

## Performance of LiCoO<sub>2</sub>-coated NiO cathode under pressurized conditions

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### Abstract

The properties of LiCoO<sub>2</sub>-coated NiO cathodes prepared by the solution impregnation technique were investigated. The electrode performance of the LiCoO<sub>2</sub>-coated cathodes were comparable with that of the conventional NiO cathode at 1, 3, and 5 atm and the prepared cathodes showed no performance decay at least for the first 1000 h at pressurized conditions. The post-analysis revealed that the LiCoO<sub>2</sub>-coated cathodes were effective in suppressing NiO dissolution up to 51% at 1 atm and 50% at 3 atm. However, the suppression of the NiO dissolution was found to be much less effective (about 11% of suppression) at 5 atm. The number of impregnations applied, in other words, the amount of LiCoO<sub>2</sub> incorporated into the NiO cathode seemed to have no significant effect on suppressing the NiO dissolution. The Ni contents in the matrix after the 1000 h operations did not vary with increasing the LiCoO<sub>2</sub> amount in the NiO cathodes from 0.25–0.8 mol%. In the cell with the co-flow configuration, the highest Ni content in the matrix was found at the gas inlet side and the Ni content in the matrix decreased along the gas flow direction. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** LiCoO<sub>2</sub>-coated NiO cathodes; Ni dissolution; MCFC

### 1. Introduction

Recently, fuel cells have been studied intensively by many research groups because of their high efficiency and extremely low emissions. Among the many types of fuel cell, the molten carbonate fuel cell (MCFC) is one of the most promising types and it faces commercialization in a near future. However, the MCFC can not be commercialized without solving the durability problem. Although, it is widely agreed that the lifetime of the MCFC for commercialization should be over 40,000 h [1], no MCFC has been successful in reaching the lifetime target so far. Only the research group in the Osaka National Research Institute was successful in completing single cell operation for 40,000 h [2].

One of the major factors limiting the lifetime of the MCFC is the dissolution and subsequent precipitation of the NiO cathode in the carbonate electrolyte. The accumulation of the Ni precipitated in the matrix eventually short-circuits the cell causing deterioration of cell performance and durability [3]. In order to solve this problem, two methods have been employed. One is to make of the electrolyte composition more basic. The NiO cathode dissolution is known to follow

a mechanism of acid dissolution under the operating conditions of MCFC and thus, increasing the basicity of the electrolyte is expected to suppress NiO dissolution. Either the adoption of Li<sub>2</sub>CO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub> instead of Li<sub>2</sub>CO<sub>3</sub>/K<sub>2</sub>CO<sub>3</sub> [4,5] or the addition of alkaline earth metal containing ingredients, such as MgO and SrO, into the Li<sub>2</sub>CO<sub>3</sub>/K<sub>2</sub>CO<sub>3</sub> or the cathodes increases the basicity of the electrolyte [6,7]. However, there is a difficulty in the trade-off problems caused by enlargement, long-term stability and low cell performance to be overcome before the practical use of this solution.

The other method is to develop alternative cathode materials. Although many materials have been investigated [8,9], LiCoO<sub>2</sub> was once considered as the most promising alternative cathode material because of its extremely low solubility [10,11]. However, the LiCoO<sub>2</sub> cathode is considered to be impractical because enlargement of the electrode area beyond 1000 cm<sup>2</sup> looks almost impossible.

Recently, a new method of making a stabilized cathode by coating LiCoO<sub>2</sub> onto a conventional NiO cathode was introduced [12]. Since then, this novel cathode has been recognized as one of the more likely candidates to solve the problem of NiO dissolution. This is due to the low NiO solubility, the sufficient electronic conductivity and the possibility to use the same fabrication process as that of the NiO cathode. Various coating techniques, such as solution

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impregnation [13], sol–gel [14], and electroplating [15] have been applied to fabricate the  $\text{LiCoO}_2$ -coated cathodes. All  $\text{LiCoO}_2$ -coated cathodes, regardless of the coating methods, worked satisfactorily in terms of NiO dissolution and electrode performance at atmospheric pressure. However, the performance of the  $\text{LiCoO}_2$ -coated cathode at elevated pressure has been reported very little. In this study, therefore, single cells with the  $\text{LiCoO}_2$ -coated cathodes fabricated by the solution impregnation method are operated at elevated pressures up to 5 atm to investigate the properties of the novel cathodes.

## 2. Experimental

### 2.1. Preparation of the $\text{LiCoO}_2$ -coated cathode

The  $\text{LiCoO}_2$ -coated cathodes were prepared by the solution impregnation technique and the procedure is depicted in Fig. 1. The precursor solution was prepared by dissolution of lithium and cobalt hydroxide ( $\text{Li/Co}=1/1$  mol) into dilute acetic acid. The concentration of the salts in the solution was 0.25 mol/l. A tape-casted and sintered porous Ni plate was dipped into the precursor solution for a few seconds and then dried in air. The dip-coating and drying process was repeated

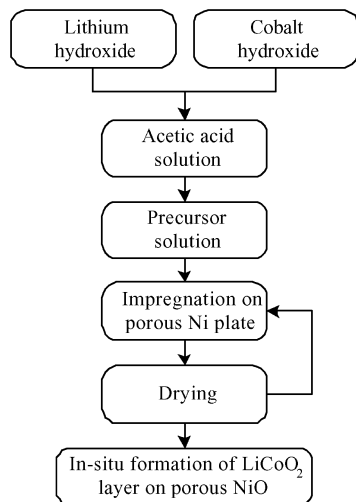


Fig. 1. Procedure for  $\text{LiCoO}_2$  coating on the porous NiO cathode.

until the desired amount of Li/Co was obtained. The amount of Co coated on the surface of the porous Ni plate was analyzed by the ICP/AA and the morphology of the coated Ni plate was characterized by the SEM. The details of the fabrication of the  $\text{LiCoO}_2$ -coated cathode are described elsewhere [13].

The Ni plate containing Co and Li salts was placed in the single cell frame with other components, such as a Ni–Cr anode and a  $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$  electrolyte. The single cell was heated up to 650 °C according to the predetermined heating schedule. During the heating process, it is expected that the porous Ni plate is oxidized and  $\text{LiCoO}_2$  is formed on the surface of the NiO cathode. The Ni content in the matrix and the distribution of the Ni precipitates after 1000 h operation were analyzed by AA and EPMA, respectively.

### 2.2. Operation of the single cell under the pressurized conditions

Single cells with an effective electrode area of 100 cm<sup>2</sup> were operated to evaluate the performance of cathodes under pressurized conditions. Fig. 2 shows the test station for the pressurized operation. The Ni–10%Cr anode and the 70:30 mol%  $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$  electrolyte were prepared according to in-house procedures. After a single cell finished the pretreatment schedule, the operating pressure was elevated to the desired level. Anode gas having  $\text{H}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in molar ratio of 72:18:10 was supplied at a flow rate equal to a  $\text{H}_2$  utilization of 0.4 at 150 mA/cm<sup>2</sup> current density. The cathode gas containing air and  $\text{CO}_2$  (70:30 in molar ratio) was fed at the flow rate of 0.4 utilization of  $\text{CO}_2$  at 150 mA/cm<sup>2</sup>. Single cells were operated continuously in the fixed

Table 1  
Single cell operating conditions

Item	Operating conditions
Effective electrode area (cm <sup>2</sup> )	10 × 10
Anode	Ni–Cr
Electrolyte	$\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$
Temperature (°C)	650
Pressure (atm)	Up to 5
Gas utilization (mA/cm <sup>2</sup> )	0.4 at 150
Anode gas	$\text{H}_2/\text{CO}_2/\text{H}_2\text{O} = 72/18/10$
Cathode gas	$\text{Air}/\text{CO}_2 = 70/30$

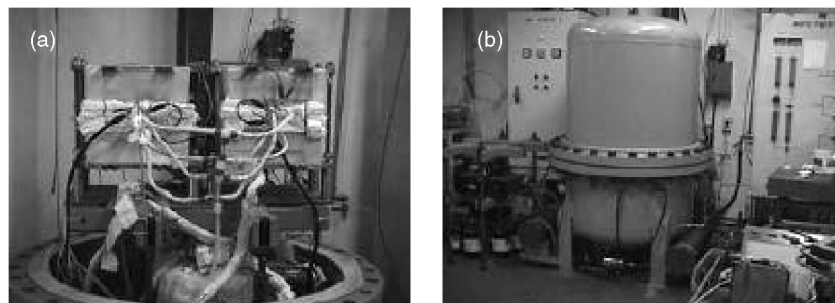


Fig. 2. Photographs of a test station for pressurized MCFC single cells.

current mode,  $150 \text{ mA/cm}^2$ , for 1000 h. Table 1 summarizes the details of the single cell operating conditions.

### 3. Results and discussion

#### 3.1. Composition and morphology of the cathode

Fig. 3 shows the morphology change of the porous Ni plate before and after the solution impregnation. As shown in Fig. 3(a), Ni particles of 2–3  $\mu\text{m}$  in diameter formed the skeleton of the porous Ni plate and various sizes of the pore were observed within the skeleton. When coated once, the Li/Co salts were mostly placed at the neck between the Ni particles (see A in Fig. 3(b)) and at the mouth of the small pores (see B in Fig. 3(b)). When coated three times or more, Ni particles were observed to be fully covered with the Li/Co salts (Fig. 3(c)) and the large pores of the five time coated sample began to be filled with the Li/Co salts (see Fig. 3(d)).

The amounts of Co in the Ni plates were analyzed by AA and the results are presented in Table 2. C1, C2 and C3 denote the number of solution impregnations, i.e. once, three times and five times, respectively. The amount of Co gained during the first impregnation was 0.25–0.3 mol%. After the first impregnation, the Co gain per impregnation was measured as about 0.13% and remained rather constant for the five-time impregnation.

#### 3.2. Cell performance

The performance of the single cells with different cathodes having a Co content from 0–0.8 mol%, were compared

Table 2  
Co contents (mol%) in the Ni plate after coating and drying process analyzed by AA

Number of coatings	Co contents in Ni plates (mol%)
C1	0.25–0.32
C3	0.50–0.60
C5	0.78–0.85

to check the effect of Co addition to the cathodes on the cell performance. As clearly seen in Fig. 4, Co addition up to 0.8 mol% was observed to have no effect on the cell performance throughout the entire experimental range. The cell performance behavior of the single cells coincided with each other even when the operating pressure increased from 1–5 atm. Also, the long-term behavior of the single cells with Co in cathode was compatible with that of the single cells with the conventional NiO cathodes.

It may be too early, without having results from longer operation than 1000 h, to conclude that the  $\text{LiCoO}_2$ -coated cathode by the solution impregnation is as good as the conventional NiO cathode. However, this  $\text{LiCoO}_2$ -coated cathode seemed to be superior to other configurations, such as  $\text{LiCoO}_2$  cathode and MgO-added cathode, in terms of the electrochemical activity.

#### 3.3. Ni precipitated in the matrices after 1000 h operation

After an 1000 h operation, the amount of Ni precipitated in the matrix of every single cell was analyzed by AA and the results were plotted against the operating pressures in

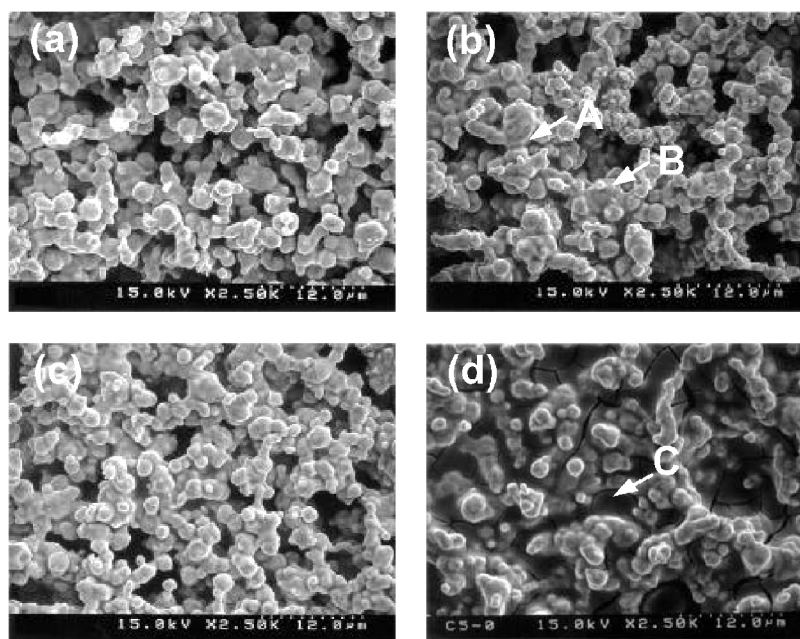


Fig. 3. Microphotographs of porous Ni plate after coating and drying process; (a) pure Ni, (b) one time coating, (c) three time coatings, and (d) five time coatings.

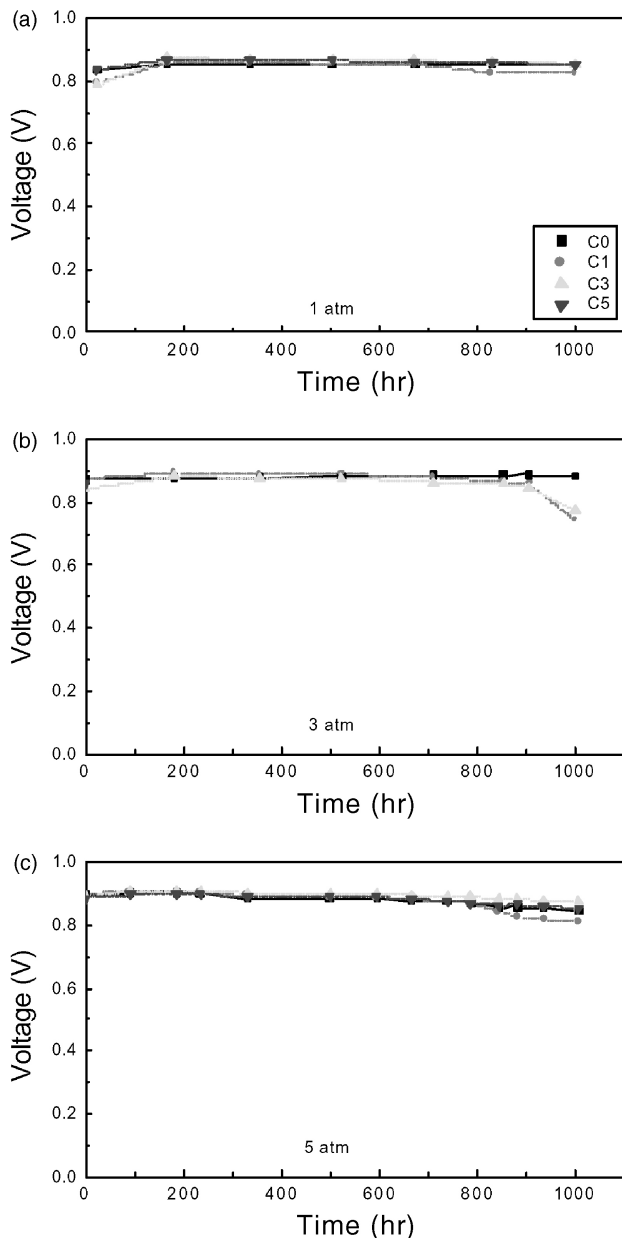
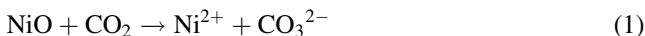


Fig. 4. Performances of single cells using coated cathodes operated at (a) 1, (b) 3, and (c) 5 atm.

Fig. 5. The amount of Ni in the matrices of the cells using the conventional NiO increased with operating pressure. This is due to the well known acid dissolution mechanism and can be expressed as:



The NiO dissolution follows the acid dissolution mechanism above 0.001 atm in a  $\text{CO}_2$  partial pressure. As reaction (1) implies, the higher the  $\text{CO}_2$  partial pressure becomes, the more NiO tends to dissolve out. The amounts of Ni precipitates in the matrix after 1000 h operation of the single cells with the conventional NiO cathode were measured as 3.2, 5.2, and 8.6 wt.% at 1, 3, and 5 atm, respectively.

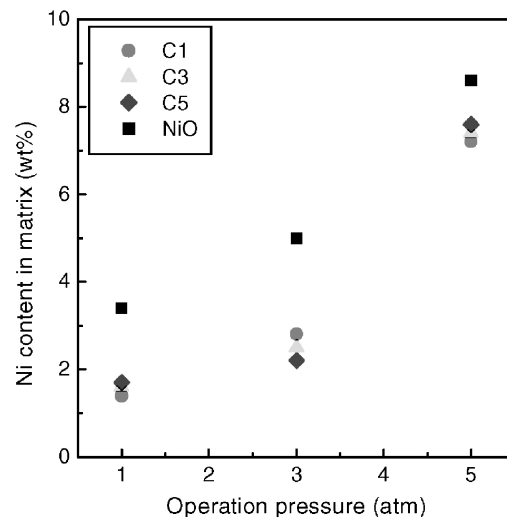


Fig. 5. Variation of the Ni amounts in the matrices with the operating pressure after 10:00 h operation.

When the  $\text{LiCoO}_2$ -coated cathodes were used, the amount of Ni precipitates in matrix were reduced to 1.4 wt.% at 1 atm and 2.9 wt.% at 3 atm which correspond to reduction of 55 and 50%, respectively. When the results from the operation at 5 atm were compared, the reduction of Ni precipitates in matrix was much less than that obtained at lower operating pressures. Ni contents in the matrix from the operations with the  $\text{LiCoO}_2$ -coated cathodes were as high as 7.4 wt.%, showing a mere 11% reduction. The reason for the decreasing effect of the  $\text{LiCoO}_2$ -coated cathode on suppressing NiO dissolution with increasing  $\text{CO}_2$  partial pressure, still remains to be solved. The comprehensive understanding of the way  $\text{LiCoO}_2$  works in the NiO cathode, is required to explain this phenomenon.

Fig. 6 which depicts the relationship between the amount of  $\text{LiCoO}_2$  incorporated into NiO and the amount of Ni

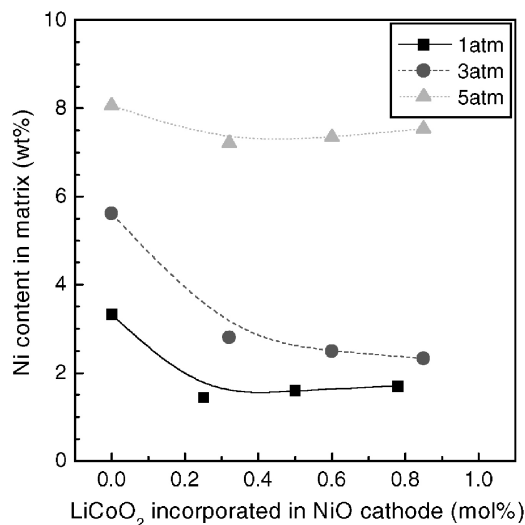


Fig. 6. Variation of the Ni amounts in the matrices with the  $\text{LiCoO}_2$  amounts in the cathodes after 10:00 h operation.

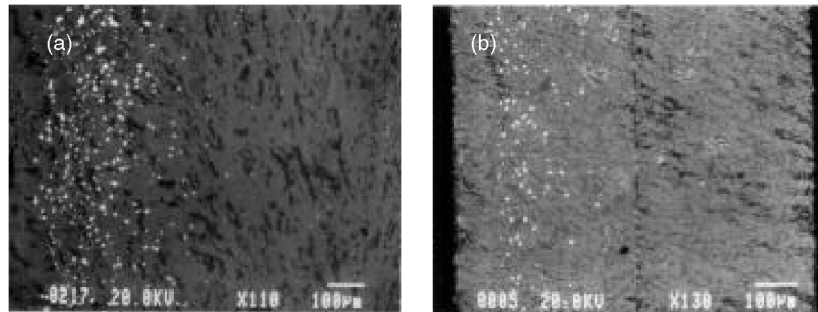


Fig. 7. Ni distributions in the matrices of the single cells using (a) NiO, (b) C3 cathode after the 10:00 h operation at 1 atm observed by EPMA.

precipitated in the matrix, indicates that  $\text{LiCoO}_2$  in cathode would suppress the NiO dissolution in a chemical way, not in a physical way. Otherwise, the Ni content in the matrix is likely to decrease as the amount of  $\text{LiCoO}_2$  incorporated in NiO increases. On the contrary, the Ni content in the matrix quickly reached a state of saturation after the  $\text{LiCoO}_2$  in cathode passed over 0.2 mol%. There is some speculation on the role of Co in suppressing NiO dissolution: Co incorporated into a NiO cathode makes the bond between Ni and oxygen stronger, consequently dissolution of NiO becomes more difficult. Further investigation is necessary to clearly explain the complicated behavior of  $\text{LiCoO}_2$ -coated cathode.

#### 3.4. Ni distribution in the matrices

After 1000 h of operation, the cross-sections of the matrices were analyzed by EPMA in order to investigate the Ni distribution in the matrices. The EPMA pictures of the matrices of the cells operated at 1, 3, and 5 atm are presented

in Figs. 7–9, respectively. The white dots in the pictures represent the Ni precipitates. The left hand side of the pictures is the cathode side and the right hand side is the anode side.

The EPMA pictures show the clear reduction of Ni precipitates in the matrices of the single cells using the  $\text{LiCoO}_2$ -coated cathodes. However, it was difficult to find the change in the amount of Ni precipitates with the amount of  $\text{LiCoO}_2$  incorporated in the NiO.

Most of the Ni existed on the cathode side of the matrices forming a narrow band and little Ni could be found in the rest of the structure. In the MCFC system, Ni precipitation is known to take place in three sub-steps, NiO dissolution into the carbonate, diffusion of Ni ions toward the anode side and reduction of Ni ions and precipitation. These sub-steps depend upon each other in a complicated manner. Thus, it is not easy to analyze the Ni precipitation mechanism. However, from the Ni band formed on the cathode side, it can be inferred that the diffusion of the Ni ions through the matrix is the rate-limiting step. The higher Ni density of the

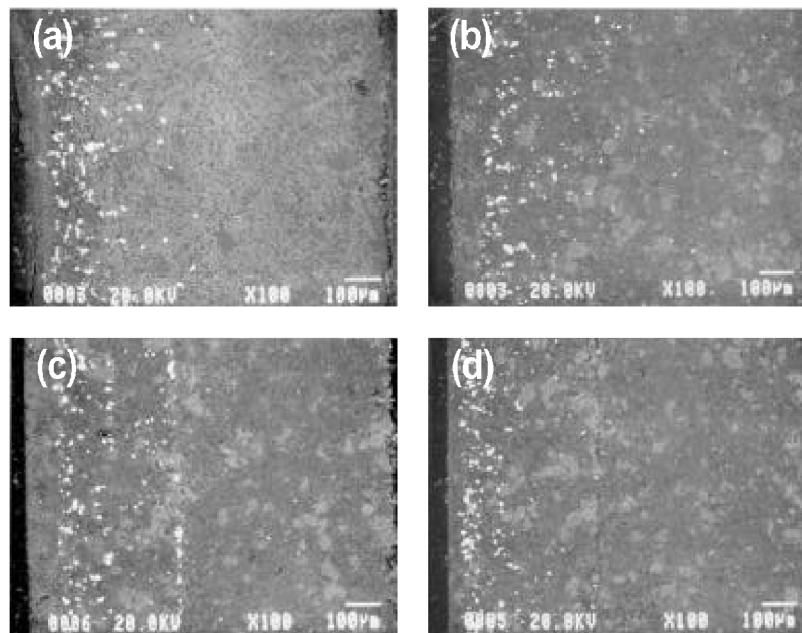


Fig. 8. Ni distributions in the matrices of the single cells using (a) NiO, (b) C1, (c) C3, and (d) C5 cathode after 10:00 h operation at 3 atm observed by EPMA.

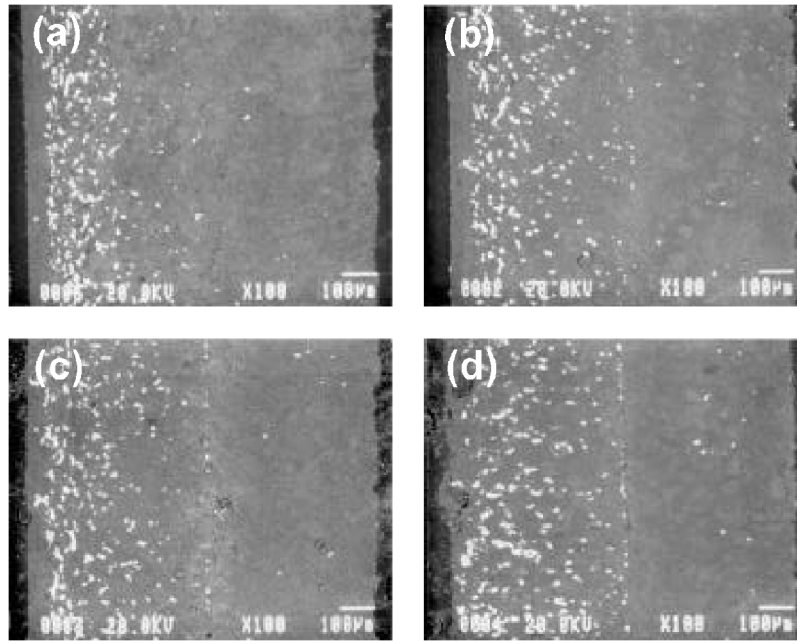


Fig. 9. Ni distributions in the matrices of the single cells using (a) NiO, (b) C1, (c) C3, and (d) C5 cathodes after the 10:00 h operation at 5 atm observed by EPMA.

band with increasing operating pressure could be another indication that is the Ni ion diffusion which would be the rate-limiting step.

### 3.5. Effect of gas flow direction

In the MCFC, the gas compositions on both anode and cathode sides vary along the gas flow direction. This is due to the electrochemical reaction that consumes the oxidant and the fuel gases. Thus, concentration profiles exist along the gas flow direction. In this study, the cell was operated in the co-flow configuration resulting in monotonically decaying  $H_2$  and  $CO_2$  concentration profiles along the gas flow direction.

In order to verify the effect of the gas concentration profile on NiO dissolution and Ni precipitation, pieces of the matrices were taken from the gas inlet, the center of the cell and the gas outlet. Table 3 summarizes the Ni content in the matrix after 1000 h of operation at 5 atm. The highest Ni content in the matrix was found at the gas inlet and the Ni composition decreased along the gas flow direction. This can be confirmed by the EPMA analysis shown in Fig. 10. The EPMA pictures in Fig. 10 shows the pieces of matrix from the gas inlet, the center and the gas outlet of the same single

Table 3

Amount of Ni (mol%) precipitated at gas inlet side, center of the cell and gas outlet side in the matrix of the cell operated at 5 atm

	NiO	C1	C3	C5
Gas inlet	8.63	8.40	7.82	8.87
Center	8.60	7.17	7.39	7.55
Gas outlet	6.94	6.05	6.85	6.30

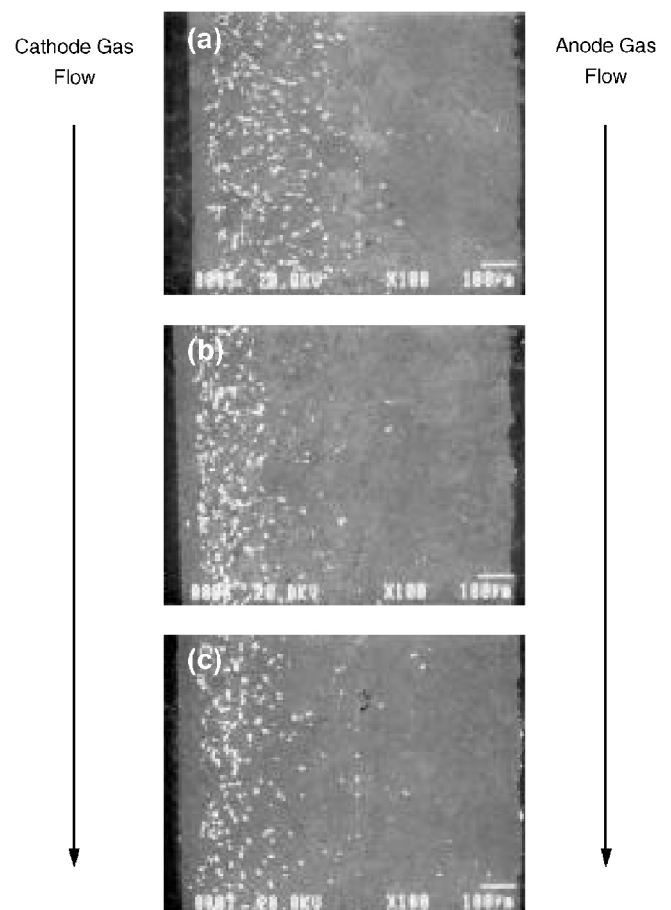


Fig. 10. The variation of the Ni concentration along the gas flow direction in the matrix of the single cell using NiO cathode after the 10:00 h operation at 5 atm observed by EPMA: the matrix at the (a) gas input, (b) center, and (c) gas output.

cell. It is clearly shown that the Ni content in the matrix decreased along the gas flow direction. The higher CO<sub>2</sub> partial pressure at the gas inlet was from the acidic NiO dissolution mechanism, as predicted.

#### 4. Conclusions

LiCoO<sub>2</sub>-coated NiO cathodes were prepared by the solution impregnation technique. Single cell tests were carried out at 1, 3, and 5 atm in order to investigate the performance of the prepared cathodes. The electrode performances of the LiCoO<sub>2</sub>-coated cathodes were comparable with that of the conventional NiO cathode in terms of electrochemical activity for 1000 h. Although the suppression mechanism of NiO dissolution is not clear yet, the LiCoO<sub>2</sub>-coated cathodes did suppress the NiO dissolution by about 50% at 1 and 3 atm. However, the suppression of the NiO dissolution was much less effective, only by 15%, at 5 atm. Another interesting finding is that NiO dissolution was independent of the amount of LiCoO<sub>2</sub> incorporated into the NiO cathode. Beyond 0.25 mol% of LiCoO<sub>2</sub> in NiO cathode, no additional reduction in NiO dissolution was observed. Due to the CO<sub>2</sub> concentration profile along the gas flow direction, the highest Ni content in the matrix was found at the gas inlet and the Ni composition decreased along the gas flow direction.

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