A stabilized NiO cathode prepared by sol-impregnation of LiCoO$_2$ precursors for molten carbonate fuel cells

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Abstract

Layers of LiCoO$_2$ were formed on the internal surface of a porous NiO cathode to reduce the rate of NiO dissolution into the molten carbonate. A sol-impregnation technique assisted by acrylic acid (AA) was used to deposit gel precursors of LiCoO$_2$ on the pore surface of the Ni plate. Thermal treatment of the gel-coated cathode above 400 °C produced LiCoO$_2$ layers on the porous cathode. A number of bench-scale single cells were fabricated with LiCoO$_2$-coated cathodes and the cell performance was examined at atmospheric pressure for 1000 h. With the increase in the LiCoO$_2$ content in the cathode, the initial cell voltage decreased, but the cell performance gradually improved during the cell test. It was found from symmetric cathode cell test that the cathode was initially flooded with electrolyte, but redistribution of the electrolyte took place during the test and cell performance became comparable to that of a conventional NiO cathode. The amount of Ni precipitated in the matrix during the cell operation for 1000 h was significantly reduced by the LiCoO$_2$ coating. For instance, coating 5 mol% of LiCoO$_2$ in the cathode led to a 56% reduction of Ni precipitation in the matrix. The results obtained in this study strongly suggest that LiCoO$_2$ layers formed on the internal surface of the porous NiO cathode effectively suppress the rate of NiO dissolution for 1000 h.
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1. Introduction

The molten carbonate fuel cell (MCFC) is one of the most promising power generation devices in the near future owing to its high efficiency and low emissions. The recent demonstration of a 250 kW MCFC power plant shows that an electrical efficiency of about 50% can be achieved with emission levels better than the US Clean Air Standard [1]. The overall efficiency of the MCFC system combined with a gas turbine is projected to be near 70% [2]. Practical application of the MCFC, however, will not be realized until some technical problems such as electrolyte loss, instability of electrodes and corrosion of the separator are resolved [3]. For commercialization, the MCFC should show stable performance for over 40,000 h [4].

Dissolution of the state-of-the-art NiO cathode into the electrolyte and subsequent precipitation of Ni in the matrix is one of major factors limiting the lifetime of MCFC. The growth of Ni precipitates in the matrix results eventually in electric shorting between cathode and anode [5]. In order to solve this problem, alternative cathode materials have been explored. Among many materials investigated, LiCoO$_2$ was considered as the most promising alternative cathode material due to its lower solubility in molten carbonate and comparable electrochemical performance compared with NiO [6–8]. However, problems in scale-up of the electrode area and relatively high cost of Co restricted the practical utilization of LiCoO$_2$ cathode.

Recently, a number of attempts were made to cover the pore surface of NiO cathodes with layers of stable materials to alleviate NiO dissolution [9–16]. The stable materials coated on NiO surface encompass mostly LiCoO$_2$ or LiCo$_{1-x}$Ni$_x$O$_2$, but CeO$_2$ [11] and oxidized Ni–Nb alloy [14] were also tried. The coated layers were expected to reduce the surface area of NiO exposed to the carbonate melts, thereby reducing the rate of NiO dissolution and improving the cell life. These stabilized NiO cathodes have been prepared by a variety of coating techniques, such as a sol–gel [9], a solution impregnation [10,11], electroplating [12], electroless deposition [13], electrochemical reduction [14], and mechanical coating [15,16]. All of these stabilized

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NiO cathodes, regardless of the techniques, yielded lower solubility in molten carbonate than untreated NiO cathodes. However, application of such stabilized NiO cathodes in real MCFCs and analysis of Ni deposited in the matrix have not been reported widely.

In this study, we performed a number of bench-scale cell tests with $LiCoO_2$-coated cathodes. The cathode was fabricated by a sol-impregnation technique. Previously, a similar technique was used to fabricate a stabilized cathode with polyvinyl alcohol (PVA) as a chelating agent [9]. In this study, acrylic acid (AA) was adopted as a chelating agent. The sol–gel techniques assisted by various acids were explored in our laboratory to synthesize ultrafine $LiCoO_2$ powders with enhanced sintering behavior [17,18]. Performance of a single cell containing $LiCoO_2$-coated cathode was investigated at atmospheric pressure with special attention paid to the Ni precipitated in the matrix after 1000 h of cell operation.

2. Experimental

2.1. Preparation of $LiCoO_2$-coated NiO cathode

The $LiCoO_2$-coated NiO cathode was prepared by a sol-impregnation technique and the procedure is illustrated in Fig. 1. A stoichiometric amount of lithium acetate and cobalt acetate was dissolved into distilled water and mixed well
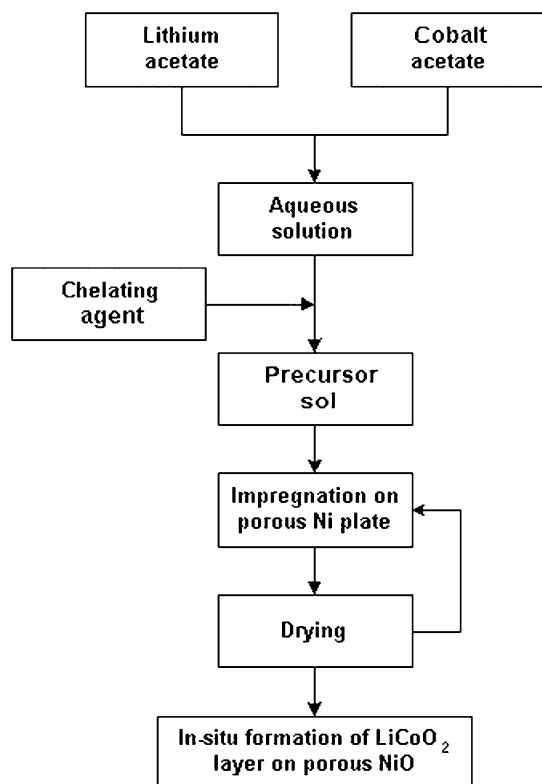

Fig. 1. Procedure for $LiCoO_2$ coating on the porous NiO cathode.

with an aqueous solution of AA. AA was used as a chelating agent to prevent segregation of metal components. The molar ratio of AA:total metal ions in the solution was 2:1. The resultant solution was then heated at 80 °C with stirring until a transparent pink sol was produced.

A porous Ni plate was fabricated by tape casting of Ni slurry and sintering of the green-sheet at 700 °C under a reducing atmosphere. The mean pore diameter, porosity, and BET surface area of the porous Ni plate were 8–10 μm, 70–80%, and 0.3–0.4 m^2/g, respectively. A vacuum impregnation technique was used to fill the pores of the Ni plate with the sol because of the relatively high viscosity of the sol. The porous Ni plate was evacuated in a chamber for a few minutes and then the sol was introduced into the chamber until the porous Ni plate was immersed in the sol. After a few minutes of immersion in the sol, the Ni plate was dried to form a gel precursor on its internal pore surface. The impregnation–drying process was repeated until a desired amount of precursor was coated in the porous Ni plate. The amount of coating was expressed in terms of the equivalent mole percent of $LiCoO_2$ contained in the NiO cathode. The porous Ni plate coated with the gel precursors was used as it was in preparing a single cell or a symmetric cathode cell without any further treatment.

2.2. Cell fabrication and test

A bench-scale molten carbonate fuel cell with 10 cm × 10 cm electrode area was prepared using a Ni–10 wt.% Cr anode, a porous Ni cathode coated with gel precursors, a γ-$LiAlO_2$ matrix and a Li/K carbonate electrolyte with a $Li_2(CO)_3$:$K_2(CO)_3$ molar ratio of 70:30. During the start-up process of the cell, it was expected that the water and other volatile species in the gel precursors were removed and the porous Ni was oxidized to NiO, forming $LiCoO_2$ layers on the pore surface of the NiO cathode.

Performance of the single cell was evaluated at 650 °C and 1 atmospheric pressure for 1000 h. A gas mixture of 72% H_2–18% CO_2–10% H_2O was supplied to the anode chamber and a gas mixture of 70% air–30% CO_2 was introduced to the cathode chamber. The total flow rate of the gas was equivalent to a gas utilization of 40% at a current density of 150 mA/cm^2.

In addition to the single cell, a symmetric cathode cell with an electrode area of 2 cm × 2 cm was fabricated and the impedance of the cell was analyzed to investigate the effect of the $LiCoO_2$ coating on cathode polarization. The cell consisted of an electrolyte matrix with two identical cathodes. A cathode gas mixture of 70% air–30% CO_2 was introduced to either side of the cell at the same flow rate. Impedance spectra were measured at open circuit potential in the frequency range of 50 mHz–70 MHz using a frequency response analyzer (Solatron 1260) and an electrochemical interface (Solatron 1287). The amplitude of the applied ac voltage was 10 mV to assure the linearity and symmetry of the system.

2.3. Characterization of the cathode and the matrix

Thermogravimetric analysis/differential scanning calorimetry (TGA/DSC, MAC Science TG–DTA 20000) were performed to investigate the thermal behavior of the gel precursors and the porous Ni cathode coated with gel precursors. TGA/DSC were carried out at a scan rate of 10 °C/min under air atmosphere. In order to confirm the formation of $LiCoO_2$ crystalline phase on the internal surface of a porous cathode, X-ray diffraction (XRD, RIGAKU Rint/DMAX-2000) was used after the sample was calcined at various temperatures for 2 h under air flow. The morphology of the cathode coated with $LiCoO_2$ gel precursors was examined by scanning electron microscopy (SEM, Hitachi S-4200). The porosity of the cathode after 1000 h cell operation was measured by Archimedes method (ASTM C378-88). The amount and distribution of Ni deposited in the matrix after 1000 h cell operation were analyzed by atomic absorption spectroscopy (Varian Spertra A 800) and electron microprobe analysis (EMPA, 5373 Link), respectively.

3. Results and discussion

3.1. Characterization of the cathode coated with $LiCoO_2$ precursors

DSC and TGA results of the gel precursors are shown in Fig. 2a and b, respectively. The weight loss of the gel precursors terminated near 520 °C and two discrete weight loss regions occurred at 20–240 and 240–520 °C. The weight loss from 20 to 240 °C corresponds to the removal of water in the gel precursors, whereas the weight loss in the temperature range of 240–520 °C is associated with the decomposition of inorganic and organic constituents in the gel precursors. The exothermic peaks in the DSC curve at 280 and 490 °C are due to the decomposition of acetates and combustion of AA, respectively. Fig. 2c shows the TGA result of the porous Ni plate coated with the gel precursors. The weight of the material decreased up to 520 °C that is similar to the result of the gel precursors. The weight gain occurred at temperatures higher than 520 °C is due to the oxidation of Ni.

Fig. 3 shows the XRD patterns of the gel-derived materials calcined at various temperatures for 2 h in air atmosphere. For the material calcined at 400 °C, impurity peaks as well as the $LiCoO_2$ phase were observed. But a significant amount of $LiCoO_2$ phase were detected when the material was calcined at 500 °C. The calcination of the material at 600 °C led to the formation of the single phase of $LiCoO_2$. The TGA and XRD results strongly suggest that in situ treatment of the porous Ni plate coated with gel precursors during the start-up process of the cell may result in the formation of a $LiCoO_2$ layer on the surface of NiO cathode.

Fig. 4 shows SEM images of porous Ni cathodes coated with gel precursors of $LiCoO_2$. Sol-impregnation technique produced layers of gel precursors completely covered on the
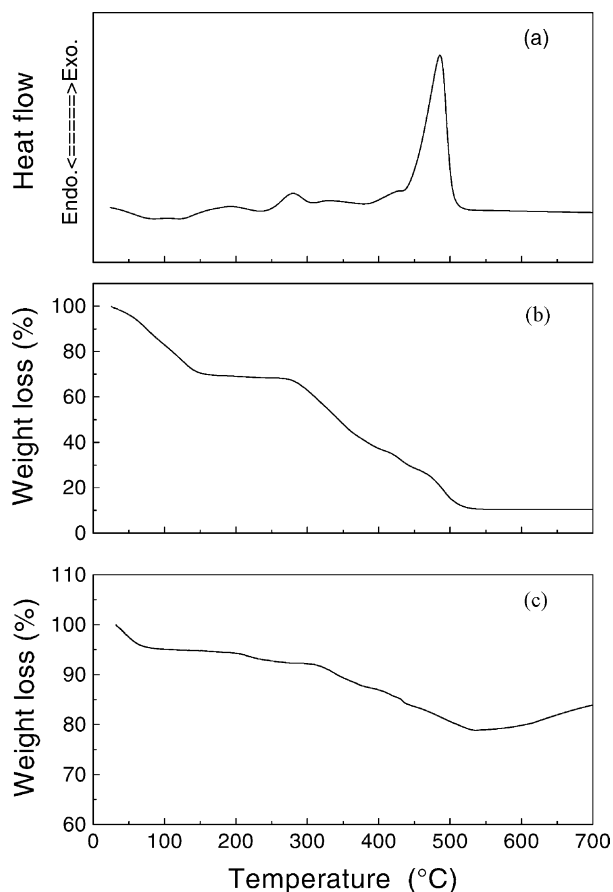

Fig. 2. Thermal analysis of gel precursors and the cathode: (a) DSC of gel precursors, (b) TGA of gel precursors, and (c) TGA of a porous Ni cathode coated with gel precursors.
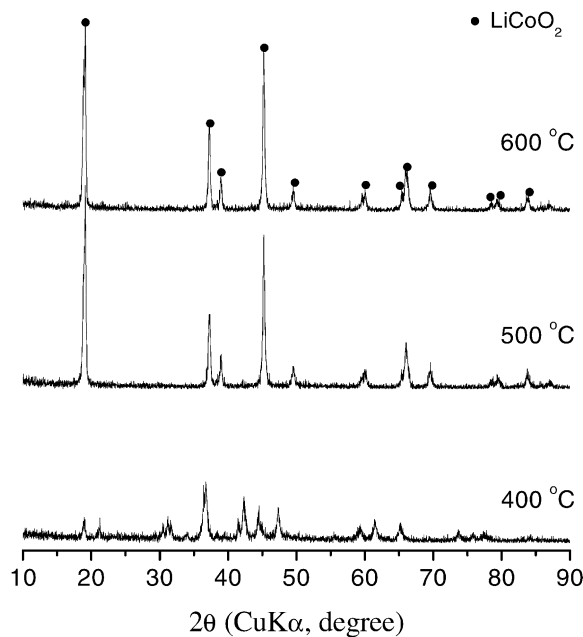

Fig. 3. XRD patterns of the $LiCoO_2$-coated NiO cathode calcined at various temperatures.
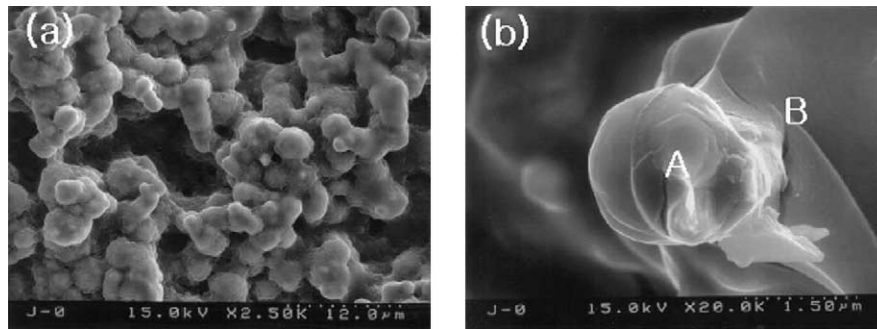
Fig. 4. SEM images of the porous cathodes coated with $LiCoO_2$ precursors (a and b).

internal surface of porous Ni as shown in Fig. 4a. The SEM images of the fractured materials are shown in Fig. 4b with higher magnification. In this SEM image, 'A' denotes the location of the fractured Ni skeleton and 'B' denotes the internal surface of the cathode covered with gel precursors. EPMA of the materials reveals that only Ni exists in location 'A', whereas Co is also observed in location 'B'. Moreover, the distribution of Co on the surface of the cathode was found to be relatively uniform. Although Li could not be analyzed by EPMA, it can be inferred from the EPMA result that precursors with uniform composition is deposited on the surface of porous Ni plate.

Fig. 5 shows XRD patterns of cathodes coated with $LiCoO_2$ gel precursors and calcined at various temperatures. When the cathode was calcined above 500 °C, XRD peaks corresponding to the (0 0 3) and (1 0 4) planes of $LiCoO_2$ was observed at 19 and 45°, respectively. The result of Fig. 5 strongly indicates that the gel precursor deposited on the skeleton of porous Ni plate can be converted to $LiCoO_2$ during the pretreatment of a single cell to operating temperature of 650 °C.
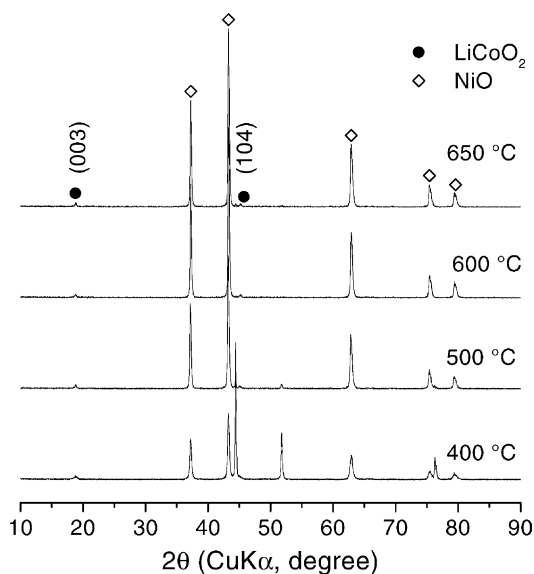
3.2. Cell performance

Fig. 6 shows the performance of single cells fabricated with NiO cathodes coated with $LiCoO_2$ precursors ($LiCoO_2$-coated NiO cathode) during 1000 h cell operation. A standard single cells fabricated with the NiO cathode showed an average cell voltage of 0.85 V at a current density of 150 mA/cm^2 and at a gas utilization of 0.4 throughout the operation. Performance of a single cell prepared with the $LiCoO_2$-coated NiO cathode was close to that of the standard cell when less than 1 mol% of $LiCoO_2$ was coated on the NiO cathode. As the $LiCoO_2$ content in the cathode increased above 1 mol%, the cell performance became lower, showing an initial voltage of 0.6–0.8 V depending on the amount of $LiCoO_2$ in the cathode. The cell performance gradually improved, however, during the cell operation, showing a voltage higher than 0.8 V after 200 h of cell operation and maintained its performance without significant performance degradation for 1000 h except for the cell fabricated with cathode coated with 8 mol% $LiCoO_2$. The performance of this cell increased continuously during
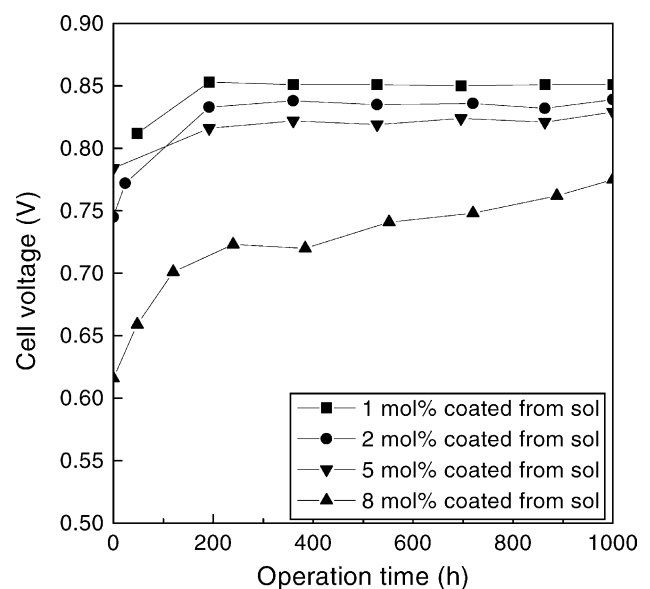

Fig. 5. XRD patterns of the $LiCoO_2$-coated cathode calcined at various temperatures.

Fig. 6. Performance of single cells at a current density of 150 mA/cm^2 fabricated with $LiCoO_2$-coated NiO cathodes.
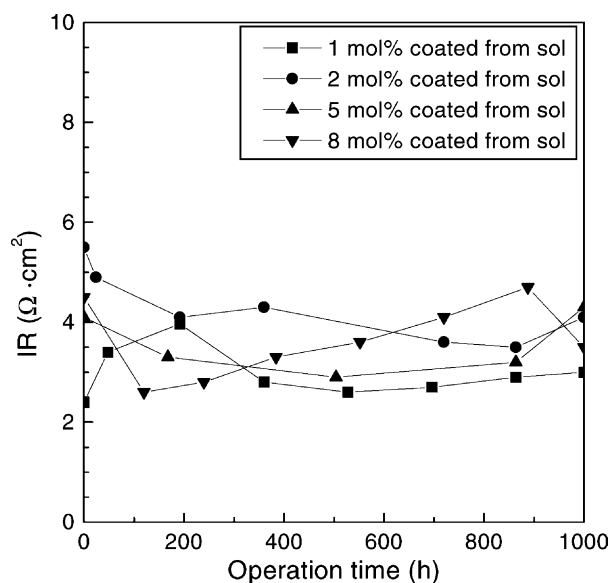
Fig. 7. Internal resistance of single cells fabricated with LiCoO$_2$-coated NiO cathodes.

Fig. 8. Impedance spectra obtained from symmetric cells prepared with various cathodes.

1000 h cell operation. There are little difference in internal resistance of cells irrespective of the amount of LiCoO$_2$ coating in the cathode as shown in Fig. 7.

The initial low voltage exhibited by the cell with LiCoO$_2$-coated cathode seems to be due to the flooding of electrolyte in the cathode side caused by the coated LiCoO$_2$ layer. As the amount of deposited LiCoO$_2$ increases, the pore size of NiO may decrease, absorbing more electrolyte because of the increase of capillary force that may lead to the flooding of cathode. To clarify the relatively low performance of the cell with LiCoO$_2$-coated NiO cathode, a symmetric cathode cell was fabricated to obtain impedance spectrum at open circuit potential. Fig. 8 shows the impedance spectra obtained from symmetric cells prepared with a number of cathodes: a LiCoO$_2$-coated NiO cathode, a standard NiO cathode and an NiO cathode flooded with electrolyte. The impedance spectra consisted of at least two arcs and the size of each arc increased with increasing the content of LiCoO$_2$ in the cathode. That is, the cathode polarization increased in proportional to the amount of coated LiCoO$_2$. The impedance spectra of the cell prepared with a cathode containing 5 mol% LiCoO$_2$ is similar to that with the flooded NiO, suggesting that the LiCoO$_2$-coated cathode is flooded with electrolyte at the initial stage of the cell operation.

Fig. 9 shows the evolution of impedance spectra with operating time for the cell fabricated with cathode having 3 mol% LiCoO$_2$. The size of the impedance arcs decreased significantly in 100–200 h and then the arc shape did not change very much. Since the impedance spectra become close to that of a standard NiO cathode, it can be inferred that the carbonate electrolyte which initially filled the pores of LiCoO$_2$-coated cathode is redistributed in 100–200 h, reducing the cathode polarization and improving of the cell performance gradually as shown in Fig. 7. In other words,
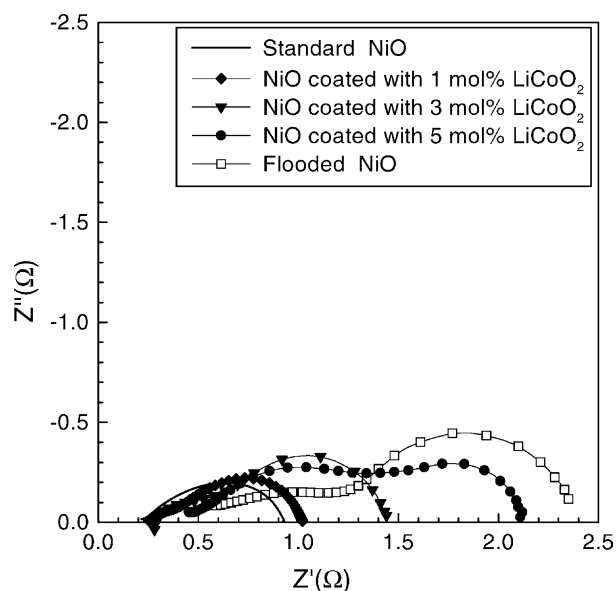
the initial induction period where the single cell performance increases gradually is attributed to the redistribution of electrolyte in the cathode.

3.3. Result from post-test analysis

Porosity of the cathode was measured after the 1000 h cell test and the results are shown in Fig. 10. The porosity of the cathode decreases with increasing the amount of the LiCoO$_2$ coating in the cathode, indicating that there may exist LiCoO$_2$ layers on the internal surface of NiO cathode after 1000 h cell operation. Since the stability of the LiCoO$_2$ layers is critical in
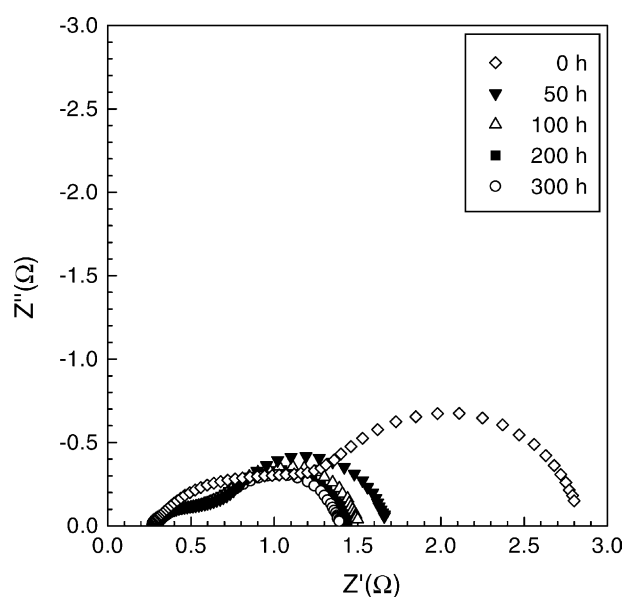

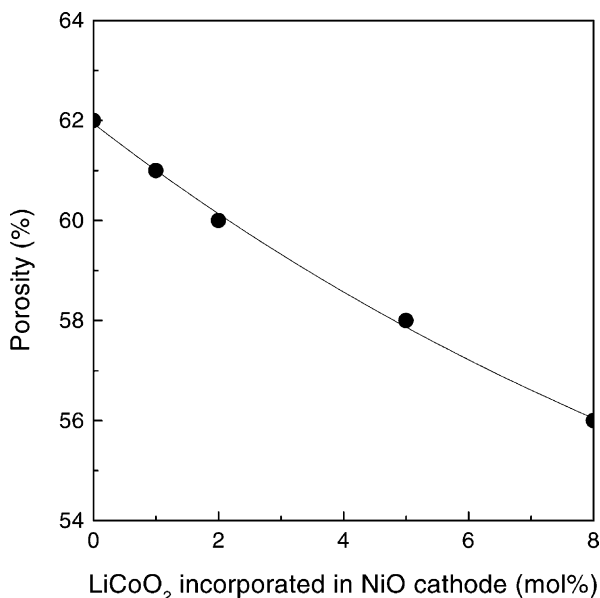Fig. 9. Evolution of impedance spectra with operation time for the cell with 3 mol% LiCoO$_2$-coated NiO cathode.

Fig. 10. Effect of LiCoO$_2$ coating on the porosity of the cathode after single cell operation of 1000 h.
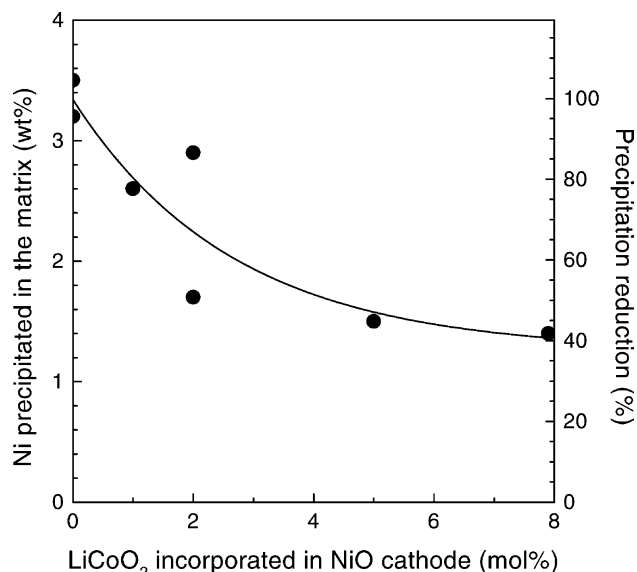
Fig. 11. Effect of LiCoO$_2$ coating on reduction of Ni precipitates in the matrix after single cell operation of 1000 h.
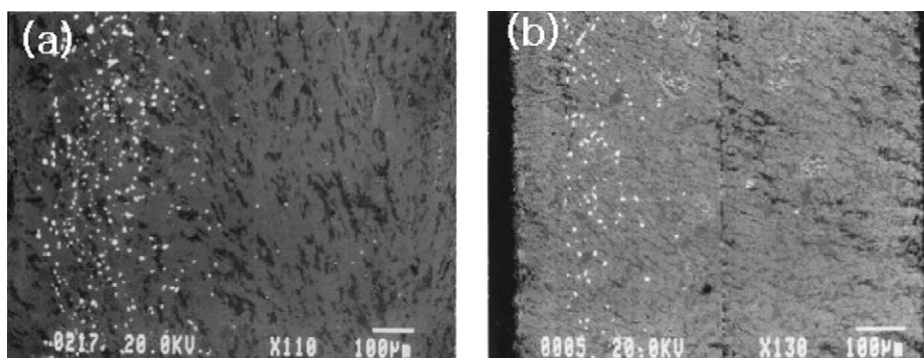

Fig. 12. EPMA of Ni precipitated in the matrix after 1000 h cell operation: (a) a cell with NiO cathode, and (b) a cell with LiCoO$_2$-coated NiO cathode.

determining the lifetime of MCFC, more work is required to confirm the long-term stability of LiCoO$_2$ layers.

The amount of Ni precipitated in the matrix during 1000 h cell operation was analyzed by atomic absorption spectroscopy and the results are summarized in Fig. 11. The amount Ni deposited in the matrix was significantly reduced by coating LiCoO$_2$ on the internal surface of the porous cathode. For instance, coating 5 mol% of LiCoO$_2$ in the cathode led to the 60% reduction of Ni precipitation. Fig. 11 apparently indicates that coating LiCoO$_2$ precursors by the sol-impregnation method is an effective way of suppressing the dissolution rate of NiO.

Fig. 12 shows the Ni distribution in the matrices after the 1000 h operation of two cells: a cell with conventional NiO cathode and a cell with LiCoO$_2$-coated NiO cathode. The left- and right-hand sides of the matrix correspond to cathode and anode, respectively. It is clear from Fig. 12 that the number of Ni clusters precipitated in the matrix is significantly reduced by using a LiCoO$_2$ coating on the NiO

cathode. In addition, the distribution of Ni in the matrix becomes narrower and confined near the cathode side of the matrix for the cell using a LiCoO$_2$-coated cathode.

Based on the above results, it can be concluded that the sol-impregnation of LiCoO$_2$ precursors on the internal surface of porous NiO cathode effectively suppresses the rate of NiO dissolution for 1000 h. Research is needed to evaluate the long-term stability of LiCoO$_2$ layer on the NiO cathode.

4. Conclusions

A stabilized NiO cathode has been fabricated by sol-impregnation of LiCoO$_2$ precursors on the internal surface of a porous Ni cathode. Acrylic acid was used as a chelating agent in preparing a precursor sol for LiCoO$_2$ coating. In situ treatment of the cathode coated with LiCoO$_2$ precursors inside a single cell resulted in the formation of LiCoO$_2$ layers on the NiO cathode. With increasing the coated

$LiCoO_2$ in the cathode, the initial cell performance decreased, but the performance was gradually improved during the cell operation. The amount Ni deposited in the matrix was significantly reduced by the $LiCoO_2$ coating. For example, coating 5 mol% of $LiCoO_2$ in the NiO cathode led to the 60% reduction of Ni precipitation. The results obtained in this study strongly suggest that $LiCoO_2$ layers formed on the internal surface of the porous NiO cathode effectively suppress the rate of NiO dissolution for 1000 h. More work is required to confirm the long-term stability of $LiCoO_2$ layer on the NiO cathode.

Acknowledgements

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