

Performance of molten carbonate fuel cell with Li-Na and Li-K carbonate electrolyte at extremely high-temperature condition

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Abstract—The cell performance of Li-K and Li-Na carbonate electrolytes was compared using a coin type molten carbonate fuel cell operated at the extremely high temperature of 800 °C. It was an acceleration test to compare the performance in a short period. Electrochemical techniques such as steady state polarization (SSP) and impedance from the Nyquist plot were used in the cell performance analysis. The initial performance of both electrolytes was similar, but the performance of the Li-K electrolyte decreased drastically after 180 h. The results from SSP showed that the total overpotential of the Li-K electrolyte increased sharply, whereas that of Li-Na electrolyte had a continuous performance up to 340 h. The impedance analysis showed that the internal resistance of the Li-K electrolyte increased with time, but that of Li-Na electrolyte remained unchanged. The remaining amount of each electrolyte was determined, and it was observed that the electrolyte loss rate of the Li-K electrolyte was 0.0072 g/hr, and that of Li-Na electrolyte was 0.0028 g/hr. This implies that the electrolyte depletion rate of the Li-K electrolyte is about 1.5 times faster than that of the Li-Na electrolyte at the high-temperature condition. Thus, the cell of a Li-Na electrolyte containing MCFC according to the consumption of electrolyte is expected to be longer than one that uses Li-K electrolyte.

Keywords: Molten Carbonate Fuel Cell, Overpotential, High Temperature, Electrolyte Amount, Impedance

INTRODUCTION

The molten carbonate fuel cell (MCFC) is expected to be a future energy source because of its low energy loss due to the direct conversion of chemical energy into electrical energy. Also, high-efficiency power generation is possible because MCFC is operated at high temperatures around 650 °C [1-5]. Due to the high-temperature characteristics of MCFC, a rare catalyst such as Pt and Ru is unnecessary [6].

In general, the MCFC uses molten salt as the electrolyte. The molten salt melts at 500 °C or over to become a liquid which serves as an electrolyte. The main advantage of liquid electrolyte is that they easily impregnate the porous material such as electrode and matrix by capillary action and prevent leakage of gases [7,8]. However, the MCFC, which is operated at high temperatures for a long time,

have some problems associated with their usage and these include corrosion of cell components and electrolyte consumption. A previous study on electrolyte consumption [9] reported that the electrolyte depletion resulted in an increase in internal resistance and polarization resistance of a bench-type MCFC. Therefore, the reduction of cell life due to electrolyte consumption is a serious problem in the commercial MCFCs. It is, therefore, necessary to research into and find solutions to reduce electrolyte consumption rate in MCFC.

In this study, two electrolytes of Li-K ($\text{Li}_2\text{CO}_3 : \text{K}_2\text{CO}_3 = 62 : 38$ mol%) and Li-Na ($\text{Li}_2\text{CO}_3 : \text{Na}_2\text{CO}_3 = 52 : 48$ mol%) were used to investigate the effect of electrolyte species on the cell life. The Li-Na electrolyte has very similar properties as the Li-K electrolyte; it was reported that it could be used as a substitute for Li-K electrolyte [10].

According to Table 1, the ionic conductivity of Li-Na electrolyte

Table 1. Properties of each electrolyte [11]

	$\text{Li}_2\text{CO}_3 : \text{Na}_2\text{CO}_3 = 52 : 48$ mol%	$\text{Li}_2\text{CO}_3 : \text{K}_2\text{CO}_3 = 62 : 38$ mol%
Density (g/cm^3)	1.96	1.94
Conductivity (S/cm)	2.4	1.65
O_2 gas solubility ($\text{mol}/\text{cm}^3 \cdot \text{atm} \times 10^{-7}$)	~1	~2
Surface tension (mN/m)	243	217
Vaporization loss (g/cm^3)	-1.9×10^{-10}	-1.5×10^{-9}

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is 2.4 S/cm, which is about 1.5-times higher than the ionic conductivity of Li-K electrolyte. It means that the Li-Na electrolyte is expected to have a lower internal resistance than that of Li-K electrolyte. However, since the O_2 gas solubility is half lower than that of Li-K electrolyte, therefore higher mass transfer resistance at the cathode is expected to occur in Li-Na electrolyte. Due to the high surface tension of Li-Na electrolyte, there will be a low wetting at the anode because of the large contact angle between the electrolyte and the anode [7,8]. These problems cause an increase in mass-transfer resistance and a reduction in reaction surface area. However, due to the vaporization loss which is ten-times lower than that of Li-K electrolyte, it could be expected to have high stability against long-term operation at high temperature as compared with a cell using Li-K electrolyte. Thus, longer cell life in high-temperature condition may be expected when Li-Na electrolyte is used.

The high temperature of operating condition for an MCFC causes serious metal corrosion, and then increases the electrolyte depletion [12]. However, evaluation of the cell performance, including the problems, requires quite a long time over years. The extremely high-temperature condition of 800 °C could be an experimental way to accelerate metal corrosion and electrolyte depletion because the corrosion and electrolyte depletion are a function of temperature.

In this study, we compared the performance and cell life characteristics of Li-K and Li-Na electrolytes at 800 °C.

EXPERIMENTAL

A coin-type MCFC was used for the simplification of the experiment. A porous Ni-Al alloy was used as an anode, and in situ oxidized NiO was used as the cathode. The matrix used was made of $LiAlO_2$. The electrode and matrix were fabricated with the support of Korea Institute of Science and Technology (KIST). The electrodes were made circular constituting a diameter of about 3 cm. Gas conditions at anode were 125 : 25 : 25 cm^3/min flow rate of 72 mol% H_2 , 14 mol% CO_2 , and 14 mol% H_2O , respectively. At the cathode, a flow rate of 300 : 130 cm^3/min was supplied at a ratio of 70 mol% Air and 30 mol% CO_2 . All cells were operated under atmospheric pressure and 800 °C for the acceleration test. More details of cell preparation and operations are described in a previous work [13].

The electrolytes used in this work were $(Li+K)_2CO_3$ and $(Li+Na)_2CO_3$. Each electrolyte was made using the lowest eutectic point composition. In the case of Li-K electrolyte, 62 mol% of Li_2CO_3 and 38 mol% of K_2CO_3 were used, and for the Li-Na electrolyte, 52 mol% of Li_2CO_3 and 48 mol% of Na_2CO_3 were used. All cells were operated with 3 g of the electrolyte.

The cell performance was measured using electrochemical measurement method via steady-state polarization (SSP) and electrochemical impedance spectroscopy (EIS). The SSP measures the relation between voltage and current from 0 to 150 mA/cm^2 current density. The EIS measures the impedance by applying a 5 mV AC signal from 10 kHz to 10 mHz under open circuit state.

To estimate remaining amount of electrolyte in the cell after operation, the weight reduction ratio of the cells was calculated. The cell component after several hours of operation was dissolved into 300 mL of 10 wt% acetic acid for 24 h, and the weight before and

after dissolution was measured. The difference between the WBD (weight before dissolution) and the WAD (weight after dissolution) expressed as a percentage of the WBD is said to be the carbonate electrolyte's reduction ratio. Thus, WRR (weight reduction ratio) indicates the remaining amount of electrolyte in the cell [14].

$$WRR = \frac{WBD - WAD}{WBD} \times 100\% \quad (1)$$

RESULTS AND DISCUSSION

Figs. 1 and 2 show the cell performance analysis of cells using 3 g of each electrolyte with time. The acceleration test used a temperature of 800 °C and 1 atm pressure. The continuous line represents the open circuit potential, the dotted line represents the polarization potential at 150 mA/cm^2 , and the short-dashed line represents the internal resistance. Each of the electrolytes was tested twice.

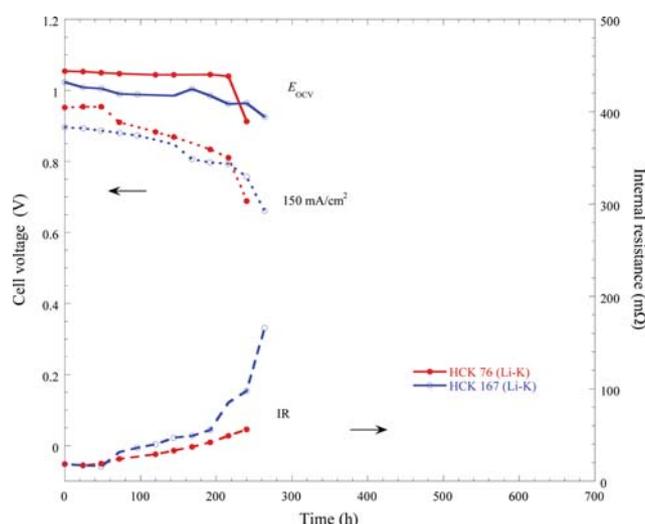


Fig. 1. The cell performance of 3 g Li-K electrolyte with time at 800 °C.

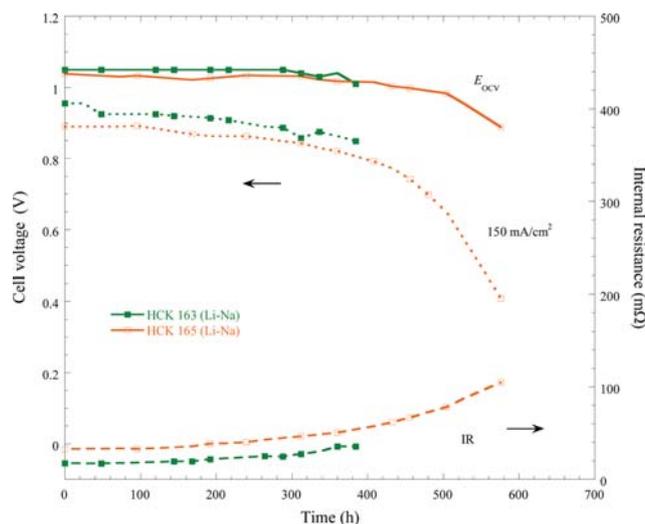


Fig. 2. The cell performance of 3 g Li-Na electrolyte with time at 800 °C.

Theoretically, the open circuit potential (E_{OCV}) of the MCFC is a function of the gas pressures and from Nernst Eq. (2) as follows:

$$E_{OCV} = E^0 + \frac{RT}{2F} \ln \left(\frac{p(\text{H}_2)p(\text{CO}_2)_{ca}p(\text{O}_2)^{0.5}}{p(\text{H}_2\text{O})p(\text{CO}_2)_{an}} \right) \quad (2)$$

where E^0 is the standard potential; T is the temperature of the operation; F is Faraday's constant; and subscripts an and ca represent the anode and the cathode, respectively. However, the actual voltage of the MCFC is smaller than the E_{OCV} , can be said to be due to the overpotential by the reaction and the resistance of cell components.

$$V = E_{OCV} - \eta_{tot} \quad (3)$$

Eq. (3) shows that the actual potential of the cell. The η_{tot} is expressed as $\eta_{ca} + \eta_{an} + \eta_{IR}$, the η_{IR} is the ohmic loss; η_{ca} and η_{an} are the overpotential due to the electrochemical reactions in the anode and cathode, respectively. When the polarization potential is increased by increasing the current density, the total overpotential is increased. This means that actual cell potential decreases also as observed from Eq. (3). Thus, the performance of the cell can be analyzed when the cell is operated for a long period of time. Through the analysis of the internal resistance and total overpotential, the electrolyte reduction in the cell and the performance decrease of the cell components due to the corrosion can be determined.

In Fig. 1, the E_{OCV} for the Li-K electrolyte is 1.038 V, which is similar to the theoretical E_{OCV} , 1.042 V, calculated from Eq. (2). It can be seen that the E_{OCV} rapidly decreased after about 180 h. It is estimated that the electrolyte in the cell reduces with the time, and then reducing the overall reaction area and the cell performance. Similar behavior was observed in the polarization potential at 150 mA/cm² and the internal resistance. In the case of the polarization potential, the initial value was 924 mV. However, the polarization potential decreased gradually with time, and after 180 h, it recorded a potential of about 815 mV, and the performance decreased drastically. It was assumed that the decrease in cell performance was due to a reduction in electrolyte amount, which caused the overpotential and the internal resistance to increase at each electrode. The effect was also observed through the behavior of the internal resistance with time. Theoretically, the internal resistance was affected by the electrolyte reduction in the cell. It showed that the reaction surface area in the cell had been reduced drastically due to depletion of the electrolyte and thus the electrolyte in the cell had decreased to such an extent that the performance of the cell could not be maintained.

On the other hand, Li-Na electrolyte had an initial E_{OCV} of 1.040 V. The E_{OCV} decreased after about 340 h, which is longer than that of the Li-K electrolyte. Also, the decrease rate in the E_{OCV} of the Li-Na electrolyte is slower than that of the Li-K electrolyte [11]. It was suggested that it could be due to the vaporization loss of the Li-Na electrolyte which is ten-times lower than that of Li-K electrolyte. In the case of the polarization potential, the initial value was 922 mV, and after 340 h, the potential was 852 mV. This could be attributed to the electrolyte depletion in the cell and the total overpotential increase as observed in the Li-K electrolyte. After 400 h of cell operation, the internal resistance of the cell was increased greatly and can be said to be due to a decrease in Li-Na electrolyte amount as

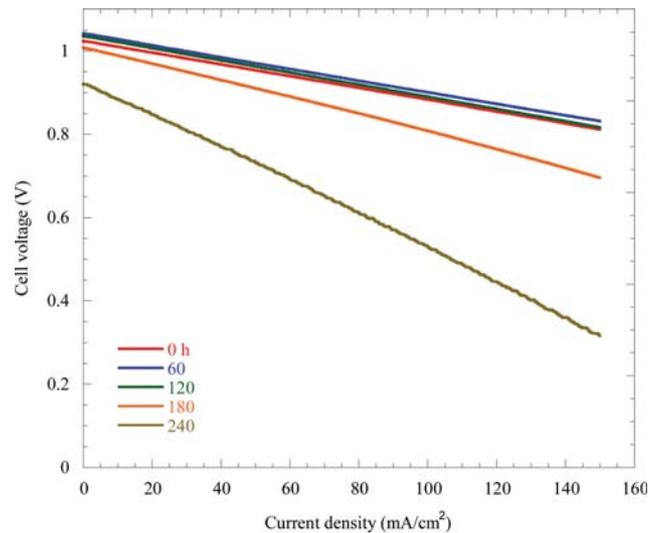


Fig. 3. Steady-state polarization behavior of 3 g Li-K electrolyte at 800 °C.

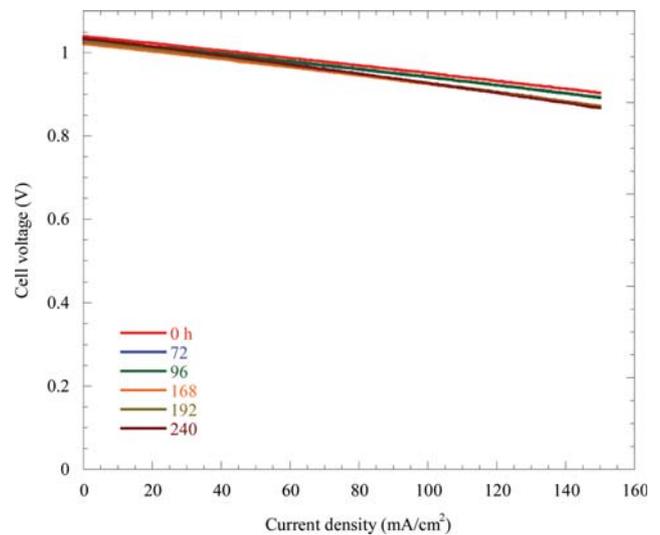


Fig. 4. Steady-state polarization behavior of 3 g Li-Na electrolyte at 800 °C.

suggested earlier in the case of Li-K electrolyte. The rate of increase in internal resistance of the Li-K electrolyte was 0.32 mΩ/h, while the Li-Na electrolyte recorded a rate of 0.11 mΩ/h. It can be seen that the Li-Na electrolyte exhibits a lower reduction rate than the Li-K electrolyte. Thus, it can be suggested that the Li-Na electrolyte can maintain a stable cell performance for longer periods of time than the Li-K electrolyte.

Figs. 3 and 4 show the steady-state polarization (SSP) behaviors of each electrolyte with the time. All cells were measured at 800 °C and atmospheric condition. The SSP method was used to analyze a current density range from 0 to 150 mA/cm²; it can measure the total overpotential (η_{tot}) in the cell using Eq. (3).

In Fig. 3, initial total overpotential of the Li-K electrolyte was 126 mV. The overpotential was almost unchanged at 115 mV until after 120 h. However, after 180 h, the overpotential was 188 mV,

which was an increase of about 60 mV compared with the initial performance. Also, after 240 h, the overpotential was 591 mV, indicating that the performance rapidly decreased within a short time. It was suggested that the overpotential in the cell was greatly increased due to the electrolyte depletion with time.

On the contrary, the initial overpotential of the Li-Na electrolyte was 135 mV. Unlike the Li-K electrolyte, the overpotential increased only about 33 mV after 200 h. It shows that the rate at which the total overpotential increased was slower compared with the Li-K

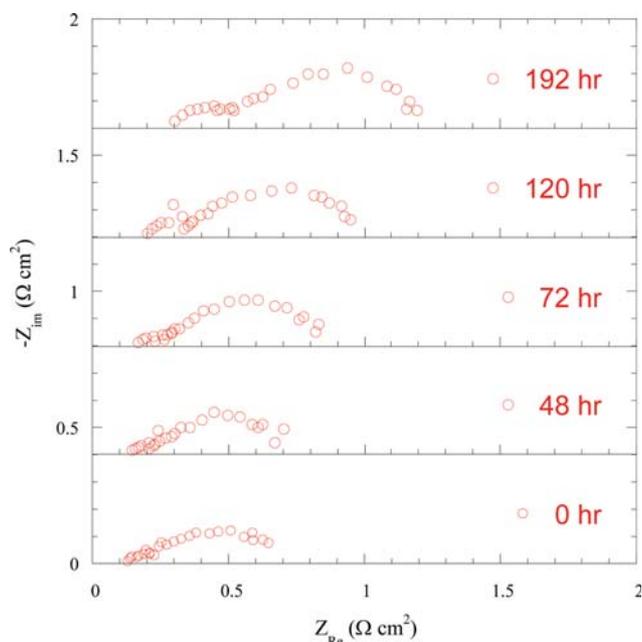


Fig. 5. Impedance behavior with 3 g of Li-K electrolyte according to the time at 800 °C.

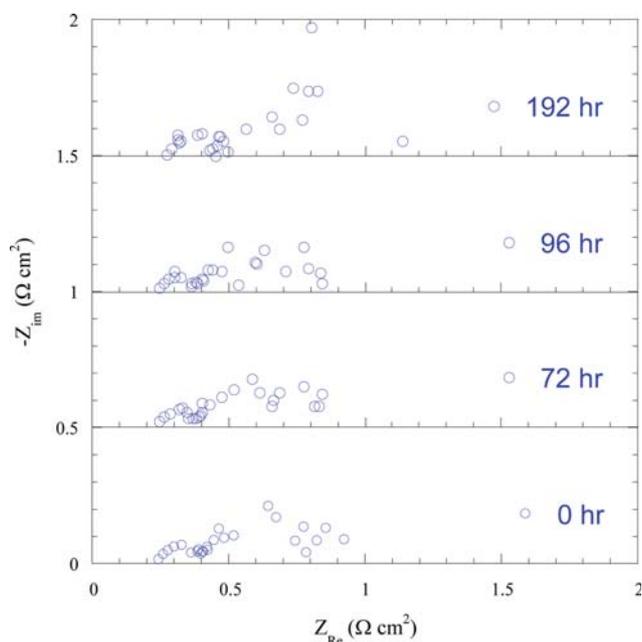


Fig. 6. Impedance behavior with 3 g of Li-Na electrolyte according to the time at 800 °C.

electrolyte. After 400 h, the overpotential was 221 mV, and then the cell performance began to increase rapidly. After 570 h, the total overpotential was 530 mV, and the performance dropped sharply. It can be seen that the rate at which the overpotential increases in the Li-Na electrolyte is lower than that of Li-K electrolyte.

This result is similar to the overall performance graphs shown in Figs. 1 and 2. Therefore, as the electrolyte in the cell is consumed, the reaction area decreases, leading to an increase in the mass-transfer resistance. The performance of a cell decreases sharply when the electrolyte is depleted by a certain amount or more.

Figs. 5 and 6 show impedance behavior of Li-K electrolyte and Li-Na electrolyte, respectively. In a previous study [15], the impedance behavior of the MCFC was divided by the three sections; the real resistance range from 0 to the starting point of the semi-circles represents the internal resistance due to the cell components, the half circle of high frequency represents cathodic overpotential due to the mass-transfer resistance through the liquid electrolyte, and the low-frequency semi-circle represents anodic overpotential due to the reaction resistance. Thus, it is possible to analyze the performance change of the cell with time through the impedance behavior.

In Fig. 5, the internal resistance and total overpotential at 0 h were $0.14 \Omega \text{ cm}^2$ and $0.65 \Omega \text{ cm}^2$, respectively. As time passed, an increase in internal resistance and total overpotential was observed. After 192 h, the internal resistance and the total overpotential were $0.29 \Omega \text{ cm}^2$ and $1.22 \Omega \text{ cm}^2$, respectively. It showed that the internal resistance and total overpotential increased to about two-times the internal resistance and total overpotential at the 0 h. This was because the electrolyte in the cell decreased with time, causing the internal resistance and the overpotential at the electrodes to increase due to depletion of the reaction area.

On the contrary, the internal resistance and total overpotential of the Li-Na electrolyte at 0 h were $0.23 \Omega \text{ cm}^2$ and $0.92 \Omega \text{ cm}^2$, which were larger than that of Li-K electrolyte. However, unlike the Li-K electrolyte behavior after 192 h, the internal resistance and total overpotential of the Li-Na electrolyte remained unchanged at all times. It means that the long-term cell performance of the Li-Na electrolyte is more stable than that of Li-K electrolyte due to the electrolyte consumption.

$$\begin{aligned} \text{Li-K electrolyte: Remaining electrolyte (g)} \\ = 0.147 \times \text{Weight reduction ratio (\%)} - 1.048 \end{aligned} \quad (4)$$

$$\begin{aligned} \text{Li-Na electrolyte: Remaining electrolyte (g)} \\ = 0.144 \times \text{Weight reduction ratio (\%)} - 0.996 \end{aligned} \quad (5)$$

Eqs. (4) and (5) are the relations between weight reduction ratio and remaining amount of electrolyte suggested in a previous study [14]. Fig. 7 shows the relationship between the total operation time and the remaining amount of electrolyte in each cell after the operation.

In Fig. 7, the electrolyte depletion rate of the Li-K electrolyte is 0.0047 g/h, and that of Li-Na is 0.0028 g/h. That is, the reduction rate of Li-Na electrolyte is about 1.5-times slower than that of Li-K electrolyte. As a result, the long-term characteristics of the Li-Na electrolyte are higher than that of Li-K electrolyte. Therefore, if Li-Na electrolyte is used, more long-term operation of the cell is expected compared with the Li-K electrolyte.

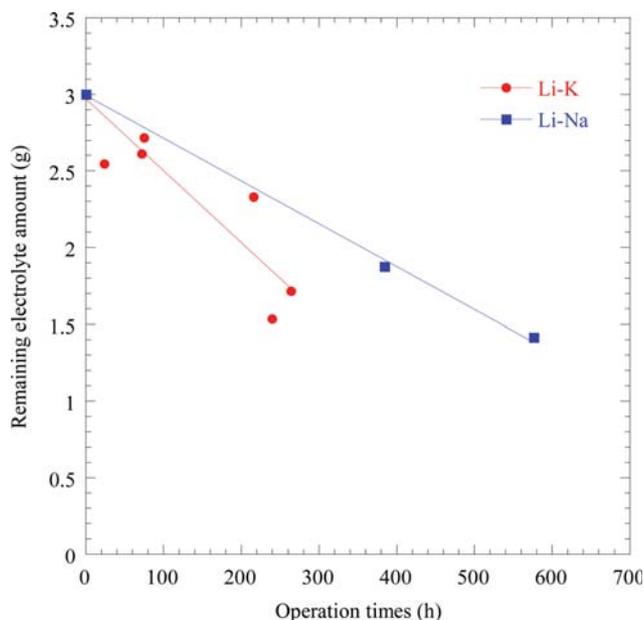


Fig. 7. Relationship between the remaining amount of electrolyte and total operation time at 800 °C.

CONCLUSION

We focused on the cell life characteristics with Li-K and Li-Na electrolyte in a molten carbonate fuel cell operated at the extremely high-temperature of 800 °C condition. The initial performance of both electrolytes was similar, but that of the Li-K electrolyte decreased after 180 h, and the Li-Na electrolyte was continuous for over 340 h. The SSP results show that the total overpotential of the Li-K electrolyte increased from 126 mV to 188 mV after 180 h, but the Li-Na electrolyte increased from 135 mV to 168 mV. Also, the impedance behavior showed that the internal resistance and total overpotential of the Li-K electrolyte at 0 h increased to about two-times after 180 h, whereas the internal resistance and total overpotential of the Li-Na electrolyte remained almost unchanged even after 300 h. As a result of calculating the remaining amount of electrolyte in the cell, the electrolyte loss rate of the Li-K electrolyte was about 0.0047 g/h, and that of the Li-Na electrolyte was about 0.0028 g/h. Thus, the electrolyte depletion rate for the Li-Na elec-

trolyte is about 1.5-times slower than that of Li-K electrolyte. So, longer cell life and better cell performance would be expected if Li-Na electrolyte is used than when the Li-K electrolyte is used.

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