

# Properties of NiO cathode coated with lithiated Co and Ni solid solution oxide for MCFCs

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## Abstract

The short circuit of cells due to the dissolution and the deposition of NiO in a molten carbonate is a big problem that has to be resolved if we want to use Molten Carbonate Fuel Cells (MCFCs) for long-term operation. To resolve this problem, we have proposed a new cathode structure in which NiO grains have been coated with LiCoO<sub>2</sub> grains by usual tape casting method, because LiCoO<sub>2</sub> is more stable in a carbonate melt than NiO. CoO/NiO composites with 5 to 20 mass% Co could be formed by using the CoO/Ni composite particles. As confirmed by SEM, these composites consisted of NiO cores covered with the outer layer of Li(Co, Ni) oxide. The stability of the lithiated CoO/NiO composite with 5 mass% CoO was significantly improved in comparison with that of conventional NiO for MCFCs. The lithiated CoO/NiO composite was also successfully formed by in-situ oxidation and lithiation process. We thought that this composite cathode material consisting of NiO core covered with Li(Co, Ni) oxide will be adopted as the new cathode for MCFCs. © 2000 Elsevier Science S.A. All rights reserved.

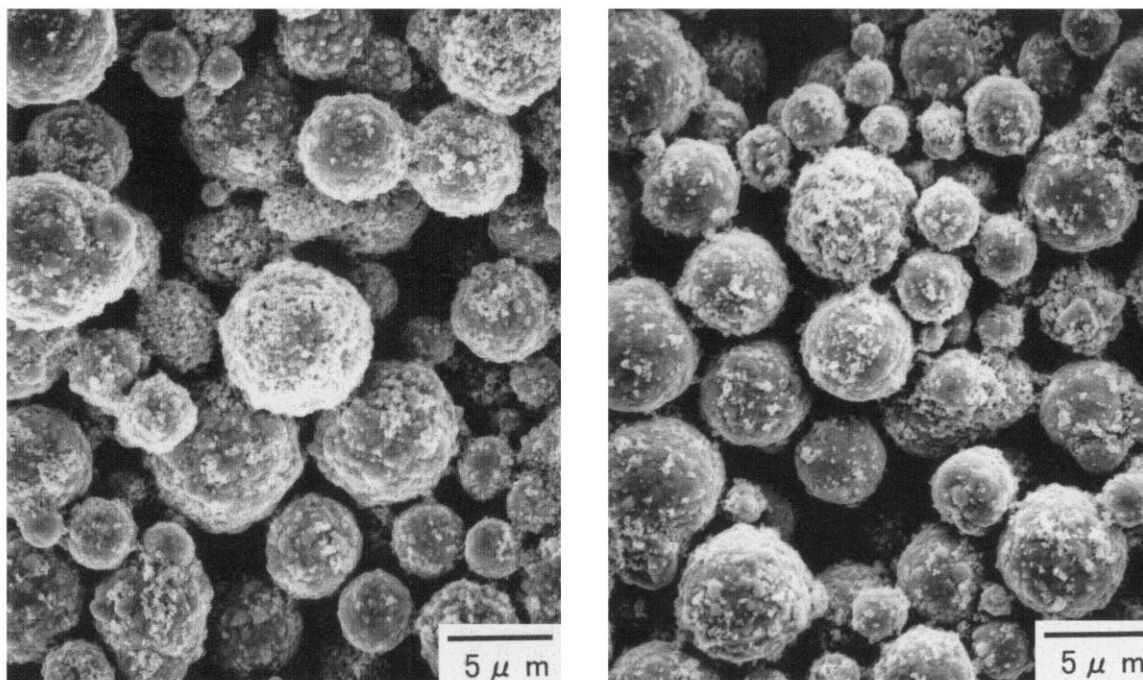
*Keywords:* Molten Carbonate Fuel Cells; New cathode structure; LiCoO<sub>2</sub>; Solubility

## 1. Introduction

Nickel oxide (NiO) is commonly used as the cathode material for the Molten Carbonate Fuel Cells (MCFCs) because of its high stability in a molten carbonate at 650°C and high activity of the cathode. However, the NiO cathode fabricated from Ni powder has not satisfied long-term stability over 10,000 h of operation; the cells are short circuited due to the dissolution and the deposition of NiO in the molten carbonate. To improve the stability of NiO, alkaline earth metal salts have been added to the molten carbonate electrolyte [1,2] and new cathode materials, such as LiCoO<sub>2</sub> and LiFeO<sub>2</sub>, have been developed [3–5]. So far, we have examined LiCoO<sub>2</sub> as an alternative cathode material for MCFCs [6,7]. The solubility and the deposition properties of this material have been studied in more detail. Our previous studies showed that LiCoO<sub>2</sub> is more stable in a carbonate melt than NiO. However, application

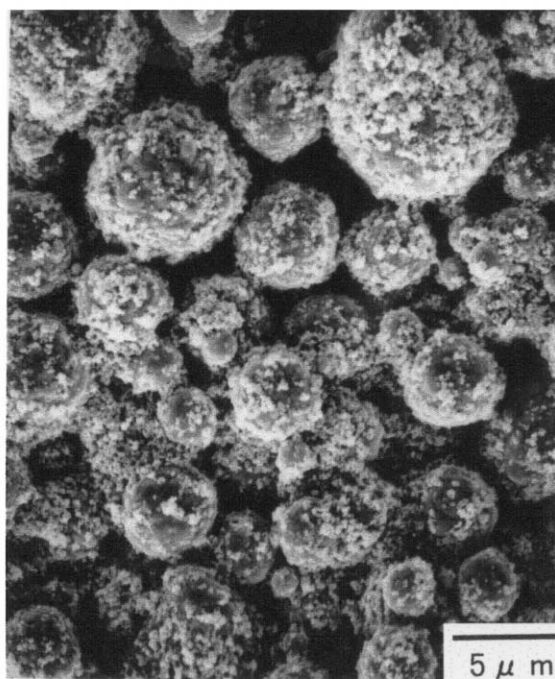
of LiCoO<sub>2</sub> as a new cathode material is still limited for producing large electrodes because of its brittleness and higher manufacturing cost than the Ni-based cathode. In general, the large sized NiO cathodes with an area of 1 m<sup>2</sup> have been prepared by the usual tape casting method. For the practical use of LiCoO<sub>2</sub>, the usual tape casting method can be applied to prepare cathodes from new cathode materials. Therefore, to overcome dissolution and deposition problems we propose a new cathode structure in which NiO grains have been coated with LiCoO<sub>2</sub> grains by using the usual tape casting method [8]. In this proposal, CoO/Ni composite particles, where fine CoO particles are densely distributed over the Ni particle surface, have been used as a cathode starting material. In our previous study, we already confirmed that it was possible to design a new structure where NiO grains are coated with an outer layer of lithiated Co and Ni solid solution oxide (Li(Co, Ni) oxide) by using these composite particles as the starting materials [8]. In this study, we examine the effect of Co content in CoO/Ni composite particles on the structure of a new cathode and the solubility of these new cathode materials. Moreover, we have tried to prepare this new cathode structure consisted of the NiO core with

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**(a)**

**(b)**



**(c)**

Fig. 1. SEM photographs of the CoO/Ni composite particles prepared by the mechanical coating method: (a) 5 mass% CoO, (b) 10 mass% CoO, (c) 20 mass% CoO.

the outer layer of Li(Co, Ni) oxide by in-situ oxidation and lithiation at 650°C in a (Li, K)CO<sub>3</sub> melt.

## 2. Experimental

### 2.1. Preparation of CoO / Ni composite particles

Ni powder (average particle size: about 8 μm) and fine CoO powder (about 0.3 μm) were used as starting materials. Ni particles were covered with fine CoO particles mechanically by the Mechanofusion system [9] (HOSOKAWA MICRON). Mechanofusion system is an equipment designed to produce composite particles by the dry coating method. Coat particles are physically bonded to core particles by high shear and compressive forces produced in this machine. The mass ratios of CoO to Ni were 5 to 20 mass%. The CoO and Ni mixture powders were treated for 30 min by the Mechanofusion system. The prepared powders (CoO/Ni composite particles) were observed by a scanning electron microscopy (SEM, Hitachi, S-800) with an energy dispersive analysis of X-ray (EDAX, Philips, PV9900).

### 2.2. Preparation of the composite cathode and solubility test

The CoO/Ni composite particles were uniaxially pressed at 30 MPa to form compacts. These compacts were heated at 850°C in air. Then the sintered samples (CoO/NiO composites) were immersed into a (Li<sub>0.62</sub>-K<sub>0.38</sub>)<sub>2</sub>CO<sub>3</sub> melt in 30% CO<sub>2</sub>-70% air atmosphere for 400 h at 650°C. Concentrations of Co and Ni dissolved into a carbonate melt were analyzed by ICP-AES (Nippon Jarrell-Ash) during immersion of sintered samples into a carbonate melt and the saturation concentration of Co or Ni was regarded as the solubility. Moreover, the compact with 5 mass% CoO was sintered at 950°C in 5% H<sub>2</sub>-argon atmosphere and then the sintered sample (Co/Ni composite) was oxidized and lithiated in-situ at 650°C in a (Li<sub>0.62</sub>K<sub>0.38</sub>)<sub>2</sub>CO<sub>3</sub> melt in 30% CO<sub>2</sub>-70% air atmosphere for 400 h. Also, the solubility of this sample was measured by ICP-AES. The structure of the samples was analyzed by SEM-EDAX and X-ray diffraction analysis (XRD).

## 3. Results and discussion

### 3.1. Morphology of the composite particles and CoO / NiO composites

The SEM photographs of the CoO/Ni composite particles with 5, 10 and 20 mass% CoO prepared by the mechanical coating method are shown in Figs. 1 and 2.

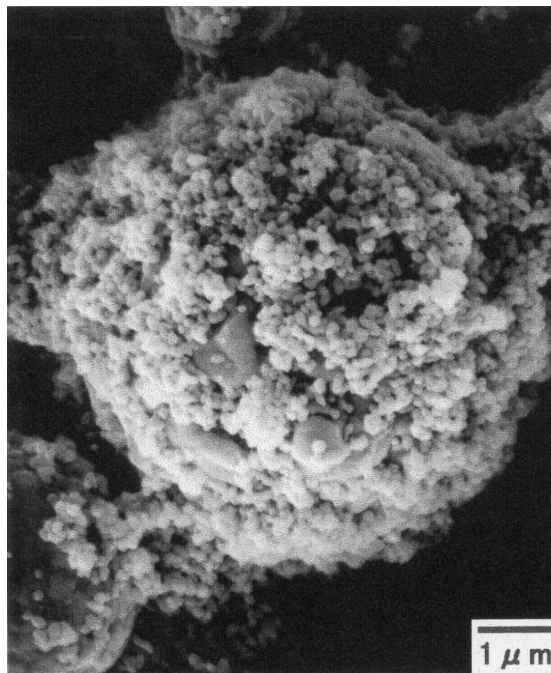


Fig. 2. SEM photographs of CoO/Ni composite particles with 5 mass% CoO.

From these figures, we can see that Ni particles are covered with fine CoO particles. In Fig. 2, fine CoO particles homogeneously covering a Ni particle are shown. From these SEM observations, we confirmed that CoO/Ni composite particles could be prepared by this mechanical method. The quantity of the fine CoO particles on the surface of Ni particles increased with increasing CoO content, up to 10 mass%. In the case when the Co content is more than 10 mass%, some lost particles of CoO can be observed among Ni grains coated with CoO particles. It is thought that further investigation is necessary to get more insight into coating of Ni particles if the content of CoO is higher than 10 mass%.

Fig. 3 shows the SEM photographs of CoO/NiO composites obtained by treatment of CoO/Ni compacts at 850°C, where Ni particles were oxidized during the heat treatment. From Figs. 1–3, we can see that the surface of these CoO/NiO composites changes evenly with increasing CoO content. It was already confirmed that grains of CoO/NiO composite consist of NiO grains that make up the skeleton core of the structure, and the outer layer of Co and Ni solid solution oxide ((Co, Ni)O), that coat to NiO core [8]. Therefore, it can be predicted that the Co concentration in the outer layer of these composites increase with increasing CoO content.

### 3.2. Solubility test

CoO/NiO composites with 5, 10, 20 Co were immersed into (Li<sub>0.62</sub>K<sub>0.38</sub>)<sub>2</sub>CO<sub>3</sub> melt at 650°C in 30%

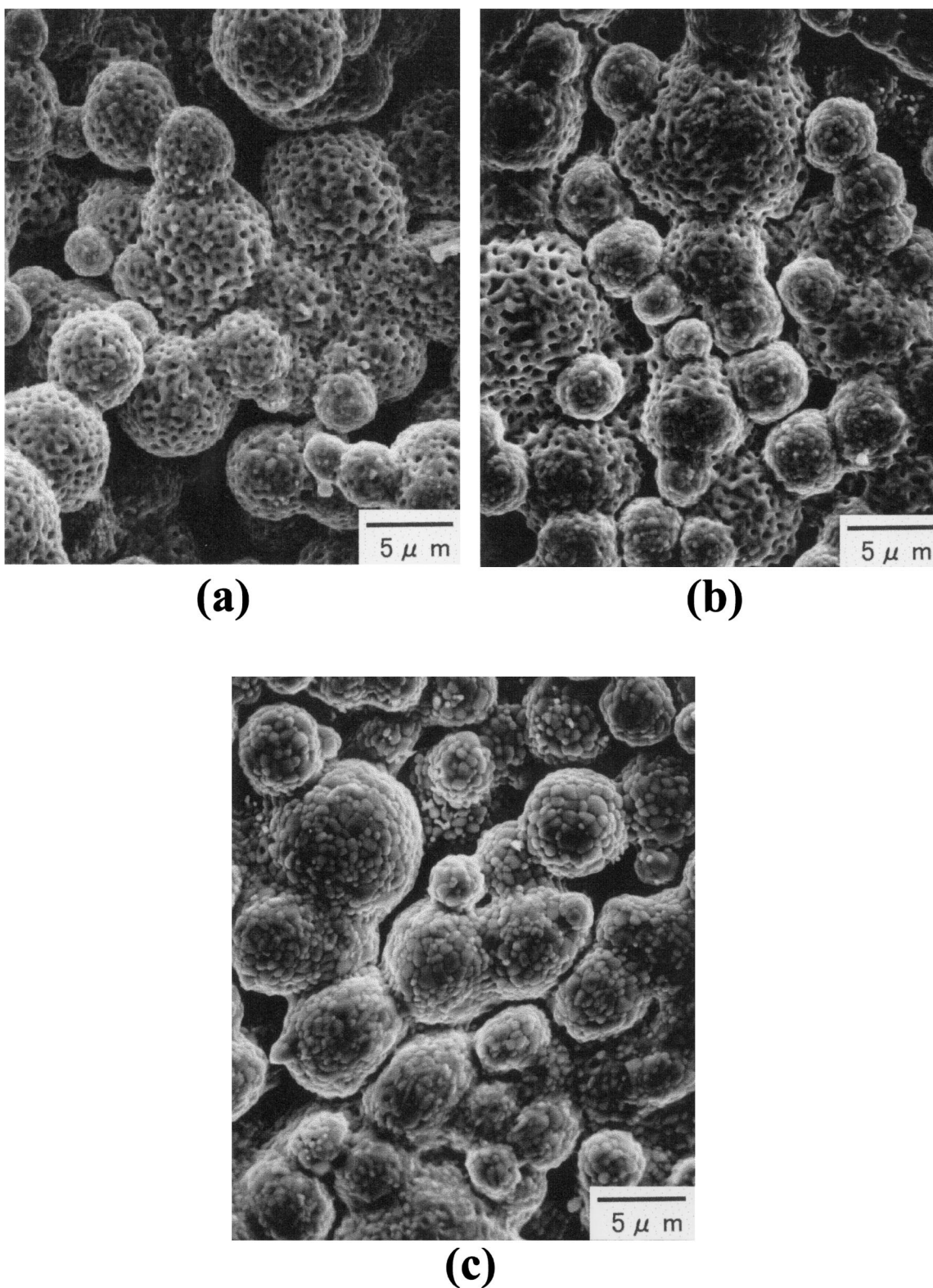


Fig. 3. SEM photographs of CoO/NiO composites obtained at 850°C: (a) 5 mass% CoO, (b) 10 mass% CoO, (c) 20 mass% CoO.

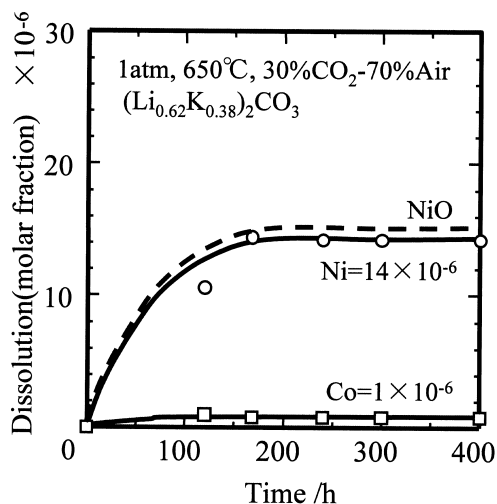


Fig. 4. Dissolution of 10 mass% CoO/NiO composite and NiO in  $(\text{Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3$  melt at 650°C in 30%  $\text{CO}_2$ -70% air atmosphere.

$\text{CO}_2$ -70% air atmosphere. Fig. 4 shows dissolution of 10 mass% CoO/NiO composite and NiO. Dissolution of both materials increases with time and reaches constant values after 150 h, which were regarded as the solubility. Fig. 5 shows Ni and Co solubility of CoO/NiO composites as a function of the Co content. Ni solubility of the composite with 5 mass% CoO decreases to two-thirds of that of NiO. No Co in 5 mass% CoO/NiO composite was found dissolved in the carbonate. However, Ni solubility of the composite with 10 and 20 mass% CoO is the same as that of NiO. Co solubility of these composite also increases with Co content. Then, Co solubility of 20 mass% CoO/NiO composite is the same as that of  $\text{LiCoO}_2$ .

### 3.3. Morphology of lithiated CoO/NiO composites

The CoO/NiO composites were lithiated in this solubility test. Fig. 6 shows SEM photographs of the lithiated CoO/NiO composites with 5, 10, 20 mass% CoO. Morphology of CoO/NiO composites changes with lithiation. In 5 mass% CoO/NiO composites, many hexagonal crystals are formed on the surface of grains after lithiation. Co oxide is easy to lithiate in  $(\text{Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3$  melt at 650°C because  $\text{LiCoO}_2$  is the stable phase in Li and K carbonate melt. On the other hand, NiO cannot be lithiated easily in a carbonate melt at 650°C. Generally, the lithium content in a NiO cathode in-situ oxidized and lithiated at 650°C is about 2 to 4 mol% [10]. Therefore, it was thought that (Co, Ni)O of the outer layer in 5 mass% CoO/NiO composite was only lithiated in a carbonate melt at 650°C and lithiated Co and Ni solid solution oxide ( $\text{Li}(\text{Co, Ni})$  oxide) was formed on the surface of the Ni oxide core. This result remains unexplained and is being investigated further. It is considered that the improvement in stability of the com-

posite cathode material into the carbonate melt results in the formation of this outer layer on the surface of NiO. In contrast, many fine grains are formed on the surface of 20 mass% CoO/NiO composite after lithiation. If the content of Co in these composites is higher, the outer layer of (Co,Ni)O is separated from the NiO core when it is lithiated. In other words, it is thought that lithiated CoO/NiO composites with 20 mass% CoO consists of NiO grains and fine  $\text{Li}(\text{Co,Ni})$  oxide grains. In Fig. 5, Ni and Co solubility in the 20 mass% CoO/NiO composites are the same as that of NiO and  $\text{LiCoO}_2$ . Therefore, we predict that no improvement in the solubility of 20 mass% CoO/NiO composite will be caused by the separation of the outer layer from the core.

### 3.4. In-situ oxidation and lithiation

Lithiated CoO/NiO composite was obtained by in-situ oxidation and lithiation at 650°C in a  $(\text{Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3$  melt in 30%  $\text{CO}_2$ -70% air atmosphere for 400 h. Fig. 7 shows the SEM photograph of the lithiated composite. From this SEM photograph, the surface of the lithiated CoO/NiO composite obtained by in-situ oxidation and lithiation is very smooth in comparison with that of the composite obtained by heat treatment at 850°C and lithiation. This difference in the morphology is caused by the difference of the preparation process. In the in-situ process, firstly, Co/Ni composite is formed by sintering in a reducing atmosphere. Secondly, Co/Ni composite is in-situ oxidized and lithiated in a carbonate melt. Therefore, it is predict that the morphology of the outer layer in lithiated CoO/NiO composite obtained by this in-situ process will differ from that of the composite by lithiation after heat treatment at 850°C. We need to make more investigations

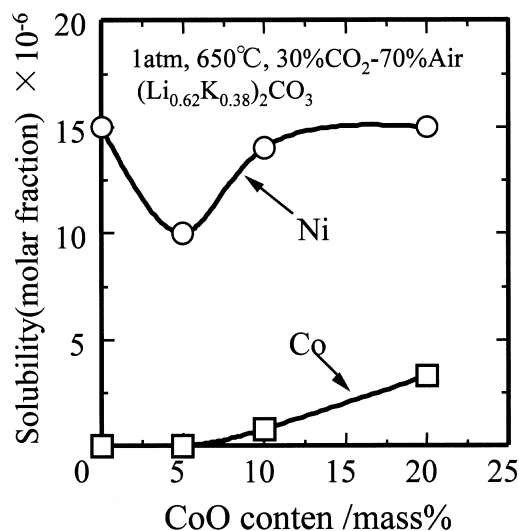


Fig. 5. Ni and Co solubility of the CoO/NiO composites as a function of CoO content.

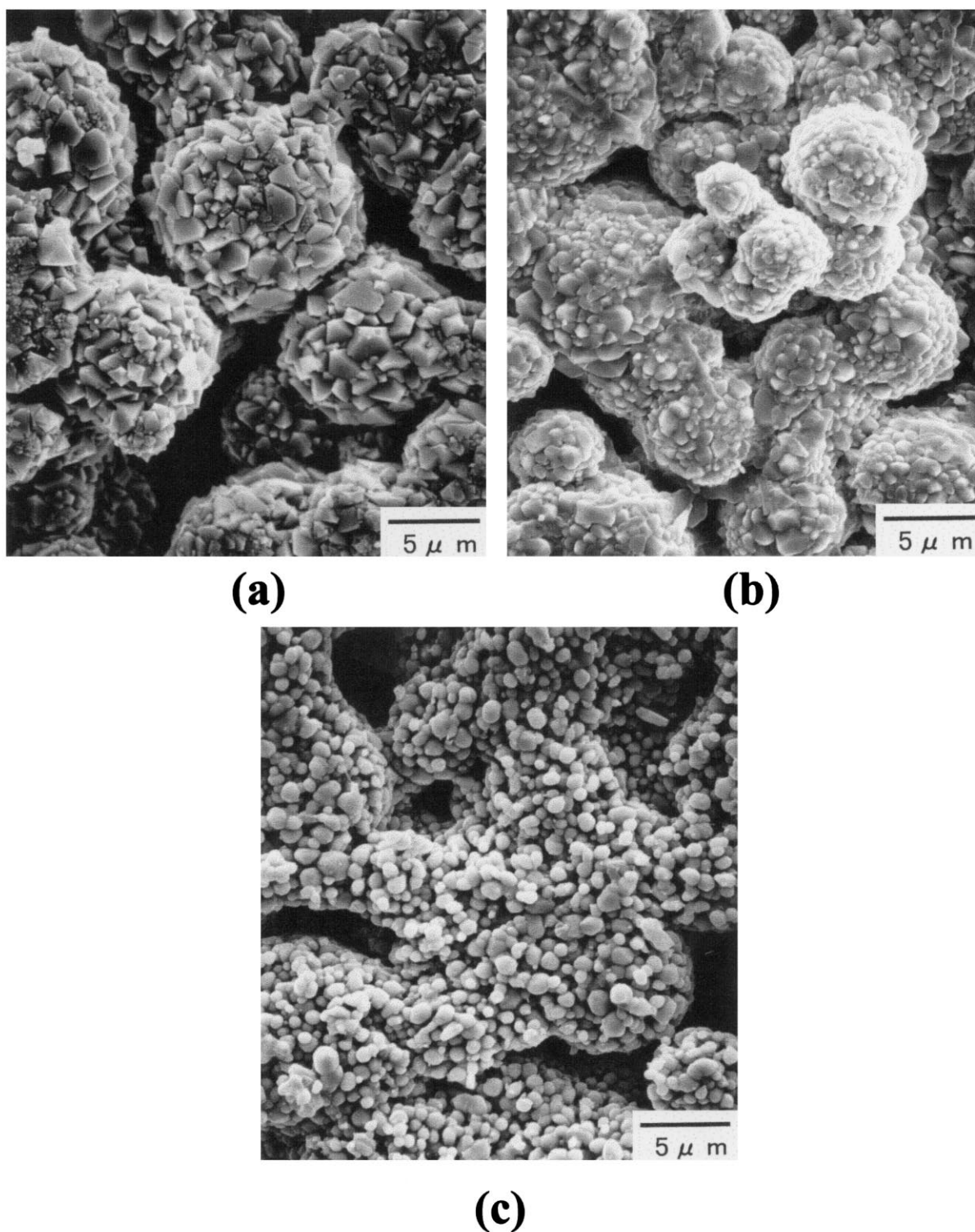


Fig. 6. SEM photographs of lithiated CoO/NiO composites obtained by lithiation into  $(\text{Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3$  melt at 650°C in 30%  $\text{CO}_2$ -70% air atmosphere: (a) 5 mass% CoO, (b) 10 mass% CoO, (c) 20 mass% CoO.

into the formation of the lithiated composite by this in-situ process and will report more detail later. However, Ni solubility of the lithiated 5 mass% CoO/NiO composite

by in-situ process was almost same as that of the 5 mass% CoO/NiO composite by lithiation after heat treatment at 850°C. We could confirm the improvement in the stability

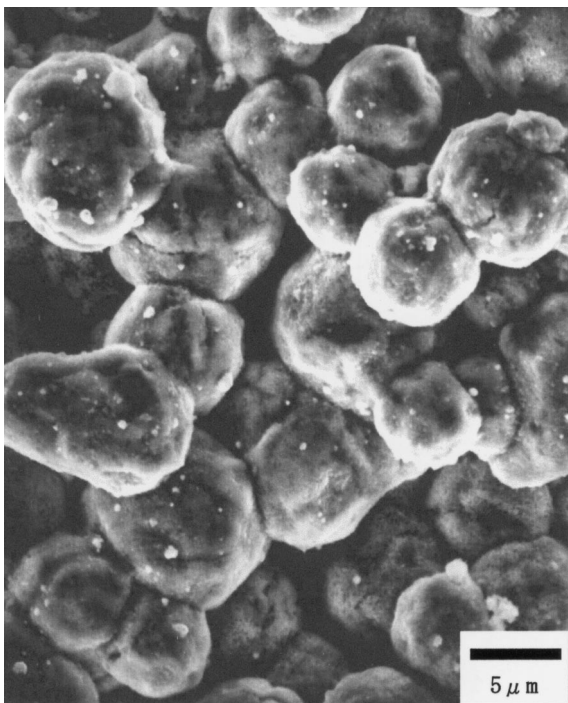


Fig. 7. SEM photographs of lithiated CoO/NiO composites obtained by in-situ oxidation and lithiation into  $(\text{Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3$  melt at  $650^\circ\text{C}$  in 30%  $\text{CO}_2$ –70% air atmosphere.

in the carbonate melt of the composite by this in-situ treatment.

#### 4. Conclusions

CoO/NiO cathodes with 5 to 20 mass% Co in the composite could be formed by using the CoO/Ni composite particles. As confirmed by SEM-EDAX, these composites consisted of NiO cores covered with an outer layer of Li(Co, Ni) oxide, where NiO grains are well connected. In the lithiated 5 mass% CoO/NiO composite, the stability in a carbonate melt was also improved in comparison with that of conventional NiO used for MCFCs. Moreover, the lithiated CoO/NiO composite was successfully formed by an in-situ oxidation and lithiation process. Finally, we thought that this composite cathode material consisting of

a NiO core covered with Li(Co, Ni) oxide could be adopted as the new cathode for MCFCs.

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