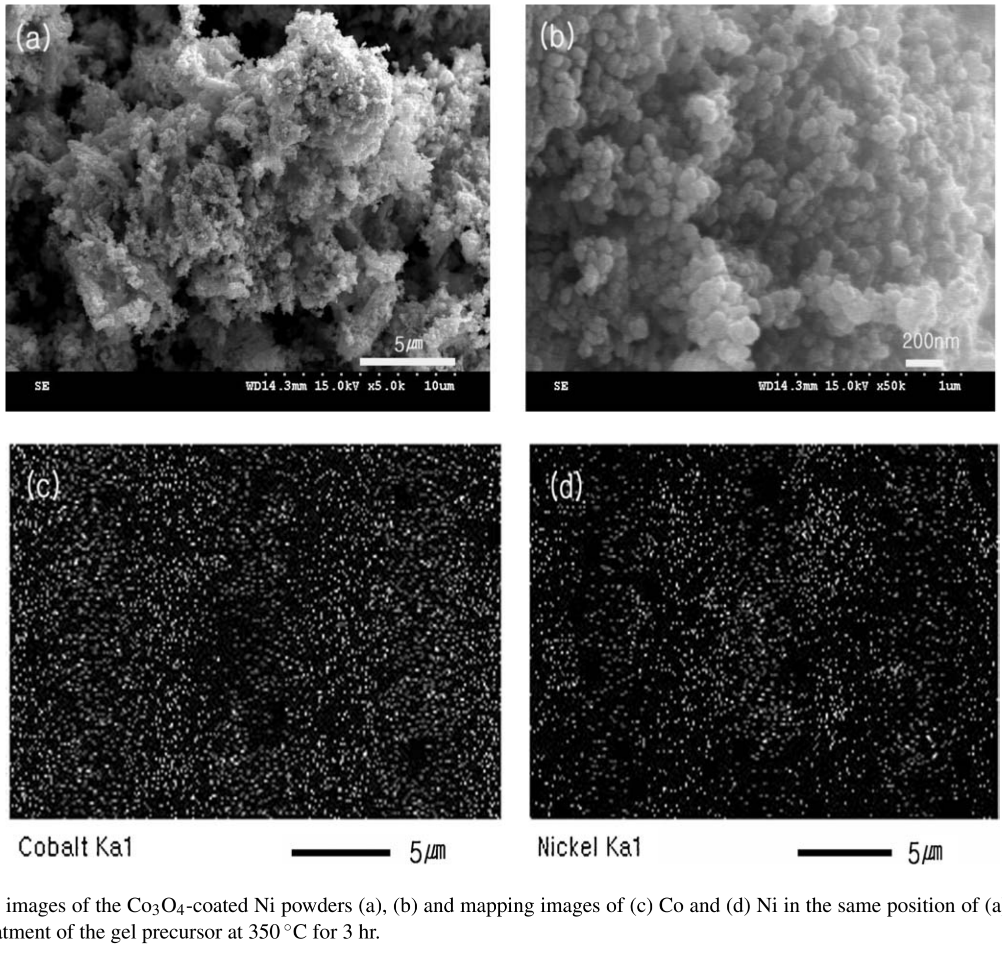

Figure 2 SEM images of the Co_3O_4-coated Ni powders (a), (b) and mapping images of (c) Co and (d) Ni in the same position of (a) obtained after calcination treatment of the gel precursor at 350 °C for 3 hr.

treatment at 350 °C. Fig. 2 shows the SEM images and mapping images of the Co_3O_4-coated Ni powders. From these SEM images, it is confirmed that Co_3O_4 particles do not cause a significant change in Ni particle size (6–12 μm, Fig. 2a) and the Co_3O_4 particles are well dispersed on the surface of the Ni particle (Fig. 2b). The average size of the Co_3O_4 grains determined from the micrographs was about 100 nm. Fig. 2c and d are Co and Ni mapping images at the same position in Fig. 2a. There is no difference in the distribution of Co and Ni in any mapping area in Fig. 2c and d. The results suggest that the Co_3O_4 particles homogeneously covered the Ni particle surface after calcination treatment of the gel precursors.

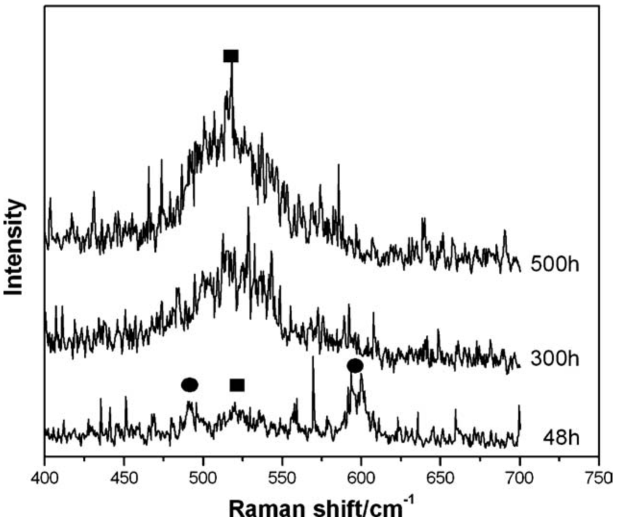

Figure 3 Raman spectra of the Co-coated Ni cathode obtained after immersion in the molten carbonate under CO_2:O_2(67:33%) atmosphere at 650 °C for different times: (●: $LiCoO_2$, ■: $LiCo_{1-y}Ni_yO_2$).

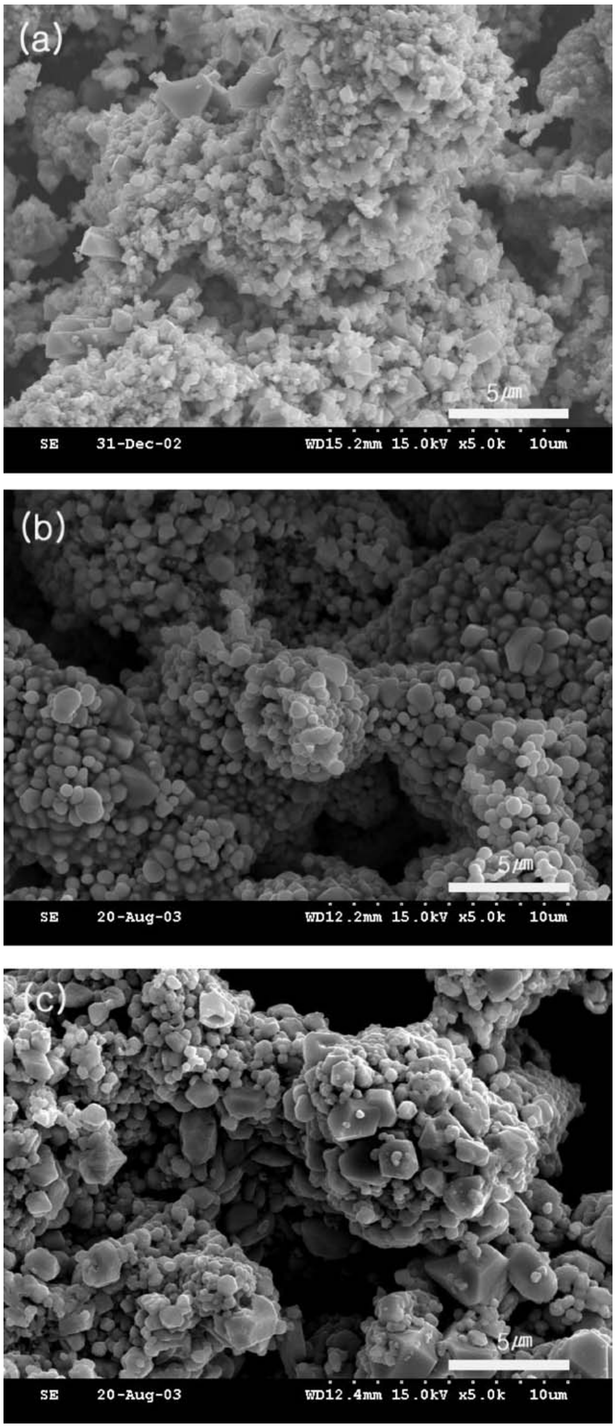

Figure 4 SEM images of the Co-coated Ni cathode obtained after immersion in the molten carbonate under CO_2:O_2 (67:33%) atmosphere at 650 °C: (a) 48 hr, (b) 300 hr, and (c) 500 hr.

In order to investigate the phase changes of the Co-coated Ni cathode which was fabricated from the Co_3O_4-coated Ni powders in the molten carbonate, the lithiation treatment was performed at different times in $(Li_{0.62}K_{0.38})_2CO_3$ under CO_2:O_2 (67:33%) atmosphere. Fig. 3 shows the Raman spectra of the Co-coated Ni cathode obtained after immersion in molten carbonate for different times. The spectra for $LiCoO_2$ were dominated by strong bands located at 485 cm^{-1} and 597 cm^{-1} which from the group factor analysis of the D^5_{3d} spectroscopic symmetry were attributed to the A_{1g} and E_g species, respectively [9]. A broad band located around 510 cm^{-1} dominates the spectrum for $LiCo_{1-y}Ni_yO_2$ [9, 10]. Fig. 3 shows that both of the strong $LiCoO_2$ bands and the broad $LiCo_{1-y}Ni_yO_2$ band were observed after 48 hr. As time passed, however, the 485 cm^{-1} and 597 cm^{-1} bands disappeared gradually while a broad band around 510 cm^{-1} appeared due to the formation of $LiCo_{1-y}Ni_yO_2$ phase. Fig. 4 shows the SEM images of the Co-coated Ni cathode obtained after immersion in the molten carbonate for different times. On the whole, the sample kept the network structure of primary NiO well and the surface of the NiO particle was covered with many tiny $LiCoO_2$ and $LiCo_{1-y}Ni_yO_2$ grains as shown in Fig. 4a. From the SEM images in Fig. 4b and c, the $LiCo_{1-y}Ni_yO_2$ morphology can be increasingly seen because of the formation and the agglomeration of a lithiated Co-Ni solid solution. Considering SEM analysis and the Raman result, we can conclude that a stable $LiCo_{1-y}Ni_yO_2$ phase is formed on the surface of the cathode in molten carbonate under cathodic operating conditions.

To summarize, a schematic description of the phase changes of the Co_3O_4-coated Ni powders during the experiment is shown in Fig. 5. The Co_3O_4-coated Ni powders have been successfully synthesized using polymeric precursor based on the Pechini method. Using this method, a scaled-up cathode can be manufactured easily and economically. As the experimental time passed, the NiO is coated with lithiated Co-Ni solid solution oxide ($LiCo_{1-y}Ni_yO_2$) in molten carbonate [11]. Therefore, we may infer that the solubility of Ni from the $LiCo_{1-y}Ni_yO_2$ layer into the molten carbonate will considerably decrease much more than that of the NiO used as a cathode for MCFC. It is suggested that this factor would lengthen the lifetime of MCFC and that the $LiCo_{1-y}Ni_yO_2$-coated NiO has a promising structure as an alternative cathode. The details for the solubility and electrochemical performance are still under investigation.

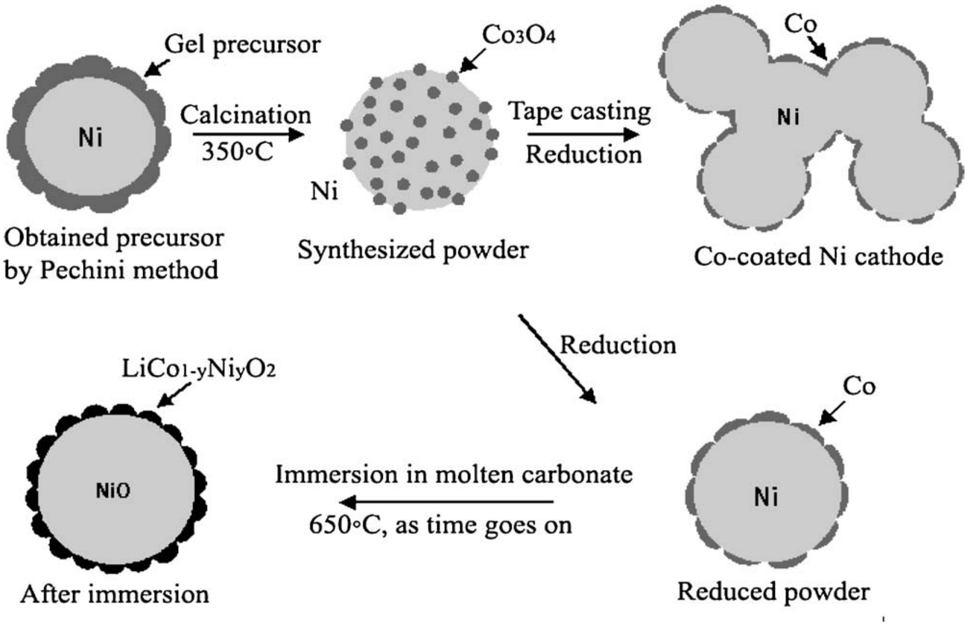

Figure 5 Schematic diagram of the phase changes of the Co_3O_4-coated Ni powders during the experiment.

Acknowledgments

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