

## Effects of fluoride on the performance of MCFCs

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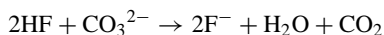
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### Abstract

To evaluate the effects of fluoride on the performance of molten carbonate fuel cells (MCFCs), bench-scale cell tests and half-cell experiments have been performed with fuel gas containing HF. The cell voltage does not change due to the addition of HF. According to the following reaction, most of the added HF reacts with carbonate ion to form fluoride ion, which accumulates in the electrolyte.



Hence, the carbonate loss and the decrease of the electrolyte volume have a negative effect on the cell-life expectancy. Moreover, a large number of fluoride ions causes corrosion on the cathode current collector. However, the MCFCs can generate electricity even if the electrolyte contains 40 mol% of LiF. There are no obvious effects of fluoride ion on the anode and cathode reaction.

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**Keywords:** Coal gas; Fluoride; HF; LiF; MCFC

### 1. Introduction

Coal gas is expected to serve as the primary fuel for MCFCs. Biomass gas and gasification gases derived from municipal solid waste are expected to reduce the dependence on fossil fuels. However, these gases contain many contaminants such as H<sub>2</sub>S, HCl, HF, NH<sub>3</sub> [1–3]. For example, coal gas without the cleanup contains approximately 200–1500 ppm H<sub>2</sub>S, 3–150 ppm HCl, 3–35 ppm HF and 200–1700 ppm NH<sub>3</sub>. Therefore, many of the contaminants have to be removed to meet acceptable concentration levels. The amount of contaminants is influenced by the fuels and the gasification process employed. The effects of H<sub>2</sub>S, HCl, and NH<sub>3</sub> on the cell performance and the cell-life expectancy have been reported [4–10]. However, the effects of HF on the cell performance are not clear. It has been reported that HF react with the carbonate to cause the carbonate loss; the results of corrosion tests [8] have also been reported. However, there is no report regarding the cell performance and the cell-life expectancy.

In this study, bench-scale cell tests and half-cell experiments are performed with fuel gas containing HF. The aim is to evaluate the effect of fluoride on the MCFC performance and the behavior of fluoride in the cell.

### 2. Experiments

#### 2.1. Long-term power generating tests

To evaluate the effects of HF on cell life, cell performance data have been obtained by using bench-scale cells with a 100 cm<sup>2</sup> effective electrode area manufactured by Hitachi Co. Ltd. The cathodes were made of lithiated NiO, and the matrices, which were made of LiAlO<sub>2</sub>, supported a mixture of lithium carbonate and sodium carbonate [Li/Na = 53/47 mol%], which was used as the electrolyte. The anodes were Ni-based alloys. The cathode current collectors were SUS316L, and the anode current collectors were Ni201. The basic operating conditions were: temperature, 650 °C; pressure, 0.49 MPa; current density, 150 mA cm<sup>-2</sup>; fuel gas, H<sub>2</sub>/CO/N<sub>2</sub> + Ar/CO<sub>2</sub>/H<sub>2</sub>O = 10.5/25.9/12.9/21.7/30; oxidant gas, air/CO<sub>2</sub> = 70/30; fuel utilization: 60%; and oxidant utilization: 40%.

For the test, during which fluoride was added to the fuel, gas cylinders containing Ar and F<sub>2</sub> (1000 ppm) were prepared, and the flow rates of the main gas (H<sub>2</sub>/CO/N<sub>2</sub>/CO<sub>2</sub>/H<sub>2</sub>O) and sub-gas (Ar/F<sub>2</sub>) were regulated for a target concentration of F.

According to the result of the thermodynamic calculation by MALT2, most of the added F<sub>2</sub> changes to HF in the conditions described above. For example, when 5 ppm F<sub>2</sub> is added to the fuel gas, there are HF 10.4 ppm, HCOF

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$6.67 \times 10^{-13}$ ,  $\text{CH}_3\text{F}$   $4.01 \times 10^{-14}$  and  $\text{F}_2$   $3.25 \times 10^{-41}$  at the anode inlet. Therefore, fluoride in fuel gas is assumed to be HF in the following discussion.

The concentration of HF in the inlet and outlet gases was analyzed by using gas analyzers manufactured by Kyoto Electronics Manufacturing Co. Ltd. It was confirmed that the concentration of HF in the inlet gas was approximately 10 ppm when 5 ppm  $\text{F}_2$  was added to the fuel gas.

## 2.2. Aptitude tests of the electrolyte

To investigate the effects of electrolyte, cell performance data of short-term tests has been obtained by using bench-scale cells with a  $9 \text{ cm}^2$  effective electrode area, which can decrease the testing time in comparison with  $100 \text{ cm}^2$  scale cell. The anodes were made of Ni-based alloys, and the cathodes were made of lithiated NiO. The matrices, which were made of  $\text{LiAlO}_2$ , supported the mixtures of lithium carbonate, sodium carbonate and lithium fluoride, which were used as the electrolyte. The mixture ratios were varied, however, according to the rule that the ratio of Li to Na in the electrolyte was constant [ $\text{Li}/\text{Na} = 53/47$  mole ratio]. The cathode current collectors were SUS316L [11], and the anode current collectors were Ni201 [12]. The basic operating conditions were: temperature,  $650^\circ\text{C}$ ; pressure, 0.10 MPa; and current density,  $100 \text{ mA cm}^{-2}$ .

## 2.3. Half-cell experiments

To investigate the effects of fluoride on the anode and cathode reaction, half-cell experiments were performed. Fig. 1 shows the schematic diagram of the experimental cell. The

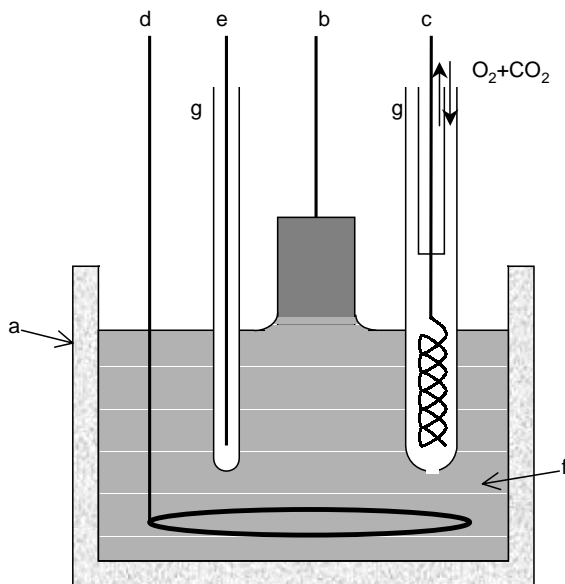


Fig. 1. Schematic diagram of experimental cell: (a)  $\text{Al}_2\text{O}_3$  crucible, (b) working electrode, (c) reference electrode, (d) counter electrode, (e) thermocouple, (f) electrolyte, (g)  $\text{Al}_2\text{O}_3$  tube.

chamber containing the cell was especially designed for controlling the atmosphere. There were four types of working electrodes. Those were two gold plates ( $\phi = 5 \text{ mm}$ ,  $t = 0.1 \text{ mm}$  and  $20 \times 20 \times 0.1 \text{ mm}$ ), a nickel plate ( $20 \times 20 \times 0.1 \text{ mm}$ ) and a porous nickel oxide plate ( $30 \times 10 \times 1 \text{ mm}$ ). The counter electrode is a gold-ringed wire. Potentials were referred to an Au ( $\text{O}_2/\text{CO}_2 = 33/67\%$ ) reference electrode. The mixtures of lithium carbonate, sodium carbonate and lithium fluoride,  $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3$  (53/47 mol%) and  $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3/\text{LiF}$  (22/38/40 mol%), were used as the electrolytes. The supplied gases were mixtures of  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2$  and  $\text{O}_2$ .

## 3. Results and discussions

### 3.1. Effects of HF on cell life

To evaluate the effects of HF on cell life, long-term tests with fuel gas containing 10 ppm HF and without HF were performed using  $100 \text{ cm}^2$  scale cells. Fig. 2 shows the changes in cell voltage and internal resistance. According to the diagram, the cell voltage and the internal resistance with 10 ppm HF and without HF do not differ.

The result of the anode outlet gas analysis in the test with 10 ppm HF is shown in Fig. 3. The anode outlet gas composition does not change much due to the addition of HF. The concentration of HF in the anode outlet gas is stable at the level corresponding to approximately 11% of the added HF.

After completing the tests, the solidified electrolyte was analyzed by X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and inductively coupled plasma (ICP) spectrometry. Fig. 4 shows AES and XPS spectra of the

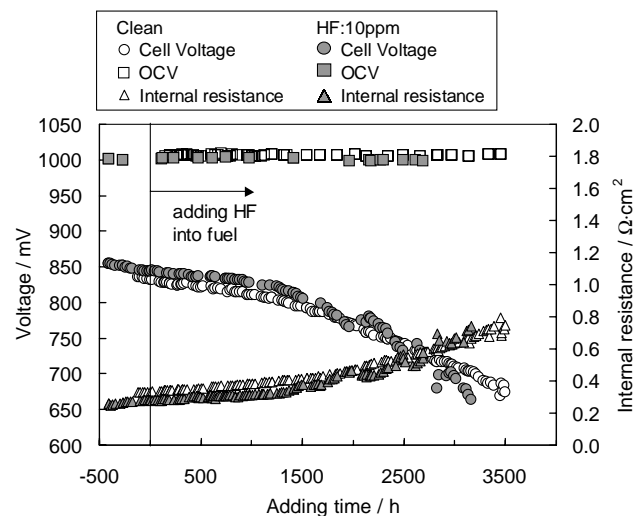


Fig. 2. Changes of cell voltage and internal resistance in two single cells operated at  $150 \text{ mA cm}^{-2}$  and  $650^\circ\text{C}$  with HF and without HF in the fuel gas. Fuel gas composition:  $\text{H}_2/\text{CO}/\text{N}_2 + \text{Ar}/\text{CO}_2/\text{H}_2\text{O} = 10.5/25.9/12.9/21.7/30$ ; fuel utilization: 60%; oxidant gas composition:  $\text{N}_2/\text{O}_2/\text{CO}_2 = 55/15/30$ ; oxidant utilization: 40%; pressure: 0.49 MPa.

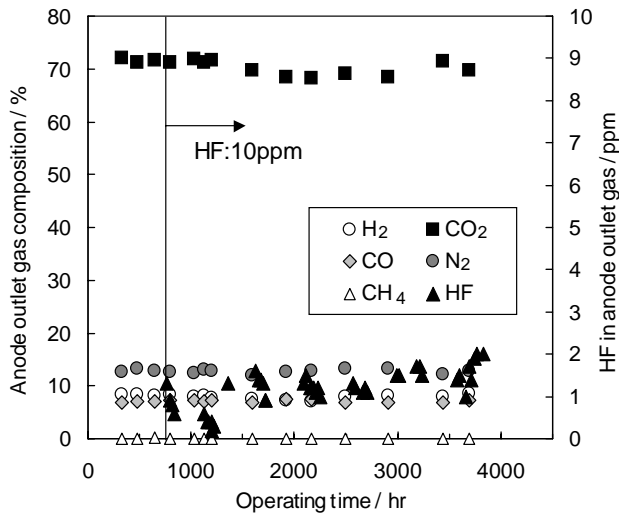
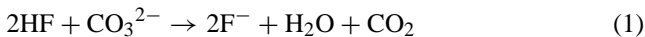


Fig. 3. Changes of anode outlet gas composition.

fluoride in the solidified electrolyte. The peak of NaF could not be detected by AES, whereas F 1s peak was observed at the binding energy, attributable to LiF, in the XPS spectrum. Therefore, the fluoride ion is considered to exist in the liquid electrolyte.

According to the result of the ICP analysis, the total amount of fluoride in the electrolyte was determined to be approximately 85% of the total HF added in the test with 10 ppm. It is considered that most of the added HF dissolves in the electrolyte and reacts with the carbonate ion to form fluoride ion according to the following reaction:



Moreover, it is clear that most of the added HF accumulates as fluoride ion in the electrolyte except for the HF passed through the cell. The accumulation of fluoride ion in the electrolyte is owing to the low vaporization of LiF and NaF [13]. When the fluoride compound in the

Table 1  
Concentration of LiF in electrolyte

Anode	28.4 mol%
Electrolyte plate	10.8 mol%
Cathode	8.6 mol%
Total	11.8 mol%

Table 2  
Electrolyte composition (mol%)

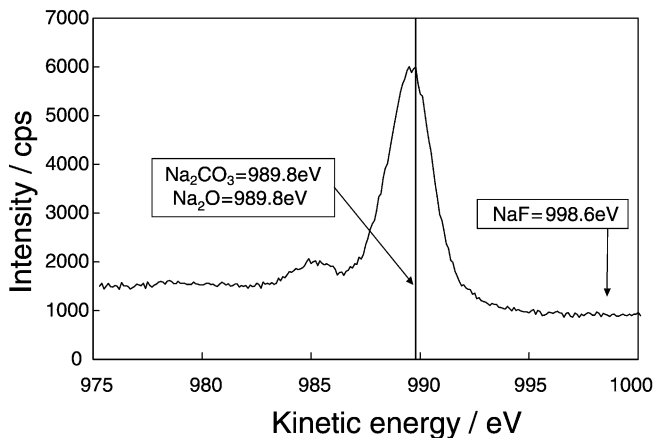
Cell	Li <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>	LiF	Li/Na ratio
1	53	47	0	53/47
2	45	45	10	53/47
3	38	43	19	53/47
4	26	39	35	53/47
5	22	38	40	53/47

electrolyte is assumed to be LiF, by the XPS and AES results, the amount of LiF in the electrolyte at each component is listed in Table 1. The total concentration of LiF in the electrolyte is about 12 mol%. Therefore, if the electrolyte contains 12 mol% of LiF, the cell performance is almost the same as that in the test without fluoride.

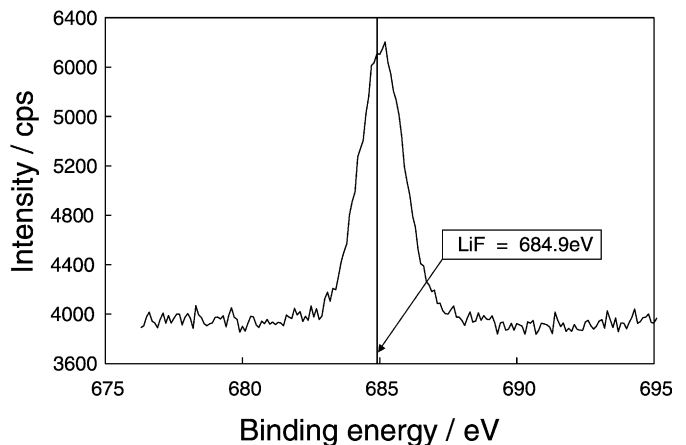
Furthermore, because the volume ratios of 2[LiF]/[Li<sub>2</sub>CO<sub>3</sub>] and 2[NaF]/[Na<sub>2</sub>CO<sub>3</sub>] are about 0.69 and 0.75, respectively [13], the volume of the electrolyte decreases by the reaction (1). Hence, when the operating time is long and the concentration of HF in fuel gas is high, the carbonate loss and the decrease of the electrolyte volume are thought to decrease the cell-life expectancy.

### 3.2. The effects of fluoride ion on the MCFC performance

To evaluate the effects of fluoride ion on the MCFC performance, the generating tests of electricity were performed with the electrolyte containing several different levels of LiF and using 9 cm<sup>2</sup> scale cells. Table 2 lists the electrolyte com-



(a) AES spectrum from Na-KLL transition



(b) XPS spectrum for F 1s

Fig. 4. AES and XPS analyses of fluoride in electrolyte.

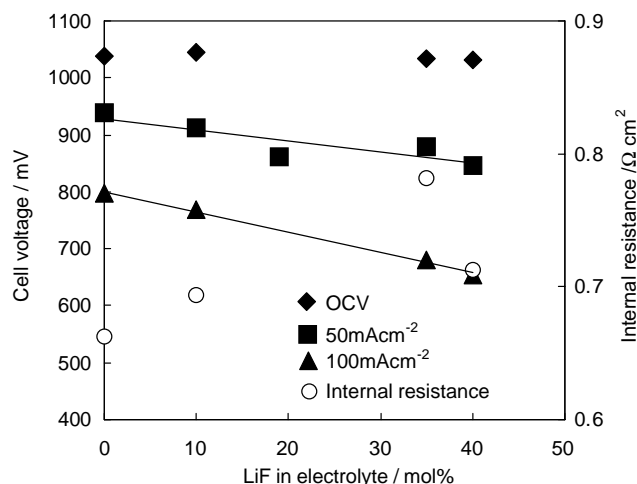


Fig. 5. Relationship between cell voltage and LiF concentration in electrolyte. Fuel gas composition:  $\text{H}_2/\text{CO}_2/\text{H}_2\text{O} = 67/19/14$ ; fuel utilization: 40%; oxidant gas composition:  $\text{air}/\text{CO}_2 = 65/35$ ; oxidant utilization: 63%; temperature:  $650^\circ\text{C}$ ; pressure: 0.10 MPa.

position of each cell. Cell 5, in which the electrolyte contains 40 mol% of LiF, was assumed to be operated for about 12,000 h with fuel gas containing 10 ppm HF. Fig. 5 shows the relationship between the cell voltage and the concentration of LiF in the electrolyte. A MCFC can generate electricity over  $0.065 \text{ W cm}^{-2}$ , even if the electrolyte contains 40 mol% of LiF. However, the cell performance decreases at a higher LiF concentration. Moreover, the internal resistances of the cell with LiF are higher than those of the cell without LiF.

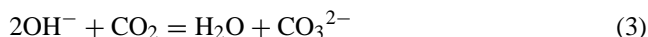
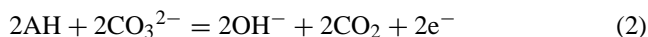
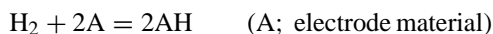
After completing the tests, it was confirmed that the concentration of LiF in the electrolyte did not change by ICP analysis. Moreover, the corrosion of the cathode current collectors was analyzed. Fig. 6 shows the cross sectional SEM images of the cathode current collectors of the cell with 40 mol% of LiF (cell 5) and without LiF (cell 1). The corrosion in the cell with LiF is more severe than that in the cell without LiF. Moreover, the corrosion in the cell with LiF ought to cause the creepage of the electrolyte and an

increase of the electrolyte loss. Hence, the corrosion and the electrolyte loss are some of the causes for the cell voltage drop caused by fluoride ion.

### 3.3. The effects of fluoride ion on the anode and cathode reaction

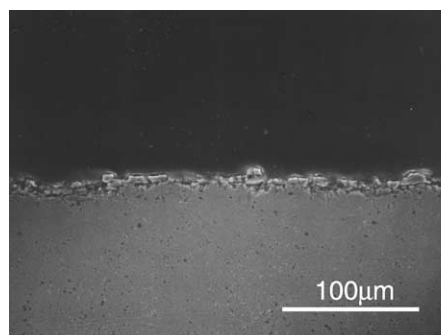
Other causes for the cell voltage drop provoked by fluoride ion are supposed to be the decrease of  $\text{CO}_3^{2-}$  activity and the increase of anode and cathode reaction resistance. To evaluate these fluoride ion effects, half-cell experiments were performed.

First, the behavior of fluoride in the electrolyte and the effect of fluoride ion on the anode reaction were investigated by applying a cyclic voltammetry. A cyclic voltammetry was carried out on a disk Au electrode ( $\phi = 5 \text{ mm}$ ,  $t = 0.1 \text{ mm}$ ) in a  $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3$  and a  $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3/\text{LiF}$  melt. The Au disk electrode was fully immersed in the electrolyte. Fig. 7 presents the cyclic voltammograms in  $\text{H}_2/\text{CO}_2/\text{H}_2\text{O} = 57/29/14$  at  $650^\circ\text{C}$ . The cyclic voltammograms have the same curves, and an effect of fluoride ion on the cyclic voltammogram cannot be observed. At around  $-1.1 \text{ V}$ , the rising of the anodic current is due to the oxidation of  $\text{H}_2$ , according to the following reactions [14]:

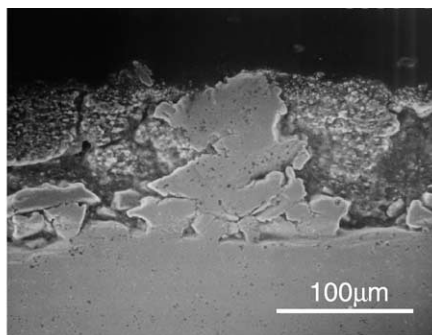


Because the peak current of the cyclic voltammogram is in direct proportion to the concentration and the square root of the diffusion coefficient of the reacting species [15], fluoride ion does not affect the diffusion coefficient and the solubility of  $\text{H}_2$  in the electrolyte.

Second, the effects of fluoride ion on the oxidation of hydrogen and the reduction of oxygen have been evaluated by the steady-state polarization method. Fig. 8 shows the steady-state polarization curves of hydrogen oxidation for Au plate in  $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3$  and  $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3/\text{LiF}$  melt. Two types of Au electrodes were used; a disk plate



(a) No.1 cell,  $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$



(b) No.5 cell,  $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-LiF}$

Fig. 6. Cross sectional SEM images of the cathode current collector.

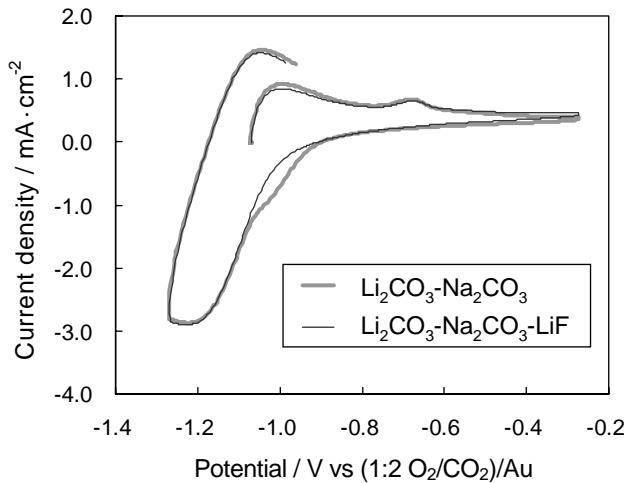


Fig. 7. Cyclic voltammograms for Au electrode in  $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3$  eutectic melt and  $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3/\text{LiF}$  melt. Electrolyte composition:  $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3 = 53/47$  mol%;  $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3/\text{LiF} = 22/38/40$  mol%; scan rate:  $0.2 \text{ V s}^{-1}$ ; inlet gas composition:  $\text{H}_2/\text{CO}_2/\text{H}_2\text{O} = 57/29/14$ ; temperature:  $650^\circ\text{C}$ ; pressure:  $0.10 \text{ MPa}$ .

( $\phi = 5 \text{ mm}$ ,  $t = 0.1 \text{ mm}$ ) and a square plate ( $20 \times 20 \times 0.1 \text{ mm}$ ). The Au disk electrode was fully immersed in the electrolyte, whereas the Au square electrode was partially immersed (5 mm) in the electrolyte. The immersed depth is defined as the distance from the electrolyte surface to the bottom of the electrode, as shown in Fig. 9. Regarding both Au electrodes, the steady-state polarization curve in the electrolyte containing LiF is almost the same as that in the electrolyte without LiF. Moreover, regarding all steady-state polarization curves, the current is saturated at over  $-950 \text{ mV}$ .  $\text{H}_2$  oxidation depends on the  $\text{H}_2$  supply in the electrolyte as described by Uchida and Nishina [14]. Hence, it is speculated that the decrease of  $\text{CO}_3^{2-}$  activity does not affect the oxidation of  $\text{H}_2$ .

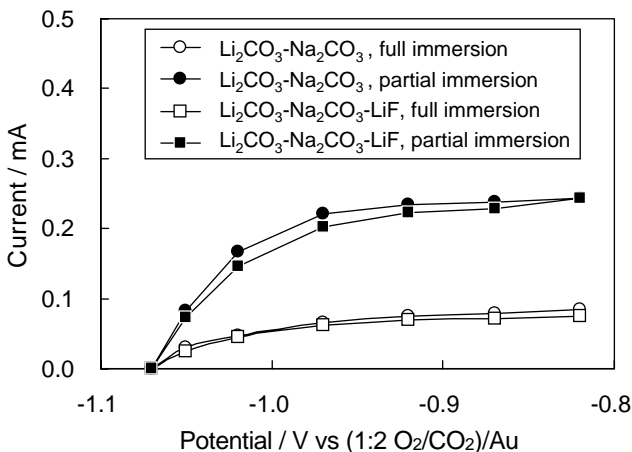


Fig. 8. Steady-state polarization curves of hydrogen oxidation for Au electrode in  $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3$  eutectic melt and  $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3/\text{LiF}$  melt. Electrolyte composition:  $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3 = 53/47$  mol%;  $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3/\text{LiF} = 22/38/40$  mol%; inlet gas composition:  $\text{H}_2/\text{CO}_2/\text{H}_2\text{O} = 57/29/14$ ; temperature:  $650^\circ\text{C}$ ; pressure:  $0.10 \text{ MPa}$ .

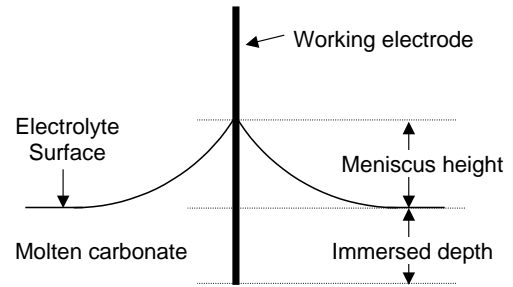


Fig. 9. State of working electrode in electrolyte.

Furthermore, Fig. 10 shows the steady-state polarization curves of oxygen reduction for a porous NiO electrode in a  $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3$  and a  $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3/\text{LiF}$  melt. The immersed depth of the porous NiO electrode was  $0.2 \text{ mm}$ . The pores of the NiO electrode were filled with electrolyte due to capillary force. The steady-state polarization curve regarding the electrolyte containing LiF is also almost the same as that in the electrolyte without LiF. Hence, the effect of fluoride ion on the oxygen reduction is also considered to be small.

Third, the effects of fluoride ion on the wetting characteristics of Ni have been evaluated. The measurement method of electrode wetting was that used earlier by the authors [16]. The electrode was immersed as shown in Fig. 9. The steady-state meniscus height was observed on a television monitor via a telescope and a charge coupled device (CCD) camera. Meniscus height data corresponds to the average value of three measurements recorded at different immersion depths of the same sample. Fig. 11 shows the effect of fluoride ion on the meniscus height. The wetting characteristic of Ni in the electrolyte containing LiF is almost the same as that in the electrolyte without LiF.

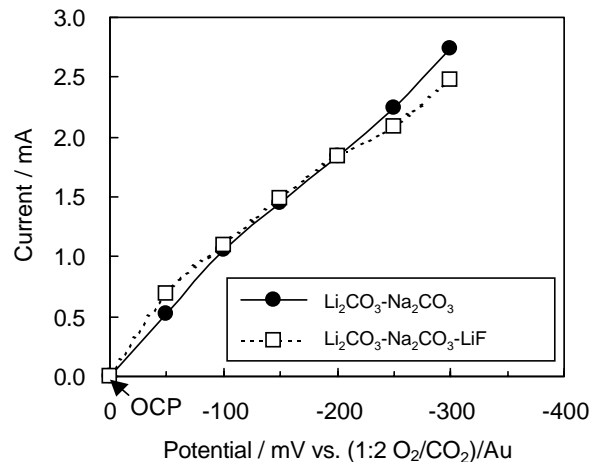


Fig. 10. Steady-state polarization curves of oxygen reduction for NiO electrode in  $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3$  eutectic melt and  $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3/\text{LiF}$  melt. Electrolyte composition:  $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3 = 53/47$  mol%;  $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3/\text{LiF} = 22/38/40$  mol%; inlet gas composition:  $\text{O}_2/\text{CO}_2 = 34/66$ ; temperature:  $650^\circ\text{C}$ ; pressure:  $0.10 \text{ MPa}$ .

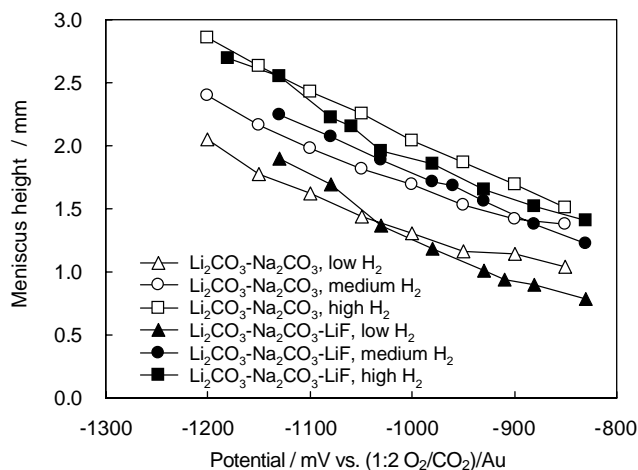


Fig. 11. Meniscus height variation with  $H_2$  partial pressure at  $650\text{ }^\circ\text{C}$ . Electrolyte composition:  $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3 = 53/47$  mol%;  $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3/\text{LiF} = 22/38/40$  mol%; inlet gas composition: low  $H_2$ ,  $H_2/\text{CO}_2/\text{H}_2\text{O} = 8/78/14$ ; medium  $H_2$ ,  $H_2/\text{CO}_2/\text{H}_2\text{O} = 29/57/14$ ; high  $H_2$ ,  $H_2/\text{CO}_2/\text{H}_2\text{O} = 69/17/14$ .

As the result of the half-cell tests, there are no obvious effects of fluoride ion on the anode and cathode reaction. The corrosion of the cathode current collector and the electrolyte loss are the main causes for the cell voltage drop caused by fluoride ion. Moreover, the decrease of the electrolyte volume and the carbonate loss, which are caused by changing  $\text{M}_2\text{CO}_3$  into  $\text{MF}$  (M: Li, Na), are also affecting the cell-life expectancy.

### 3.4. Acceptable concentration of HF

The MCFC development targets of the cell life and the degradation of the cell voltage are 40,000 h and  $0.3\%/1000$  h at  $200\text{ mA cm}^{-2}$ , respectively [17,18]. It was reported that the MCFC stack, which has 10 cells with a  $1\text{ m}^2$  effective electrode area, was operated for 10,000 h and the degradation rate of the cell voltage was about  $0.3\%/1000$  h [19]. When the cell such as the above MCFC, which has a high performance for the cell life, is operated in the same condition as in Fig. 2, the acceptable concentration of HF has been discussed in this section.

The cell performance with 10 ppm HF contained in the fuel gas is almost equal to that without HF for about 3000 h, as shown in Fig. 2. In the cell with 10 ppm HF, the mole ratio of  $\text{F}^-/(\text{F}^- + \text{CO}_3^{2-})$  in the electrolyte is about 0.12. Therefore, when the acceptable mole ratio of  $\text{F}^-/(\text{F}^- + \text{CO}_3^{2-})$  is defined as the condition that the cell performance with HF is almost equal to that without HF, the acceptable mole ratio of  $\text{F}^-/(\text{F}^- + \text{CO}_3^{2-})$  is 0.12. Moreover, when all of the added HF is assumed to accumulate in the electrolyte, the concentration of HF in the fuel gas should be kept below 0.67 ppm, to keep the mole ratio of  $\text{F}^-/(\text{F}^- + \text{CO}_3^{2-})$  from exceeding 0.12 until 40,000 h.

On the other hand, because a MCFC, in which the electrolyte contains 40 mol% of LiF, can generate electricity over  $0.065\text{ W cm}^{-2}$ , as shown in Fig. 5, the acceptable mole ratio of  $\text{F}^-/(\text{F}^- + \text{CO}_3^{2-})$  is assumed to be 0.4. In order to keep the mole ratio of  $\text{F}^-/(\text{F}^- + \text{CO}_3^{2-})$  from exceeding 0.4 until 40,000 h, the concentration of HF in the fuel gas should be kept below 2.3 ppm.

## 4. Conclusions

The cell performance with 10 ppm HF contained in the fuel gas is almost equal to that without HF. A small amount of added HF passes through the cell. Most of added HF reacts with carbonate ion to form fluoride ion. Moreover, fluoride ion accumulates in the electrolyte because of the low vaporization of LiF and NaF. Furthermore, MCFCs can generate electricity over  $0.065\text{ W cm}^{-2}$ , even if the electrolyte contains 40 mol% of LiF. There are no obvious effects of fluoride ion on the anode and cathode reaction.

However, the cell performance decreases at a higher LiF concentration. The internal resistances of the cell with LiF are also higher than those of the cell without LiF. The corrosion and the electrolyte loss caused by fluoride ion are the main causes for the cell voltage drop.

Therefore, when the operating time is long and the concentration of HF in fuel gas is high, the corrosion, the carbonate loss and the decrease of the electrolyte volume could be a problem for the cell-life expectancy. When the cell with HF is required to have the same performance as that without HF, the acceptable concentration of HF in the fuel gas is about 0.67 ppm to operate the MCFCs for 40,000 h.

## Acknowledgements

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