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The formation of $LiCoO_2$ on a NiO cathode for a molten carbonate fuel cell using electroplating

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Lithiated NiO cathode dissolution has been a major problem for the development of molten carbonate fuel cells (MCFCs). Many studies have been contributed to find new alternative cathodes; here, lithium cobalt oxide, $LiCoO_2$, was coated onto the commonly used NiO cathode by the electroplating method and the resulting cathode showed much reduced solubility compared with that of the common nickel oxide cathode. Thin film lithium cobalt oxide was prepared by the oxidation of Co metal deposited on a nickel plate in molten $(Li,K)_2CO_3$ at 650 °C under a CO_2–O_2 (2 : 1 vol%) atmosphere. When this coated nickel plate was oxidized, the open circuit potential (OCP) decayed gradually, indicating two well-defined potential plateaux; the oxide films produced at each potential plateau were identified by X-ray diffraction methods. The surface product at the first plateau was CoO. $LiCoO_2$ was formed at the second OCP plateau [around −0.47 V *vs.* CO_2–O_2 (2 : 1 vol%) reference electrode]. By the same method, $LiCoO_2$ was coated onto a porous nickel cathode in order to produce a MCFC.

For 300 h steady operation of the cells, the mean voltages of the cells were 0.80 V using a NiO cathode and 0.85 V for a LC-NiO(EP) cathode at a current density of 150 mA cm^{-2}. In addition to the cell efficiency improvement, the solubility of the LC-NiO(EP) cathode was much lower than that of the NiO cathode.

Introduction

The molten carbonate fuel cell (MCFC) is an energy-producing electrochemical system, which is expected to become commercial in the near future.[1–3] The MCFC produces an electric current from a fuel, such as hydrocarbons, and an oxidant at 650 °C and consists of a lithiated nickel oxide cathode, a $(Li,K)_2CO_3$ electrolyte, a $LiAlO_2$ matrix and a Ni–Cr or Ni–Al alloy anode. The lithiated NiO cathode is generally formed by *in situ* oxidation and subsequent lithiation of a presintered porous nickel plaque. The NiO cathode prepared by this method presents a porous structure and a high electrical conductivity, which ensures the efficient performance of the electrode. However, the dissolution and precipitation of the NiO cathode in the matrix is one of the factors that limit the operation time of the MCFC. There is also a risk that dissolved nickel will precipitate in the matrix on the anode side and cause a short-circuit in the cell. This problem, originated by the tendency of the Ni ions to dissolve in the electrolyte mixture, should not be a heavy limitation on the cell lifetime, because the solubility equilibrium of Ni^{2+} in the $(Li,K)_2CO_3$ solution is reached at an ion concentration of 30–50 ppm.[4] In practice, the formed Ni^{2+} ions can diffuse through the matrix structure towards the anode where the reducing conditions enhance the precipitation of Ni metal particles.

Two main ways have been adopted to solve this problem. One is to modify the molten carbonate, *e.g.* adding alkaline earth metal salts (such as Ba, Sr) to the melt, adopting Li–Na eutectic carbonates instead of Li–K carbonates as the electrolyte, which make the molten carbonate more basic, thereby reducing the solubility of NiO.[5] Another way is to develop an alternative cathode material. Lithium cobalt oxide, $LiCoO_2$, is used as one of the alternative materials for the MCFC cathode because its solubility is small and the rate of dissolution is slower than that of NiO. However, the electronic conductivity of $LiCoO_2$ is lower than that of NiO and its cost is higher. Thus, coating the NiO cathode with $LiCoO_2$ may be an attractive option. Through various coating methods, cheaper alternative cathodes, which have higher conductivities than $LiCoO_2$ and lower solubilities than NiO, can be produced. In a previous paper we coated NiO cathodes, which have higher electrical conductivity, with stable $LiCoO_2$ in carbonate by a PVA-assisted sol–gel method and obtained a LC-NiO(SG) cathode.[6] Hong *et al.*[7] synthesized films of $LiCoO_2$ on the surface of the porous NiO cathode by a solution–gel technique. Acrylic acid was added as a chelating agent and acrylic acid solutions of various concentrations were used in the experiment. Fukui *et al.*[8] proposed a new cathode structure in which NiO grains are coated with $LiCoO_2$ by using the usual tape casting method, *in situ* oxidation and lithiation at 650 °C in a $(Li,K)CO_3$ melt.[9] They prepared Ni powder covered with fine CoO particles mechanically by the Mechanofusion system.[10]

Another method of coating $LiCoO_2$ onto a NiO cathode is the electroplating method. Yamada and Uchida[11] coated Co metal onto a gold plate, with the electroplating method, from which they produced a $LiCoO_2$ coated gold plate after oxidation in molten salt at 650 °C. The merits of the electroplating method include *in situ* oxidation, control over the coating thickness and low cost. In the present study, $LiCoO_2$, which is stable in molten salts, coated NiO cathodes were prepared by the electroplating method. Surface analysis, unit cell tests and solubility tests were carried out in order to investigate how the $LiCoO_2$-coated NiO (which will be referred to as LC-NiO(EP)) cathode affected the cell performance and solubility. The structure change of the cathodes during the fabrication procedure was investigated by X-ray diffraction (XRD) and Raman spectroscopy. The unit cell test was performed to examine the electrochemical performance and the solubility of metal oxide coated NiO cathodes, using induc-

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tively coupled plasma atomic emission spectroscopy (ICP-AES).

Experimental

Preparation of $LiCoO_2$-coated Ni substrates

$LiCoO_2$-coated substrates were obtained after the oxidation in carbonate melts of Co metal electroplated on various substrates. A Ni metal plate and a porous Ni electrode for MCFC were used as the substrates. For this coating procedure, the Watts solution was prepared by mixing 0.4 M $CoCl_2{\cdot}7H_2O$, 0.4 M $CoSO_4{\cdot}6H_2O$ and 0.1 M H_3BO_3 solutions. Fig. 1 shows the device for electroplating Co metal onto a Ni substrate. The counter electrode was a Pt plate (1.5×1.5 cm^2) and an Ag/AgCl reference electrode was used. The supplied current and time for the electroplating of Co metal were determined according to the Faraday equation. After the electroplating process, the substrates coated with Co metal was heated at 650 °C in a carbonate melt of Li_2CO_3–K_2CO_3 (62 : 38 mol%). The CO_2–O_2 gas mixture (67 : 33 vol%) was supplied at 650 °C for oxidation of Co metal. Fig. 2 shows the apparatus used for oxidation of Co-coated substrates and to measure the changes in the open circuit potential (OCP) during the oxidation process. The Ni metal plates coated with Co metal of various thicknesses (0.01–0.1 μm) were used as the working electrodes. The reference electrode was a 1.5×1.5 cm^2 gold plate and the counter electrode was a gold wire of 1.0 mm diameter. The OCP values were monitored with a charge–discharge cycler, Arbin BT-2042.

Characterization

The surface structures of various LC-NiO(EP) substrates were identified using an X-ray diffraction system (XRD, MAC Science MXP3A-HF) and Raman spectrometry. The XRD patterns of the samples were measured from 10 to 70° (2θ) at a scan rate of 4° min^{-1} using CuKα radiation. A Model NR-1100 Raman spectrometer from Jasco was used, and the laser source was a Coherent Innova 70 series Ar ion laser.

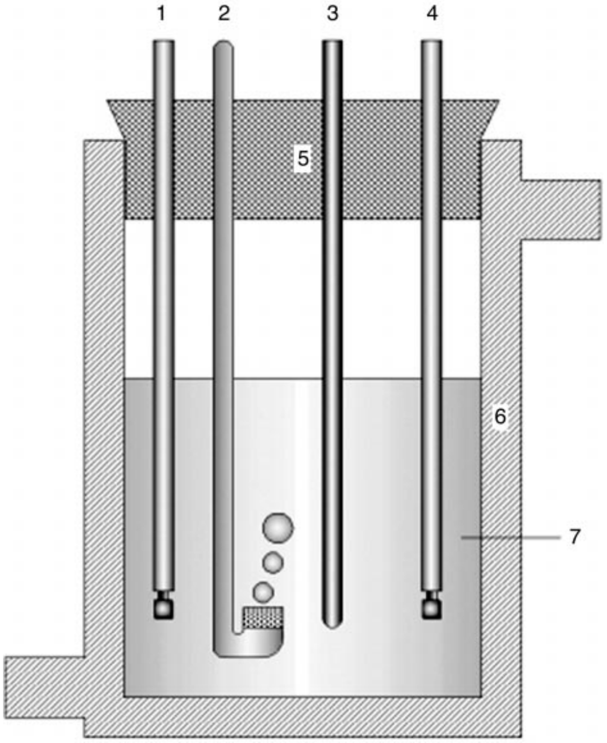

Fig. 1 The device for electroplating Co metal onto a Ni substrate: 1 counter electrode, 2 Ar blowing tube, 3 reference electrode, 4 working electrode, 5 silicon cover, 6 water jacket, 7 electrolyte.

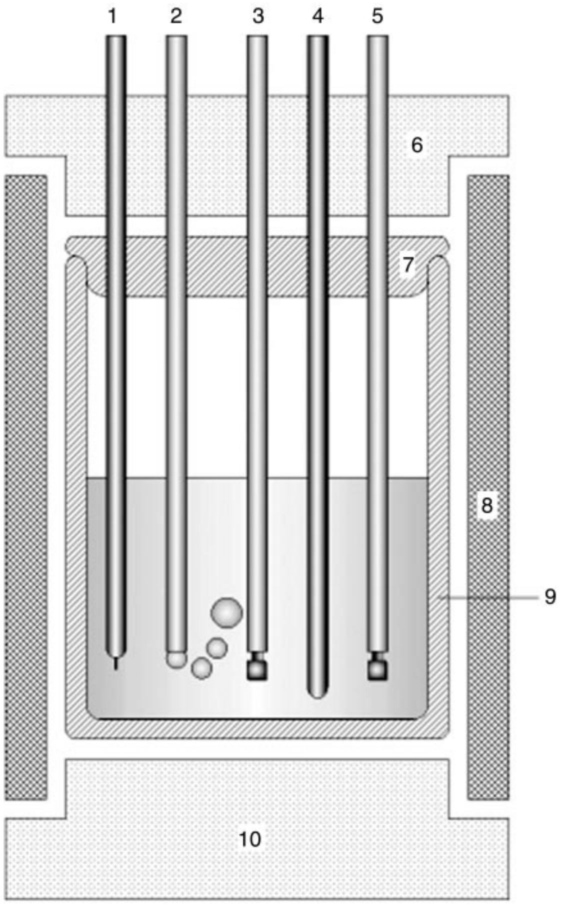

Fig. 2 The apparatus for oxidation of Co-coated substrates: 1 counter electrode, 2 gas inlet, 3 working electrode, 4 thermocouple, 5 reference electrode, 6 furnace cover, 7 crucible cover, 8 furnace, 9 crucible, 10 insulator.

The tested MCFC was a 1×1 cm^2 single cell with lithiated NiO and LC-NiO(EP) cathodes. The anode was a porous Ni–10 wt% Cr plaque, while the cathode was a porous Ni plaque oxidized *in situ* and lithiated to either NiO(Li$^+$) or LC-NiO(EP) as prepared in this study. The matrix was made of $LiAlO_2$ and the carbonate was a lithium-rich Li_2CO_3–K_2CO_3 eutectic (62 : 38 mol%). The anode current collector was a perforated nickel plate, while the cathode current collector was a perforated plate made of stainless steel (type 316L). The cell body was made with stainless steel type 316L also. These cells were operated at 650 °C under atmospheric pressure. The anode gas was a mixture of H_2–CO_2 (80 : 20) humidified at 50 °C; the cathode gas was a mixture of $CO_2 : O_2$ (67 : 33 vol%).

The solubility of the LC-NiO(EP) cathode was measured in a binary eutectic melt, Li_2CO_3–K_2CO_3 (62 : 38). Li_2CO_3 and K_2CO_3 were used as supplied from Junsei Chemical Company [analytical purity (>98%)]. 60g $(Li,K)_2CO_3$ were placed in a pure alumina crucible. A 1.5 g LC-NiO(EP) cathode sample was immersed in $(Li,K)_2CO_3$ and then the temperature was increased from ambient to 650 °C at a rate of 3 °C min^{-1}. The inlet gas, which was a mixture of $P_{CO_2} = 0.67$ atm and $P_{O_2} = 0.33$ atm, was supplied at 650 °C. Equilibrium solubility was determined by removing a ~0.3 g aliquot of molten carbonate from the melts at the appointed time using an alumina pipette. Each liquid carbonate sample was transferred to a clean alumina crucible where it solidified. The samples were analyzed for dissolved nickel by inductively coupled plasma atomic emission spectroscopy (ICP, Jobin Yvon 138 VLTRACE ICP-AES spectrometer).

Results and discussion

The reduction potential of Co metal calculated by using the Nernst equation was 0.57–0.83 V at 1, 10 and 50 mA. However, the reduction potentials measured in this study were higher than the calculated potentials. This over potential increased with the increase in supplied current because of the *I–R* drop and the concentration polarization between the working electrode and the reference electrode. The OCP data for the effect of pre-treatment before the oxidation of Co metal electroplated onto a Ni plate are given in Fig. 3. The pre-treatment was the aging process and the surface of the Co-coated Ni plate was oxidized partially in the oven at 120 °C for 24 h. As can be seen in Fig. 3(a), an OCP plateau was not found around −0.55 V for the Co-coated Ni plate obtained without any pre-treatment, as compared with Fig. 3(b). The plateau around −0.55 V involves the oxidation of Co metal. Hence, the results of Fig. 3 provide evidence that the Co metal was not coated onto the Ni plate in the absence of the pre-treatment process. Accordingly, it is reasonable to suppose that the Co metal was separated from the Ni plate in the case of no pre-treatment, because the surface area of the Ni plate was increased rapidly during the oxidation process in the molten salt. The partial oxidation decreases the diffusion rate of oxygen into the electrode during the next oxidation process. In the case of the Ni plate with a thin metallic Co layer, it is easy for oxygen to pass through and diffuse into the Ni plate. So, the Ni metal within the body of the plate is oxidized rapidly and this effect causes the separation between the Co layer and the Ni plate. After the aging process the Co-coated Ni plate has a thin CoO layer on the surface which prevents rapid oxidation of Ni metal; the coating remains strongly attached to the plate because of the formation of a Co/Ni solid solution.[6,12–14] Fig. 4 shows the OCP changes of a Ni plate coated with Co metal of various thicknesses during the oxidation in molten salt at 650 °C. The oxidation is completed before 500 s [Fig. 4(a)] and this result is in agreement with that of Malionwska who found that the OCP for the NiO obtained after oxidation of a Ni ribbon in molten salt was about −0.5 V.[15]

According to Fig. 4(d), the OCP decayed gradually *via* two potential plateaux when a thin Co film electroplated on a Ni plate was immersed into a molten (62Li+38K) mol% carbonate mixture at 650 °C. The Co metal obtained after the electroplating procedure has two packing structures, hexagonal closed packing (hcp) or face centered cubic (fcc) depending on the supplied current and the pH of the electrolyte.[16] Generally, the structure of Co metal prepared by the electroplating method has a mixed structure of hcp and fcc. However, at low

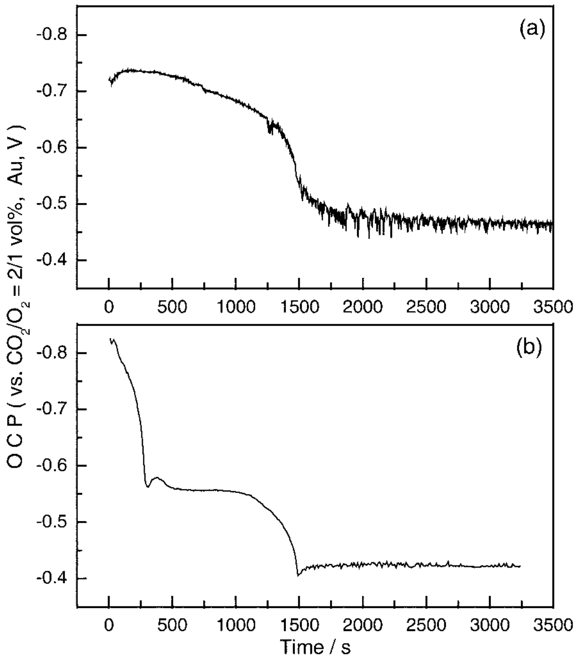

Fig. 3 OCP changes for a pre-oxidation treated Co-coated Ni plate upon oxidation in molten salt at 650 °C (a) after Co electroplating and (b) after Co electroplating and aging in an oven for 24 h.

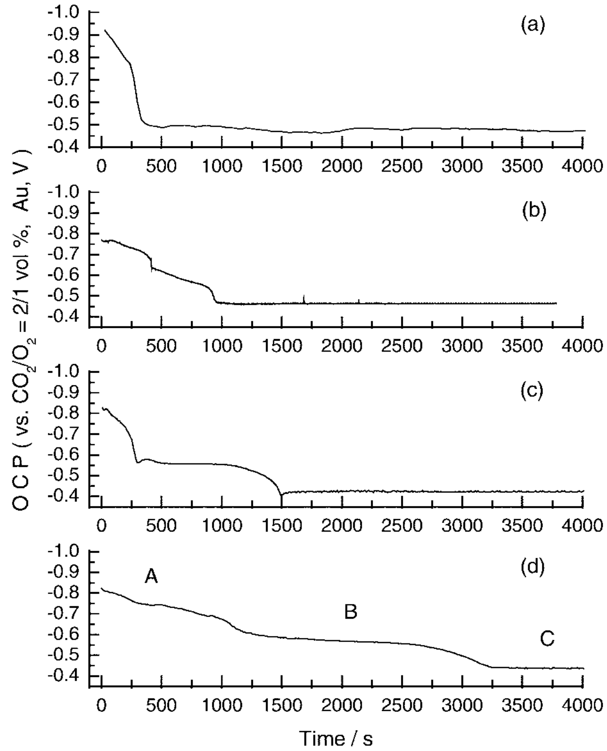

Fig. 4 The OCP changes of a Ni plate coated with various thicknesses of Co metal during the oxidation in molten salt at 650 °C: (a) uncoated, (b) 0.01 µm Co, (c) 0.1 µm Co, (d) 1 µm Co.

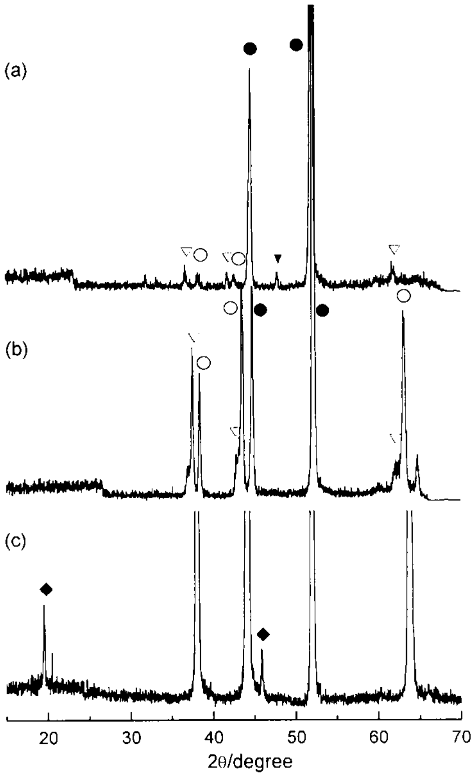

Fig. 5 XRD patterns of Co electroplated on the Ni plate during the oxidation in molten salt at 650 °C: (a) after 80 s, (b) after 2700 s, (c) after 4000 s (∇: CoO, ○: NiO, •: Ni, ▼: Co, ◆: LiCoO$_2$).

current and high pH, Co metal was precipitated with the hcp structure.[15] The Ni plates coated with Co metal produced at each potential plateau were examined by X-ray diffraction and the XRD patterns are shown in Fig. 5. Fig. 5(a) shows the XRD pattern of the Co metal electroplated on a Ni plate obtained after oxidation for 80 s in molten salt at 650 °C [A in Fig. 4(d)]. The major XRD peaks for Ni metal appear at 44.5 and 51.9° (2θ)[17] and those for Co metal are observed at 44.8 and 47.6° (2θ).[18] As seen in Fig. 5(a), small peaks for NiO and CoO are observed but those for Ni and Co metal are absent because of the pre-treatment for partial surface oxidation. The oxidation of Ni and Co metal progresses slowly from region A to region B. In B, in the case of the Co-electroplated Ni plate obtained after oxidation for 2700 s, the growth of peaks for CoO is observed at 36.6°, 42.5° and 61.9°. Yamada and Uchida[11] reported that the OCP plateau around −0.68 V involved the oxidation of Co metal to CoO. In Fig. 4(d), the OCP plateau for CoO observed around −0.6 V and the difference between this value and Yamada's report may be due to the NiO, which has an oxidation potential of −0.47 V. Thus, this result shows that Co metal was oxidized to CoO and Ni to NiO at the first plateau. The XRD pattern of the $LiCoO_2$-coated NiO [which will be referred to as LC-NiO(EP)] plate obtained after oxidation for 4000 s in molten salt at 650 °C is presented in Fig. 5(c). In region C, the diffusion of Li^+ ions into the CoO layer progressed and a $LiCoO_2$ layer was formed. From these XRD patterns, we can explain the coating process of the $LiCoO_2$ layer on the Ni metal plate. At first, oxidation of the Ni metal plate occurs simultaneously with the oxidation of Co metal to CoO around −0.6 V; then, a $LiCoO_2$ layer on the NiO plate is formed from the diffusion of Li^+ ions into the CoO layer.

The Raman spectra of Co metal electroplated on a Ni plate at various thicknesses after oxidation in molten salt at 650 °C are presented in Fig. 6. The spectrum for $LiCoO_2$ has two sharp peaks, one at 485 cm^{-1} and the other at 597 cm^{-1}. Inaba *et al.*[14] assigned the above-mentioned two peaks as A_{1g} and E_g vibrational modes. They observed the two peaks approach each other and become lower in intensity as more Ni replaces Co in $LiCo_{1-y}Ni_yO_2$. As can be seen in Fig. 6, the Raman spectrum of the Ni plate coated with a thin Co metal layer exhibits a broad band around 510 cm^{-1} because of the formation of $LiCo_{1-y}Ni_yO_2$, which is due to the formation of a Co/Ni solid solution which is then lithiated.[6] The Raman spectra of LC-NiO(EP) cathodes after oxidation in molten salt at 650 °C are given in Fig. 7. As in Fig. 6, lithiated Co and Ni solid solution oxide ($LiCo_{1-y}Ni_yO_2$) was formed on the surface of the NiO particles in the case of the NiO cathode coated with a thin $LiCoO_2$ layer [Fig. 7(a)].[8,13] Otherwise, two peaks for $LiCoO_2$ appear in the Raman spectrum of the LC-NiO(EP) cathode obtained after heat treatment of a Ni cathode coated with a thick $LiCoO_2$ layer in Fig. 7(b).[6]

The cell performance using the LC-NiO(EP) cathode with a coating thickness of 0.1 µm prepared by the electroplating method was evaluated at 650 °C for 300 h and the results are depicted in Fig. 8. The open circuit voltage (OCV) of the cell remained around 1.1 V and the closed circuit voltage (CCV) remained at ~0.85 V at 150 mA cm^{-2}. This result indicates that the cell using a LC-NiO(EP) cathode is superior to a cell using NiO. Studies of the cell performances using $LiCoO_2$ coated NiO cathodes have been carried out by many researchers. Various LC-NiO cathodes were obtained using PVA, acrylic acid or double layer tape casting methods and cell voltages of 0.8–0.85 V at 150 mA cm^{-2} were obtained.[6,7,19] Hong *et al.*[7] suggested that the cell voltage depends on the amount of $LiCoO_2$ in the cathode. As the amount of $LiCoO_2$ increases, the pore size of NiO decreases, absorbing more carbonate which leads to the flooding of the cathode. Fig. 9 shows the solubility of a LC-NiO(EP) cathode with a coating thickness of 0.1 µm prepared by the electroplating method in a Li_2CO_3–K_2CO_3 (62 : 38) melt at 650 °C under $P_{CO_2} = 0.67$ atm, $P_{O_2} = 0.33$ atm. From Fig. 9, it is observed that the solubility of the LC-NiO(EP) cathode obtained by electroplating is much

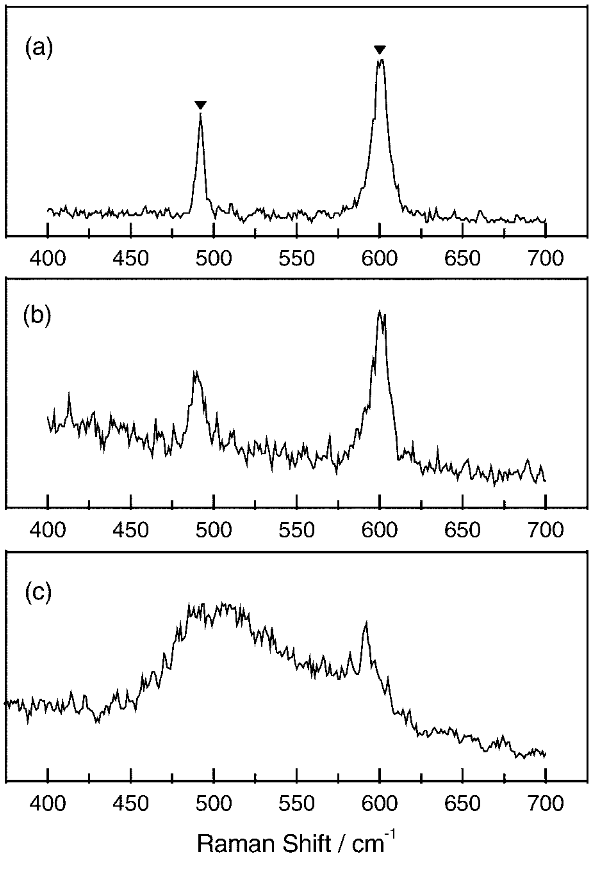

Fig. 6 Raman spectra of Co electroplated on Ni plates after oxidation in molten salt at 650 °C with thicknesses of (a) 1 µm, (b) 0.1 µm, (c) 0.01 µm (▼: $LiCoO_2$).

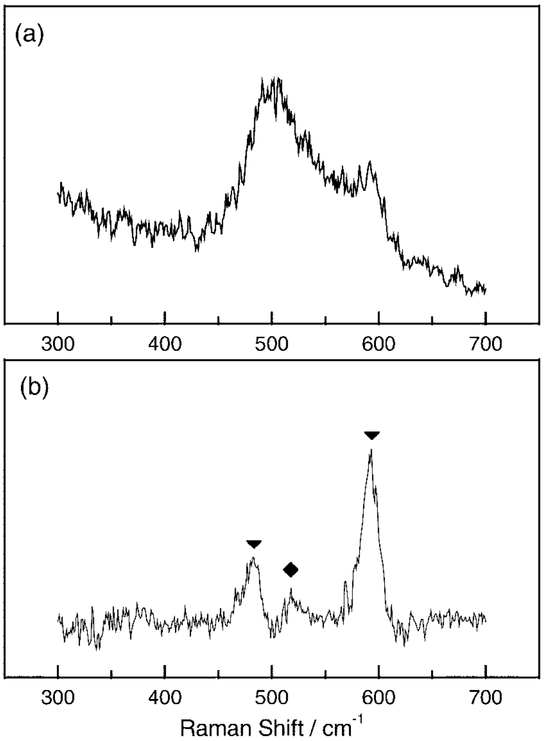

Fig. 7 Raman spectra of Co electroplated on Ni cathodes after oxidation in molten salt at 650 °C with thicknesses of (a) 0.01 µm, (b) 0.1 µm (▼: $LiCoO_2$, :◆ $LiCo_{1-y}Ni_yO_2$).

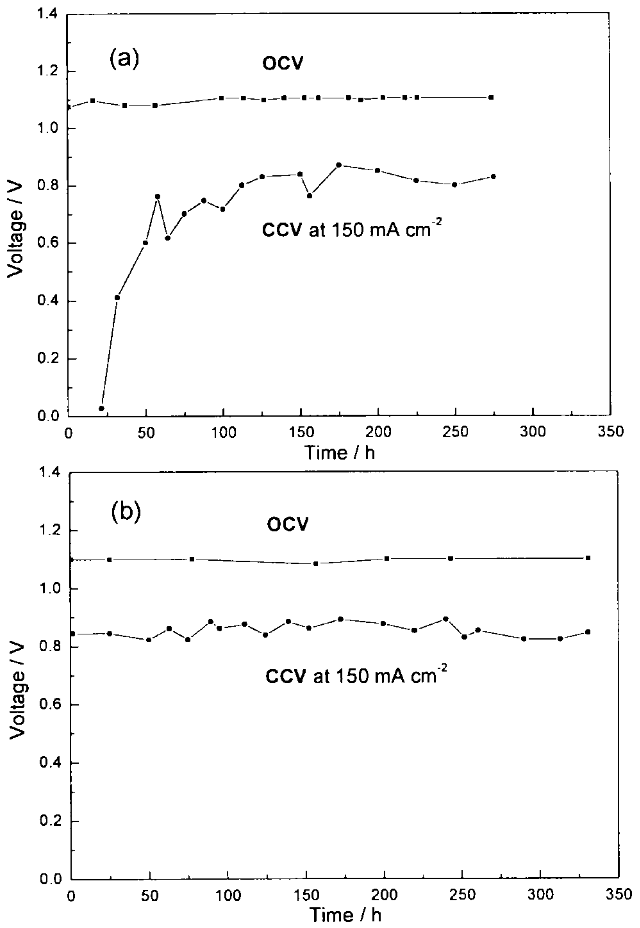

Fig. 8 Cell performance using (a) NiO cathode, (b) LC-NiO(EP) cathode.

lower than that of the NiO cathode. From the solubility test, it is suggested that the amazing decrease of the solubility is observed because the $LiCoO_2$ layer formed on the NiO cathode prevents the dissolution of nickel ions into the electrolyte. The solubilities of various LC-NiO cathodes were found to be less than half of that of the NiO cathode in previous papers. It was suggested that two factors induced the solubility decrease of LC-NiO cathodes. One factor is that the solubility of LC-NiO cathodes decreases because the $LiCoO_2$ coated on the surface of the NiO cathode has lower solubility than NiO, especially in the low-pressure atmosphere.[20–22] The other factor is the formation of a prelithiated structure. Zhang *et al.* showed that the solubility of both prelithiated NiO and prelithiated CoO was affected by its lithium content.[23] In their paper, they suggested a structure modification of NiO or CoO to a more stable form, caused by the prelithiation, and an increase of the local basicity in the interface region between the prelithiated NiO or prelithiated CoO material in the carbonate melts.

Conclusion

We have coated a Ni plate with Co by an electroplating method and obtained a LC-NiO(EP) plate after the oxidation of the plate in molten $(Li,K)_2CO_3$ at 650 °C with a CO_2–O_2 (2 : 1 vol%) atmosphere. In order to prevent the separation between the Co layer and the Ni plate, which is caused by the rapid increase of surface area of Ni metal during the oxidation process, an aging pretreatment was carried out. It was found from the XRD data that $LiCoO_2$ prepared by the electroplating method has the hcp structure only. With an increase in thickness of the Co metal layer on the Ni substrate, the amount of $LiCoO_2$ coated on the substrate increased. When this Co-coated Ni substrate was oxidized, the open circuit potential (OCP) decayed gradually, indicating two well-defined potential plateaux, and the oxide films produced at each potential plateau were identified by X-ray diffraction. At the first OCP plateau, Co metal was oxidized to CoO and Ni to NiO respectively. Then a solid solution of CoO and NiO was formed, and $LiCoO_2$ was formed at the second OCP plateau [around −0.47 V *vs.* O_2–CO_2 (1 : 2) reference electrode]. By the same method, $LiCoO_2$ was coated on the porous nickel cathode for MCFC. For 300 h of steady operation of the cells, the mean voltages of the cells were 0.80 V using the NiO cathode and 0.85 V for the LC-NiO(EP) cathode at a current density of 150 mA cm^{-2}. The solubility of the LC-NiO(EP) cathode was much lower than that of the NiO cathode at 650 °C under $P_{CO_2} = 0.67$ atm, $P_{O_2} = 0.33$ atm.

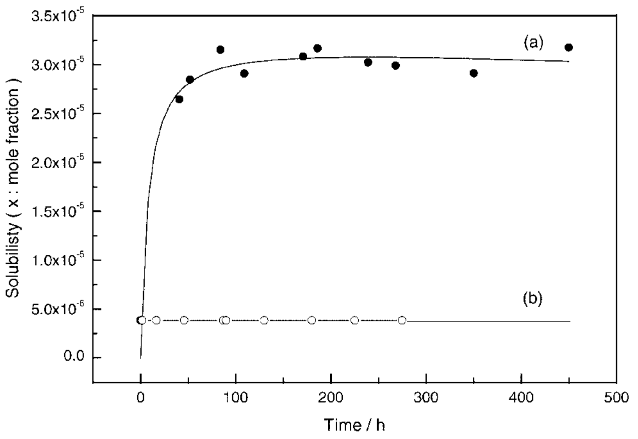

Fig. 9 The solubility of a LC-NiO(EP) cathode prepared by the electroplating method in a Li_2CO_3–K_2CO_3 (62 : 38) melt at 650 °C under $P_{CO_2} = 0.67$ atm, $P_{O_2} = 0.33$ atm. (a) NiO (solubility, 3.035×10^{-5}), (b) LC-NiO(EP) (solubility, $< 2.124 \times 10^{-6}$).

Consequently, the coating of $LiCoO_2$ on the NiO cathode for MCFC using the electroplating method was successfully conducted and this LC-NiO(EP) cathode could be used as an alternative cathode which is less soluble in the molten carbonate.

Acknowledgement

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