

# Optimization of the electrolyte composition in a $(\text{Li}_{0.52}\text{Na}_{0.48})_{2-2x}\text{AE}_x\text{CO}_3$ (AE = Ca and Ba) molten carbonate fuel cell

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## Abstract

We report that the addition of the alkaline-earth carbonates  $\text{CaCO}_3$ ,  $\text{SrCO}_3$  and  $\text{BaCO}_3$ , to an alkali carbonate mixture effectively reduced the solubility of nickel oxide in a molten carbonate. In addition, we discuss the molten carbonate fuel cell (MCFC) performance with a ternary system of  $(\text{Li}_{0.52}\text{Na}_{0.48})_{2-2x}\text{AE}_x\text{CO}_3$  (AE = Ca, Sr and Ba). Although the solubility of nickel oxide in the molten carbonate was reduced with an increase in the amount of additives, large amount of additives bring a low cell performance. We have made progress in the optimization of the carbonate composition through investigations as to durability by small-sized cell testing under a pressurized condition. The addition of  $\text{SrCO}_3$  was deemed inadequate by the failure of cell voltage within a 1000-h operating period. From the single cell operation results of periods up to 5000 h, we concluded that the addition of 9 mol%  $\text{CaCO}_3$  and 9 mol%  $\text{BaCO}_3$  to 52 mol%  $\text{Li}_2\text{CO}_3$ – $\text{Na}_2\text{CO}_3$  preserved the cell performance. This electrolyte composition is expected to yield an efficiently performing and durable MCFC.

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## 1. Introduction

A molten carbonate fuel cell (MCFC) has been developed to ramp up the distributed generation of several hundreds of kilowatts to a high power generation in the megawatt range [1]. The MCFC, which is operated at 600–650 °C possesses the advantages of high efficiency, low emissions, and the capacity to utilize various fuels such as coal, natural gas, petroleum and hydrogen.

The important issues in the commercialization of power generation systems that employ the MCFC are high performance and durability. However, the severe problem of nickel shorting causes a reduction of cell voltage in long-term operations and a failure to attain a highly efficient power generation system. To assess the nickel shorting mechanism, investigators have dissolved nickel oxide as a cathode material into molten carbonate as an electrolyte during the operation of the system; under these conditions, the diffused hydrogen of the fuel gas from the anode side reduced the dissolved nickel cation in the electrolyte, so that nickel

metal particles were deposited in the electrolyte [2,3]. When these particles grouped together like a chain, they formed an electrical path between the anode and the cathode. The resultant nickel shorting happens after an operating period of more than 10,000 h [4].

The mechanism of nickel shorting has been researched in detail [5–8]. The first step of this phenomenon is the dissolution of nickel oxide in the molten carbonate used as an electrolyte in the MCFC. When the solubility of the nickel oxide in the molten carbonate is reduced, it is thought that the nickel shorting can be delayed [9]. We chose to investigate an alternative carbonate composition [10–13]. After researching the addition of alkaline-earth carbonates, which were chemically and thermally stable in the operating conditions of the MCFC we concluded that this procedure promised a way to overcome the nickel shorting issue [14].

Although the addition of an alkaline-earth carbonate is expected to prolong the MCFC's life-time, the appropriateness of the application of this method to the MCFC must be confirmed from the viewpoint of cell performance and durability. From such a perspective, we examined the optimization potential of additional alkaline-earth carbonates introduced into the lithium carbonate and sodium carbonate mixture.

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Table 1  
Examined additive and composition

Additive	mol%
CaCO <sub>3</sub>	0, 4, 9, 13, 15, 17
SrCO <sub>3</sub>	0, 4
BaCO <sub>3</sub>	0, 4, 9, 13, 15

The additives were added to Li<sub>2</sub>CO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub> = 52/48 mol% and ternary carbonate system was investigated.

## 2. Experimental

The cell components, consisting of an anode, a cathode electrolyte, and an electrolyte supporting matrix, were fabricated in-house. The fabrication method of the matrix has already been reported [15]. The anode porous plaque was fabricated by tape casting using a nickel-3% aluminum alloy powder that was 30 μm in median particle size. The cathode porous plaque was made from a commercially available nickel powder, INCO255. The plaques were fabricated in the same way as the electrolyte supporting matrix except that a toluene/ethanol mixture was used as a solvent. After tape casting and drying, the anode green sheet was sintered for 10 h at 1000 °C under a H<sub>2</sub>/N<sub>2</sub> = 1/1 mixture humidified at 90 °C. The cathode green sheet was sintered for 10 min at 700 °C under dry N<sub>2</sub> using an electrical furnace. The current collectors' anode and cathode were perforated sheets of nickel and stainless steel type 310S, respectively. The cell frame was made of stainless steel type 310S.

Table 1 shows the compositions tested using an alkaline-earth carbonate added to a lithium carbonate/sodium carbonate eutectic (Li<sub>2</sub>CO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub> = 52/48 mol%). The tested single cell, whose effective electrode area was 81 cm<sup>2</sup>, was assembled. Table 2 shows the standard operating conditions for both atmospheric and pressurized conditions. The cell resistance was measured by an HP4720A milliohm meter operated at 1 kHz ac.

The gas composition of the anode outlet was analyzed at appropriate intervals by means of gas chromatography. After the cell operation, the amount of deposited metallic nickel in the matrix was determined by chemical analysis.

## 3. Results and discussion

### 3.1. Optimization of additives

Since an increasing amount of alkaline-earth carbonate lowers the solubility of nickel oxide in the molten carbonate, the addition of the alkaline-earth carbonate to the molten carbonate used as an electrolyte is expected to prolong the operating time of the MCFC. Fig. 1 shows the relationship between the amount of additives and the cell voltage under load at 150 mA/cm<sup>2</sup>, together with the cell resistance. An increasing amount of additive tends to reduce the cell voltage. Although a 4 mol% addition of SrCO<sub>3</sub> drastically dropped the cell voltage, its addition does not prolong the cell's life time. A 9 mol% addition of the additives CaCO<sub>3</sub> or BaCO<sub>3</sub> seemed to keep the cell voltage comparable with conditions when no additive was present.

The effect of a larger addition of CaCO<sub>3</sub> or BaCO<sub>3</sub> was confirmed by the cell's extended operating time under an accelerated atmospheric condition. Fig. 2 shows the time profile of the tested cell voltage and cell resistance when using different amounts of additional CaCO<sub>3</sub>, 9 and 15 mol%. The 17 mol% addition of CaCO<sub>3</sub> caused an unstable cell voltage under load. The cell voltage with the 15 mol% addition of CaCO<sub>3</sub> did not attain a steady state and gradually decreased. The 9 mol% addition of CaCO<sub>3</sub> produces a cell voltage profile very similar to that of the cell voltage when no additive is present.

Fig. 3 shows the cell voltage profile for the addition of BaCO<sub>3</sub>. A 15 mol% addition of BaCO<sub>3</sub> did not yield a steady state. Under load, the cell voltage decreased with a 15 mol% addition of BaCO<sub>3</sub>; at that point, the loading of the tested cell was stopped. After several hours under no load conditions, the cell performance recovered. Most likely, the behavior exhibited by this cell profile was due to the segregation of BaCO<sub>3</sub> in the molten carbonate of content 15 mol% BaCO<sub>3</sub> of the electrolyte matrix [15]. Although, at an operating temperature of 650 °C, the carbonates were uniformly mixed in a static condition, the alkali and alkaline-earth cations might be segregated under load conditions due to

Table 2  
Operation condition of 81 cm<sup>2</sup>-single cell

	Atmospheric condition		Pressurized condition	
	Standard	Accelerated	Standard	Accelerated
Pressure	0.1 MPa		0.5–0.6 MPa	
Temperature	650 °C			
Anode	H <sub>2</sub> /CO <sub>2</sub> = 80/20			
Anode humidified temperature	50 °C		130 °C	
Fuel utilization	75%			
Cathode	Air/CO <sub>2</sub> = 70/30	O <sub>2</sub> /CO <sub>2</sub> = 15/85	Air/CO <sub>2</sub> = 70/30	O <sub>2</sub> /CO <sub>2</sub> = 15/85
Oxidant utilization	40%	50%	40%	50%
CO <sub>2</sub> utilization	40%	23%	40%	23%
Load	150 mA/cm <sup>2</sup>			

Gas ratios are in vol.%.

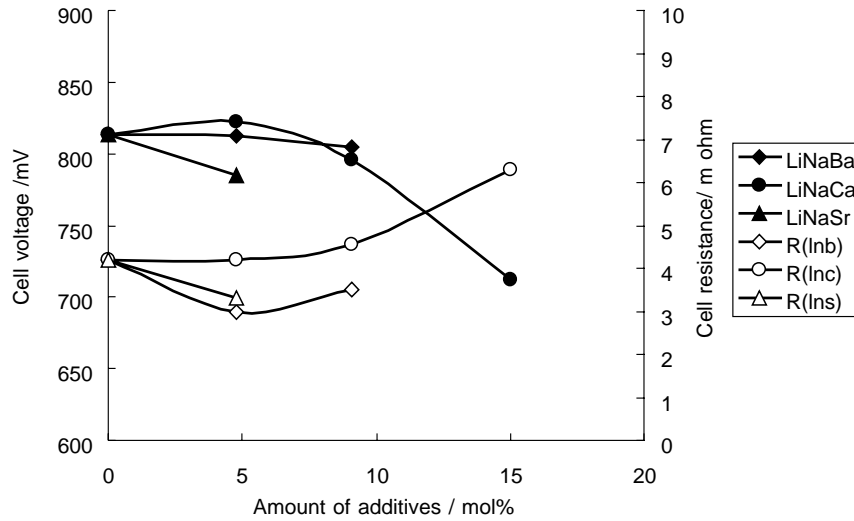


Fig. 1. The relation between the cell voltage at 150 mA/cm<sup>2</sup> and the amount of CaCO<sub>3</sub>, SrCO<sub>3</sub> and BaCO<sub>3</sub> additives to (Li<sub>0.52</sub>Na<sub>0.48</sub>)<sub>2</sub>CO<sub>3</sub> as the electrolyte.

the different mobility of the cations Li<sup>+</sup>, Na<sup>+</sup> and Ba<sup>2+</sup> in the molten carbonate. However, the tested cell with a 9 mol% BaCO<sub>3</sub> addition can be continuously operated for several thousand hours. The 9 mol% additions of CaCO<sub>3</sub> and BaCO<sub>3</sub> to 52 mol% Li<sub>2</sub>CO<sub>3</sub>–Na<sub>2</sub>CO<sub>3</sub> are expected to produce promising compositions for a long operation time.

### 3.2. Amount of additives

Although the tested cells with 9 mol% additions of CaCO<sub>3</sub> and BaCO<sub>3</sub> can be operated for several thousand hours under atmospheric conditions, the cell tested without additives also can be operated for long periods as shown in Figs. 2 and 3. The effect of additives on prolonging lifetimes is not

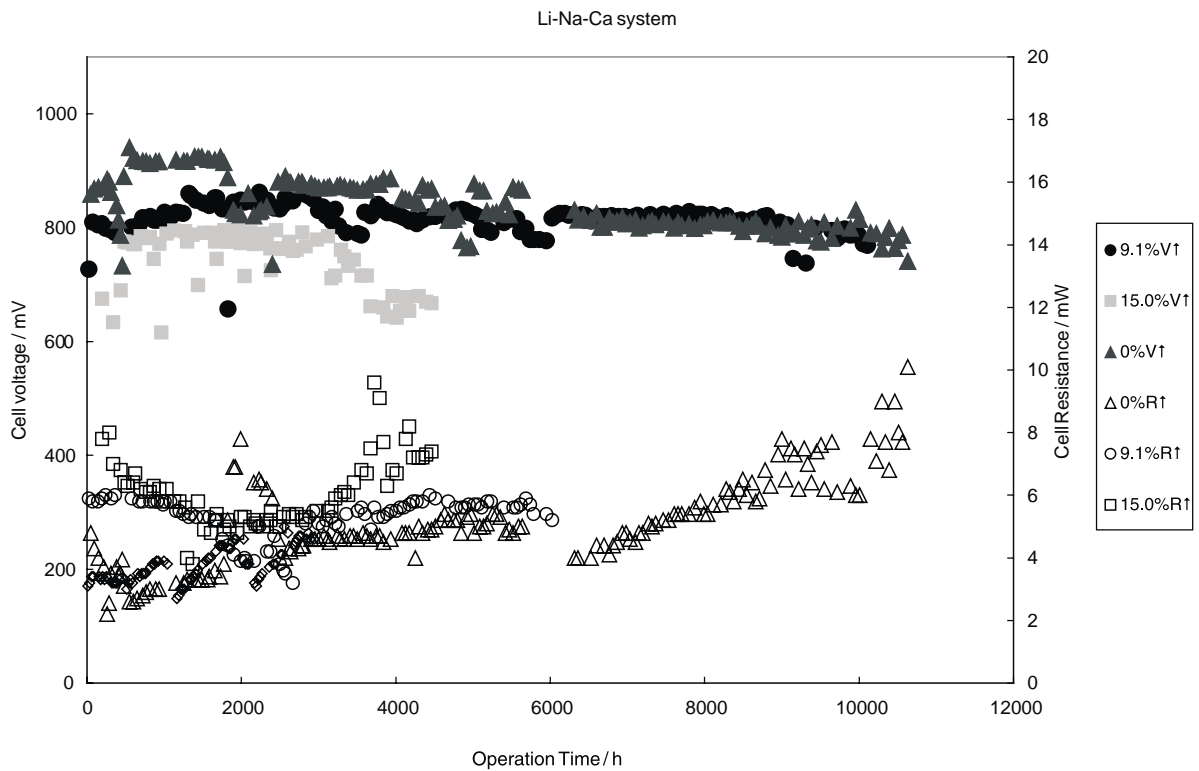


Fig. 2. Cell voltage at 150 mA/cm<sup>2</sup> and cell resistance of a 81 cm<sup>2</sup> single cell with a ternary carbonate electrolyte, Li<sub>2</sub>CO<sub>3</sub>–Na<sub>2</sub>CO<sub>3</sub>–CaCO<sub>3</sub>. The cells were operated under an accelerated atmospheric condition as shown in Table 2.

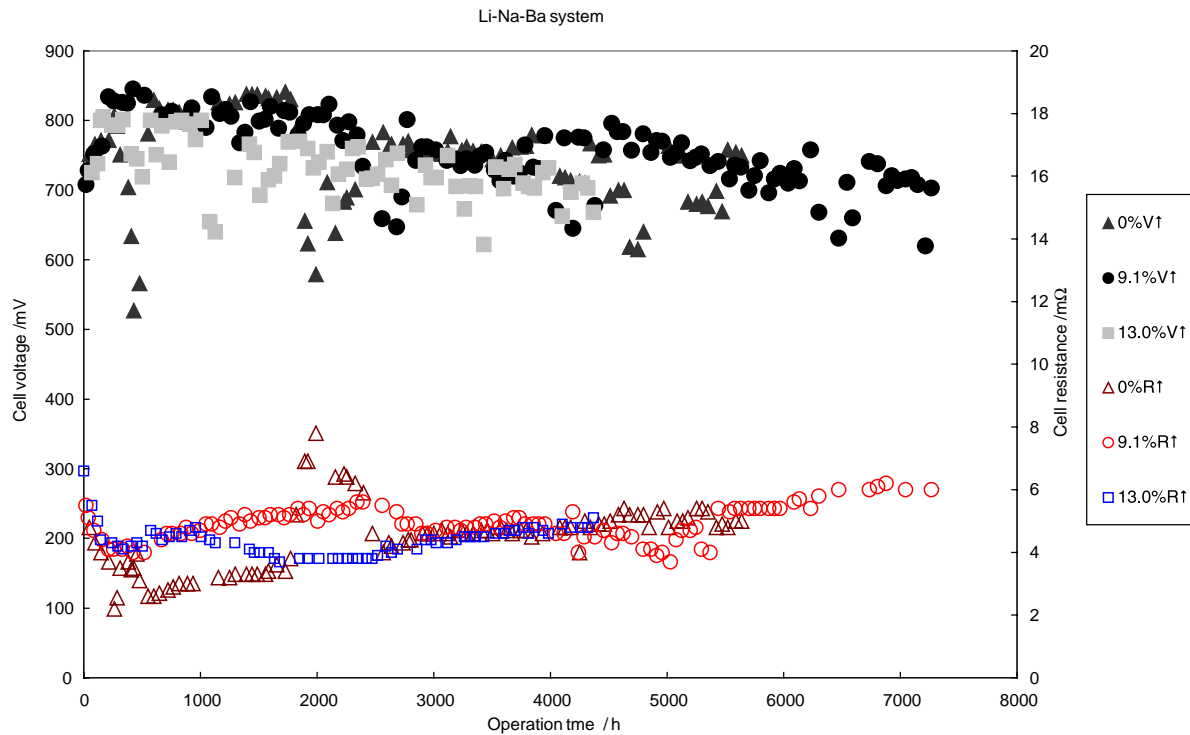


Fig. 3. Cell voltage at  $150 \text{ mA/cm}^2$  and cell resistance of a  $81 \text{ cm}^2$  single cell with a ternary carbonate electrolyte,  $\text{Li}_2\text{CO}_3\text{--Na}_2\text{CO}_3\text{--BaCO}_3$ . The cells were operated under an accelerated atmospheric condition as shown in Table 2.

clear under atmospheric conditions. The pressurized condition should lead to a reduced lifetime due to an increase in the dissolved nickel cation. This rise, in turn, is caused by an elevated NiO solubility at a higher partial pressure of carbon dioxide.

A larger amount of deposited metal nickel in the matrix led to the formation of many electrical paths, facilitating nickel shorting. When the nickel shorting occurred, the cell behavior showed a slow dropping of the OCV and a change in the anode outlet gas composition, such that the concentration of  $\text{CO}_2$  increased and that of  $\text{H}_2$  fell. The following reaction of  $\text{H}_2$  at the anode side describes the change:



When a leak, of either autoclave gas or reaction gas, took place, a degradation in the OCV was also observed. This situation may be distinguished from nickel shorting by analyzing the concentration of nitrogen in the anode outlet gas from the cathode side and/or in the autoclave gas. Table 3 shows the prolonging effect on cell life of adding 9 mol%  $\text{CaCO}_3$  or 9 mol%  $\text{BaCO}_3$  to a 52 mol%  $\text{Li}_2\text{CO}_3\text{--Na}_2\text{CO}_3$  mixture under both a pressurized and a high  $p\text{CO}_2$  accelerated condition. So that the effect of additives on the cell life might be evaluated under a pressurized and accelerated condition, the  $p\text{CO}_2$  at cathode side was 0.42–0.45 MPa. Fig. 4 shows the cell voltage profiles of the tested cell with additives of 9 mol%  $\text{CaCO}_3$  or 9 mol%  $\text{BaCO}_3$ , and with no additives. Arrows in Fig. 4 represent the onset of nickel shorting indicated by the changing point of  $\text{CO}_2$  concen-

tration at the anode. When additives were present, onset of nickel shorting was extended to 2050 h, compared with 1600 h for cells with no additives.

### 3.3. Effect of additives on the cell life

The solubility of nickel oxide in a 52 mol%  $\text{Li}_2\text{CO}_3\text{--Na}_2\text{CO}_3$  is reduced by 20% by a 9 mol% addition of  $\text{CaCO}_3$  or  $\text{BaCO}_3$ . The lifetime increased almost 15–20% as illustrated by the experimental results shown in Fig. 4. The amount of deposited nickel in the matrix after operation is presented in Table 3; here, we can see that, with additives, a larger amount of nickel is deposited, compared with conditions without additives. These results were not consistent with the expectation that a large amount of deposited nickel would cause the shorting to begin earlier. The relationship between the cell lifetime and such related properties as the amount of deposited nickel and the solubility of NiO, has

Table 3  
The additional effect of  $\text{CaCO}_3$  or  $\text{BaCO}_3$  to 52 mol%  $\text{Li}_2\text{CO}_3\text{--Na}_2\text{CO}_3$  on the nickel shorting

Composition	Shorting time (h)	Operating time (h)	Deposited Ni ( $\text{mg/cm}^2$ )
Non-additive	1655	2185	30.3
Non-additive	1624	2549	32.0
9 mol% $\text{CaCO}_3$	2059	2660	36.9
9 mol% $\text{BaCO}_3$	2031	2259	40.9

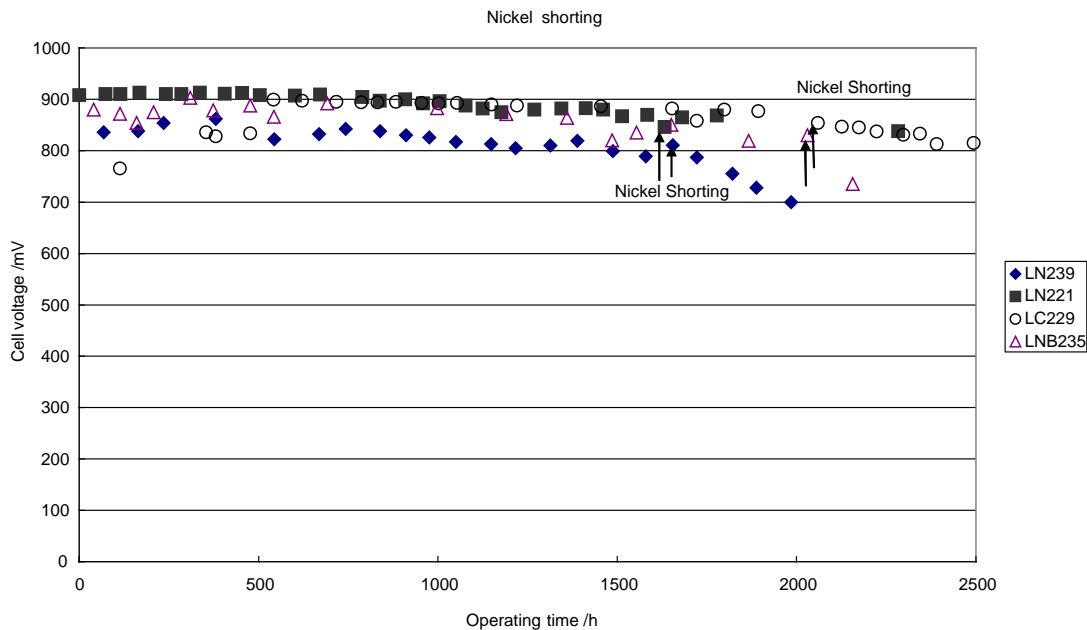


Fig. 4. Cell voltage at  $150 \text{ mA/cm}^2$  of a  $81 \text{ cm}^2$  single cell with binary and ternary carbonate electrolyte systems. LN239 and LN221 were operated using a  $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$  system. LNC229 and LNB235 were operated using a 9 mol% addition of  $\text{CaCO}_3$  or  $\text{BaCO}_3$  to the  $(\text{Li}_{0.52}\text{Na}_{0.48})_2\text{CO}_3$  system. The  $\uparrow$  symbol stands for the onset of shorting indicated by a reduction in the cell voltage. The cells were operated under a 0.58–0.60 MPa accelerated condition as shown in Table 2.

been investigated by a number of researchers. Some of them reported that the amount of deposited nickel in matrix and the shorting time were consistent with the above expectation [5,6]. There have been conflicts in the data and difficulties in explaining the long operation time results. The mechanism of nickel shorting should be clarified.

#### 4. Conclusion

The addition of an alkaline-earth carbonate to a 52 mol%  $\text{Li}_2\text{CO}_3\text{--Na}_2\text{CO}_3$  reduces the solubility of nickel oxide in the carbonates. From the cell performance data,  $\text{SrCO}_3$  is not a suitable addition due to the large cell voltage loss even at a 5 mol% concentration. The 9 mol% additions of  $\text{CaCO}_3$  and  $\text{BaCO}_3$  are promising compositions, under whose use the  $81 \text{ cm}^2$  single cell can be operated for a 15–20% longer time under an accelerated condition of 0.58 MPa and an 85%  $\text{CO}_2\text{--O}_2$  mixture at the cathode side.

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