

# Mechanical strength of porous nickel plates containing lithium and their performance as the cathode for MCFC

Seung-Goo Kim<sup>\*</sup>, Sung Pil Yoon, Jonghee Han, Suk Woo Nam,  
Tae-Hoon Lim, In-Hwan Oh, Seong-Ahn Hong

*Battery and Fuel Cell Research Center, Korea Institute of Science and Technology, Seoul 136-791, South Korea*

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## Abstract

To improve the mechanical properties of MCFC cathode materials, pre-lithiated porous nickel plates containing 1–5 mol% of lithium were fabricated by the tape casting method, and the microstructures, mechanical properties, and performance was examined. The microstructure and pore distribution was not changed until the lithium content reached 3 mol%. The sample containing 5 mol% of lithium had patch structure on the skeleton and a smaller volume of primary pores. XRD analysis showed that lithium-containing porous nickel plates can easily form solid solutions without any undesirable byproducts after the oxidation. Both the bending strength and Young's modulus of the porous plates increased with the increase of lithium content. The average bending strengths of the samples containing 1, 3, and 5 mol% of lithium were 1.29, 1.33, and 1.49 kgf/mm<sup>2</sup> which were 2.9, 3.0, and 3.4 times higher than that of pure porous nickel plate. The Young's modulus increased up to 1.35 kgf/mm in the case of the 5 mol% lithium containing sample that is 5.4 times higher than that of pure porous nickel plate. The OCV of single cells using pre-lithiated cathodes were between 1.065 and 1.067 V, and comparable cell performance was obtained for 500 h of single cell operation. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* MCFC; Cathode; Mechanical strength; Lithiated nickel oxide; Single cell performance

## 1. Introduction

To be competitive in the current electric power market, the molten carbonate fuel cell (MCFC), a most promising power generation system due to its high energy conversion efficiency accompanied by its low atmospheric emissions, should have a longer life time, improved reliability, and higher utility factor [1,2]. Recently, the stack size of MCFC has become larger to enhance the utility factor of MCFC not only by the increase in the number of layers but also in electrode area. For example, the electrode area of single cells employed in 1000 kW class MCFC power plants operated in 1999 in Kawagoe, Japan were 1.0 and 1.2 m<sup>3</sup> [3]. The most generally used cathode materials for MCFC was lithiated nickel oxide because of its high electric conductivity, electrochemical activity, and low precursor cost. Since making the large thin ceramic plate such as lithiated nickel oxide

without warping and/or cracking is difficult, the porous nickel plates were used as the cathode in the assembly of MCFC stacks [4,5]. They were oxidized and lithiated during the heating process for power generation. Since the pore size and porosity of porous nickel plates decreased during the in situ oxidation and lithiation, the porous nickel plates for MCFC cathodes should be under 800 μm in thickness and about 80% in porosity to facilitate the gas exchange during power generation. By virtue of their high porosity and slimness, the mechanical strength is compromised by the increase of electrode area.

Swarr and Trocciola had reported that the mechanical strength of nickel oxide was improved by the addition of lithium carbonate [6]. Moreover, it is found that the pre-lithiated nickel oxide had better chemical durability and comparable electrode performance than conventional cathode materials [7,8]. Those results mentioned above, however, were only for the samples made from the mixture of nickel oxide and lithium oxides and the mechanical properties of porous nickel plate containing lithium have not been reported. In practice, the mechanical properties of nickel are more important than those of nickel oxide because that is used in the assembly stage of MCFC stacks. In this research,

<sup>\*</sup> Corresponding author. Present address: Division of Chemistry and Chemical Engineering, California Institute of Technology, 1200 E. California Blvd., M/C 210-41, Pasadena, CA 91125, USA.

Tel.: +1-626-395-4255.

E-mail address: seunggoo@caltech.edu (S.-G. Kim).

therefore, we fabricated porous nickel plate containing lithium by the tape casting method, and the microstructural characteristics, mechanical properties, and electrode performances were investigated.

## 2. Experimental

The slurry for tape casting was made by the mixing of 100 cm<sup>3</sup> of water as the solvent, 1.6 g of glycerol (Junsei Chemical, Japan) as the plasticizer, 2.0 g of methyl cellulose (Junsei Chemical, Japan) as the binder, 1.6 g of Cerasperse 5468 (San Nopco Korea Ltd., Korea) as the dispersant, lithium nitrate as the source of lithium (Junsei Chemical, Japan), and 80 g of nickel powder (Type 255, Inco, USA) using a stabilized zirconia ball and polyethylene jar. The amount of lithium nitrate was fixed at 0.940, 1.88 and 2.82 g which corresponded to 1, 3, and 5 mol% of nickel, respectively. After ball milling for 24 h and de-airing, tape casting was carried out using in-house made doctor blade equipment. The clearance and casting speed of doctor blade were controlled to that the thickness of porous nickel plate after sintering was about 800 μm. Samples were heat-treated at 840 °C in hydrogen to prevent the oxidation after the drying in air for 12 h.

Scanning electron microscopy (SEM, S-4200, Hitachi, Japan) was employed to investigate the micro-morphology of sintered samples. The pore size distributions of samples were measured by the mercury porosimetry (Autopore II 9220, Micromeritics, USA) with the pressure up to 30 000 psi. The phase of sintered samples after the oxidation at 650 °C for 10 h in air was observed using X-ray diffraction (XRD, Rint/DMAX-2000, Rigaku, Japan) using Cu K $\alpha$  radiation from 10 to 90° with the interval of 0.02°. A computer program based on the least square method devised by Appleman and Evans [9] and modified by Benoit for PC was used to determine the lattice parameters of oxidized

samples from XRD data. The sintered porous nickel plates were cut into 6 cm × 4 cm to examine the mechanical strength by the universal testing machine (1127, Instron, USA). The span distance and the loading speed was fixed at 2.5 cm and 0.1 cm/s, respectively. The data was acquired with computer at 9 points/s. A minimum of 5 samples was used for each composition.

The general operation conditions for the test and evaluation of bench-scale MCFC single cell, as shown in Table 1, were employed in this research [4,5]. The fuel and oxidant gases were supplied using a mass flow controller (MFC, 1559A, MKS, USA). Single cell performance was observed at a current density of 150 mA/cm<sup>2</sup> using a digital voltmeter (3456A, HP, USA) and electric load bank (6060B, HP, USA).

## 3. Results and discussion

### 3.1. Microstructure of sintered porous nickel plates containing lithium

The microstructures of sintered porous nickel plates, presented in Fig. 1, show that the skeleton and pore morphologies of porous plates were not changed until the lithium content reached 3 mol% while the patch structure, A in Fig. 1(d), were found in the sample contain 5 mol% lithium. The pore size distributions of samples measured using mercury porosimetry were compared in Fig. 2. The pore volume of the secondary peak at about 7 μm, B in Fig. 2, was increased by the addition of lithium while the pore size of primary peak, C in Fig. 2, at about 5 μm were kept constant. The pore volume of primary pores was also unchanged until the lithium content reached 3 mol% and slightly decreased in the sample containing 5 mol% lithium. The geometric porosity of the pure porous nickel plate was 81% and decreased to 79, 77, and 76% with the increase of lithium content to 1, 3, and 5 mol%, respectively.

Table 1  
Operating conditions for MCFC single cell tests

Item	Specification	
Effective electrode area (cm <sup>2</sup> )	100	
Components	Cathode	Lithiated nickel oxide <sup>a</sup>
	Anode	Ni-10% Cr
	Electrolyte	62 mol% Li <sub>2</sub> CO <sub>3</sub> + 38 mol% K <sub>2</sub> CO <sub>3</sub>
	Matrix	γ-LiAlO <sub>2</sub>
Operating condition	Temperature (°C)	650
	Gas pressure (atm)	1
	Holding pressure (kgf/cm)	1.5
	Current density (mA/cm <sup>2</sup> )	150
Gases	Anode	72 mol% H <sub>2</sub> + 18 mol% CO <sub>2</sub> + 10 mol% H <sub>2</sub> O
	Cathode	70 mol% Air + 30 mol% CO <sub>2</sub>
Utilization	Anode (%)	40
	Cathode (%)	40

<sup>a</sup> In situ or pre-lithiated.

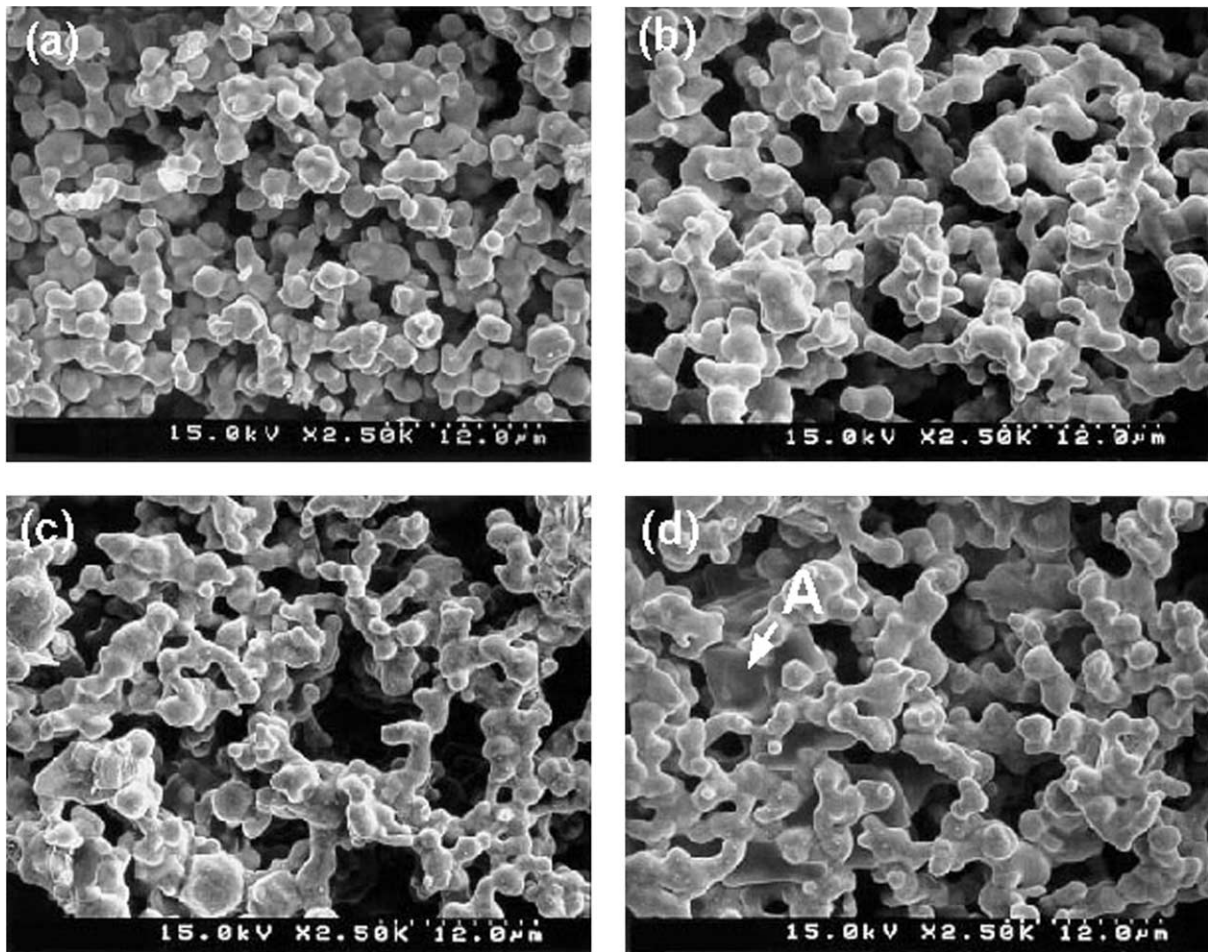


Fig. 1. SEM images of porous nickel plates containing (a) 0, (b) 1, (c) 3, and (d) 5 mol% of lithium.

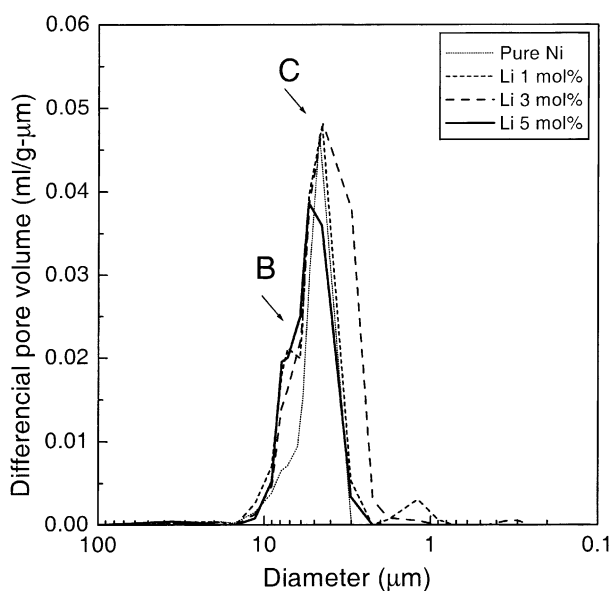


Fig. 2. Pore size distribution changes of porous nickel plates with lithium content measured using mercury porosimetry.

The XRD diffractograms of porous nickel plates after the oxidation at 650°C in air are illustrated in Fig. 3. All the peaks are corresponded to the nickel oxide with face centered cubic NaCl structure and the peak correspond to the primary peak of hexagonal type LiNiO<sub>2</sub> at about 20°, D in Fig. 3, cannot be found. Perez et al. reported that the formation of LiNiO<sub>2</sub> is undesirable due to the decomposition followed by the deterioration of electrode performance [10]. The result of XRD investigation implies that all the added lithium formed solid solution with nickel oxide and no adverse effect should be expected on electrode performance. By Vegard's law, there is a linear relationship between the composition and lattice parameter when forming a solid solution. It is known that some of the nickel amounting to the same as that of lithium in lithium-nickel oxide, Li<sub>x</sub>Ni<sub>1-x</sub>O, is trivalent (Ni<sup>3+</sup>) instead of divalent (Ni<sup>2+</sup>) to maintain electric neutrality. Therefore, the theoretical lattice parameter of lithium-nickel oxide, the solid line in Fig. 4, was calculated using Eq. (1):

$$a = 2f[xrLi^{1+} + xrNi^{3+} + (1 - 2x)rNi^{2+} + rO^{2-}] \quad (1)$$

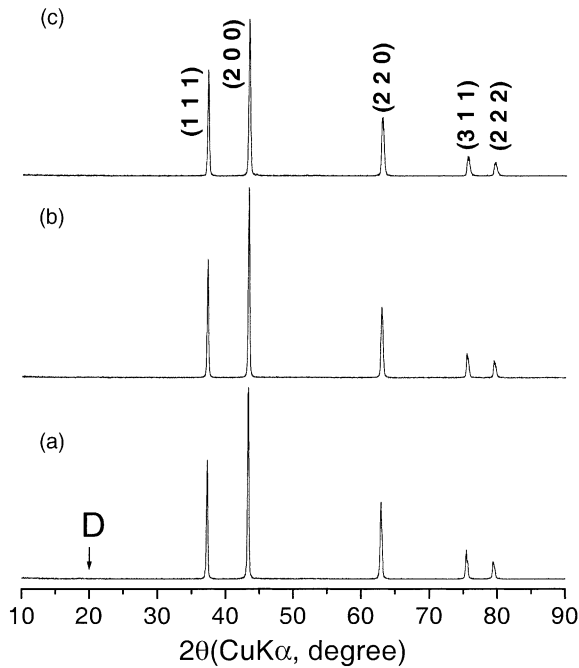


Fig. 3. XRD diffractograms of porous nickel plates containing (a) 1, (b) 3, and (c) 5 mol% of lithium after heat-treatment at 650 °C in air for 10 h.

where  $a$  is the lattice parameter of lithium–nickel oxide,  $x$  the content of lithium,  $r_{\text{Li}^{1+}}$ ,  $r_{\text{Ni}^{2+}}$ ,  $r_{\text{Ni}^{3+}}$  and  $r_{\text{O}^{2-}}$  are the ionic radii of  $\text{Li}^{1+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Ni}^{3+}$ , and  $\text{O}^{2-}$ , respectively, and  $f$ , 0.9990 in this case, is a parameter to correct the difference between the calculated and standard lattice parameter of pure nickel oxide, 4.176 Å, in JCPDS 04-0835. The ionic radii of  $\text{Li}^{1+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Ni}^{3+}$ , and  $\text{O}^{2-}$  at coordination number of six were 0.76, 0.69, 0.56, and 1.40 Å, respectively [11].

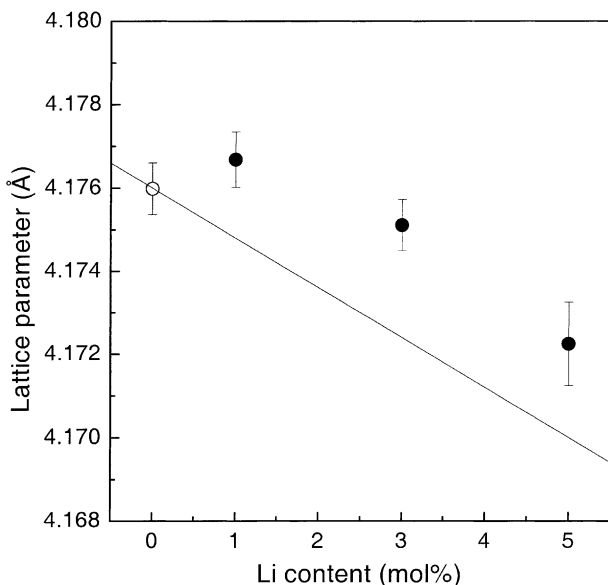


Fig. 4. Lattice parameters of oxidized porous nickel plates as a function of the amount of lithium content. The lattice parameter of pure nickel oxide was cited JCPDS 04-0835. Solid line shows the theoretical lattice parameter of nickel oxide containing lithium.

As can be seen in Fig. 4, the lattice parameters of lithiated nickel oxide measured using XRD show the same trend as the theoretical value calculated using Eq. (1) with a displacement due to the instrument error. Therefore, we believe Fig. 4 confirms that the lithiated nickel oxide,  $\text{Li}_x\text{Ni}_{1-x}\text{O}$ , with low lithium content ( $x \leq 5$ ) formed a solid solution.

### 3.2. Mechanical strength

Typical stress–strain curves of various sintered porous nickel plates containing lithium are shown in Fig. 5. Generally, metallic materials show ductile behavior following elastic deformation. For the case of porous nickel plate, however, plastic deformation was not appeared clearly due to their porous nature. In Fig. 5, the deformation curves of samples can be divided into two regions. It is considered that the porous structure deformed elastically in the lower load region, while it fractured one by one in the higher load region. Fig. 5 also shows that the Young's modulus of the porous plates, the slope of the stress–strain curves of elastic deformation region, increases as the lithium content increased. Young's modulus increased from 0.250 kgf/mm for pure nickel to 0.776, 0.822, and 1.35 kgf/mm for 1, 3, and 5 mol% lithium containing samples. The higher Young's modulus values make it easy to handle the porous plate especially when it has a large area.

Apparent 3-point bending strength of porous nickel plates, in which the porosity of the samples was not considered, is shown in Fig. 6. The bending strength of samples shows a narrow distribution with small deviation. The average bending strength of pure porous nickel plate was 0.42 kgf/mm<sup>2</sup> and the values also increased with the increase of lithium

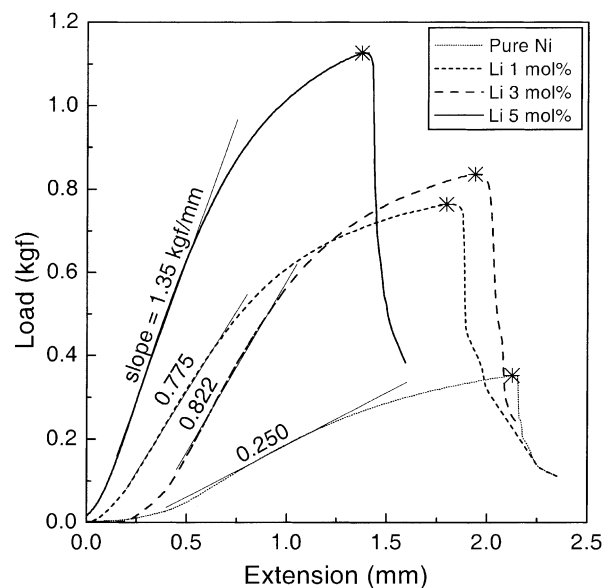


Fig. 5. Stress–strain behavior of porous nickel plates with various lithium contents. The slope of the elastic deformation range is Young's modulus of each sample.

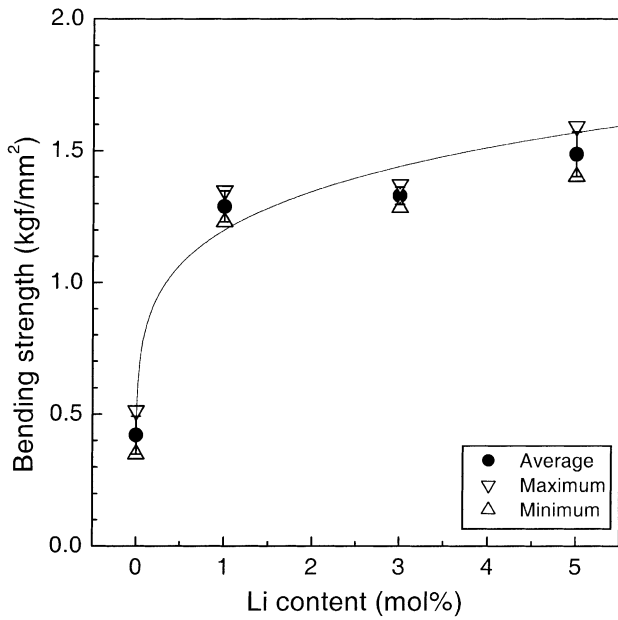


Fig. 6. Three-point bending strength of porous nickel plates as a function of lithium content.

content. The average bending strength of samples containing 1, 3, and 5 mol% of lithium was 1.29, 1.33, and 1.49 kgf/mm<sup>2</sup> which were 2.9, 3.0, and 3.4 times higher than that of pure Ni. The results shown in Figs. 5 and 6 show that the mechanical properties of porous nickel plates were improved by the addition of lithium. The results depicted in Figs. 5 and 6 were not only due to the change of microstructure as shown in Figs. 1 and 2 but also by the increase of point defects in the skeleton of the porous structure by the formation of a solid solution, as shown in Figs. 3 and 4, there inhibit the movement of dislocations required for the deformation of materials.

### 3.3. Performances of single cells

The OCV of single cells were between 1.065 and 1.067 V for 500 h which is slightly lower than the theoretical value, 1.068 V. The small difference in OCV between measured and theoretical means that there was no cross over and no wet-seal failure in single cells. It is believed that the difference was due to the inaccuracy of the temperature control of the water gas saturator at the anode gas inlet port. The cell voltage changes at 150 mA/cm<sup>2</sup> for 500 h of 10 cm<sup>2</sup> × 10 cm<sup>2</sup> single cells with various cathodes is shown in Fig. 7. The initial cell voltage was 0.791–0.816 V, and increased up to 0.838–0.845 V within 50 h of operation caused probably by the electrolyte redistribution in the pores of the matrix, anode and cathode. The single cells using a 1 and 3 mol% lithium containing cathode were 0.843 and 0.838 V, respectively, after operation of 500 h at 150 mA/cm<sup>2</sup>. These values are comparable to the performance of standard MCFC single cells using pure porous nickel plate as a cathode. The average cell voltage of standard single cells the same condition under operated in

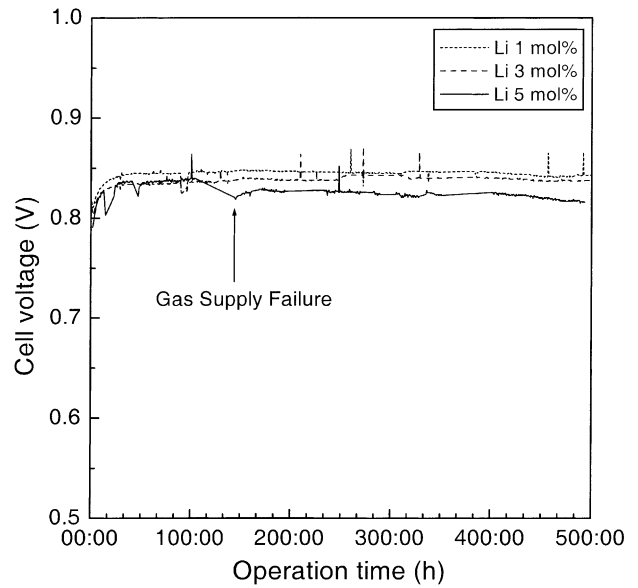


Fig. 7. Cell voltages of single cells with various cathodes at 150 mA/cm<sup>2</sup> for 500 h.

our laboratory was about 0.85 V [4,5]. During the operation of the single cell using 5 mol% lithium containing cathode, there is a anode gas supply failure after 150 h of running time. The OCV was not changed after the accident while the cell voltage at 150 mA/cm<sup>2</sup> was decreased from 0.840 to 0.821 V presumably due to the degradation of the current collector. The cell voltage of the single cell using 5 mol% lithium containing cathode was 0.817 V after operation for 500 h at 150 mA/cm<sup>2</sup>. The results of single cell operation show that the electrode performance of pre-lithiated nickel cathodes prepared in this research is comparable to the conventional cathode in spite of their 1–4% lower porosity.

## 4. Conclusion

From the present study of the microstructure, mechanical properties, and electrode performance of pre-lithiated porous nickel plates containing 1–5 mol% of lithium, the following conclusions can be drawn:

1. The samples containing 1 and 3 mol% lithium show nearly the same skeleton microstructure and primary pore volume as those of pure porous nickel plate while the sample containing 5 mol% of lithium has a patch structure on the skeleton and smaller volume of the primary pores. XRD analysis shows that lithium-containing porous nickel plates were composed of a solid solution after the oxidation without the formation of any undesirable byproduct such as LiNiO<sub>2</sub> that would deteriorate the cell performance.
2. It is observed that the Young's modulus and bending strength of the porous nickel plates can be increased by

the addition of lithium. The average bending strengths of the samples containing 1, 3, and 5 mol% of lithium were 2.9, 3.0, and 3.4 times higher than that of pure porous nickel plate. The Young's modulus also increased up to 1.35 kgf/mm in the case of 5 mol% lithium containing sample that is a 5.4 times higher value than pure porous nickel plate.

3. The OCV of single cells using pre-lithiated cathodes was over 1.065 V, and the cell voltage at 150 mA/cm<sup>2</sup> was over 0.838 V after operation for 500 h except in the case of single cells undergoing gas supply failure. Therefore, it is concluded that preparing the pre-lithiated porous nickel plate was a very effective way to fabricate the new MCFC cathode materials with high mechanical strength without any loss of cell performance.

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