

## Effect of sulfur on the cell performance in a molten carbonate fuel cell

Ki-Jeong Lee, Samuel Koomson, and Choong-Gon Lee<sup>†</sup>

Department of Chemical & Biological Engineering, Hanbat National University,  
125 Dongseodaero, Yuseong-gu, Daejeon, 34158, Korea  
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**Abstract**—This study evaluated the performance characteristics of a molten carbonate fuel cell (MCFC) under sulfur poisoning condition. A 100 cm<sup>2</sup> bench-scale MCFC was used for the performance test. The performance of the cell at the normal operation condition was measured at 620 °C under atmospheric pressure. To evaluate the sulfur poisoning effect, 50 ppm H<sub>2</sub>S/Balanced N<sub>2</sub> gas mixture at a flow rate of 30 ml/min was injected into the anode. The cell performance was analyzed via steady-state polarization (SSP) and inert gas step addition (ISA) methods. The overpotential of the cell was observed to have been changed by the injection of H<sub>2</sub>S gas, and an overpotential increase of ca. 40% was recorded after about 100 hours from the point of addition of the H<sub>2</sub>S gas. A voltage reduction rate of  $-2.62 \times 10^{-4}$  mV/s was recorded at a current density of 150 mA/cm<sup>2</sup> after about 240 hours. The steady-state polarization characteristics of the cell showed that the sulfur poisoning was relatively slow. In addition, the effect of H<sub>2</sub>S gas on the cell performance was quantitatively measured by the ISA method.

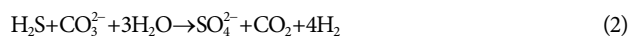
**Keywords:** Molten Carbonate Fuel Cell, Anode, Inert Gas Step Addition, Sulphur Poisoning, Overpotential

### INTRODUCTION

The molten carbonate fuel cell (MCFC) is a high-temperature fuel cell that is tagged as the next generation energy source. The MCFC converts chemical energy from chemical reactions directly into the electrical energy. This conversion occurs spontaneously at a high efficiency. Therefore, no catalyst is needed [1-5].

The main economic advantage of using MCFC is its fuel flexibility. Due to the high operating temperatures of MCFC, it is less affected by fuel gas composition. In other words, MCFC can operate using various hydrogen-based gases such as natural gas, biogas, coal gas, etc. However, some fuel gases can contain toxic substances. This contaminant can be harmful to the MCFC components, leading to a decrease in cell performance and cell-life. Sulfur compounds (H<sub>2</sub>S, COS, CS<sub>2</sub>) [6,7] and nitrogen compounds (NH<sub>3</sub>, NO<sub>x</sub>) [8] can seriously affect the cell components. Sulfur contaminants, in particular, are reported to affect reactions at the anode mainly [6,9]. The effect of sulfur-containing compounds on the performance and cell life of MCFCs has been studied using several methods [6,9-13].

The critical poisoning gas of the MCFC is known as H<sub>2</sub>S, which can react with cell components via electrode, electrolyte, and the current collector. In a previous work, it was reported that when H<sub>2</sub>S is supplied to the anode, the following reactions occur [10,11]:



H<sub>2</sub>S can react chemically with carbonate electrolyte and produce S<sup>2-</sup> or SO<sub>4</sub><sup>2-</sup> as shown in Eqs. (1) and (2), respectively. It means that

the cell performance will decrease because the carbonate ions are replaced by the sulfur-based anions. Especially, SO<sub>4</sub><sup>2-</sup> ions produced in Eq. (2) are highly involved in electrolyte consumption [13], which not only lowers the performance of the cell significantly but also shortens the life of the cell.

The MCFC cell components are made of a Ni-based metal such as Ni-Al or Cr alloy as the anode and in situ NiO as the cathode. Also, H<sub>2</sub>S can react with Ni at high temperatures over a long period of time. The reactions between H<sub>2</sub>S and Ni are as shown below [11]:



The Ni<sub>x</sub>S<sub>y</sub> on the electrode surfaces reduces the fuel gas reaction and also changes the wettability and contact angle of the anode with the carbonate electrolyte.

In summary, all reactions with sulfur compounds affect the electrochemical reaction in the anode [6]: Decrease in hydrogen oxidation reaction at the anode; change of the physical property of the anode, e.g. contact angle, wettability, ionic conductivity; covering the anode surface and porous structure. In this work, the effect of the sulfur poisoning was investigated, and the additional overpotential introduced by the impurity gas composition was quantitatively evaluated by inert gas step addition (ISA) method.

### EXPERIMENTAL

A 100 cm<sup>2</sup> bench type MCFC was used to investigate the effect of sulfur poisoning. The anode was made of Ni-Al metal powder. The cathode was made of Ni powder, and the matrix was made of LiAlO<sub>2</sub>. The electrolyte was made from a eutectic mixture of 52 mol% Li<sub>2</sub>CO<sub>3</sub> and 48 mol% Na<sub>2</sub>CO<sub>3</sub>. The choice of electrolyte was determined by a previous research done using 7 cm<sup>2</sup> coin-type

<sup>†</sup>To whom correspondence should be addressed.

E-mail: leecg@hanbat.ac.kr

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**Table 1. The gas utilization at each electrode for the normal condition**

$u_f$	0.4		0.6	
	Gas	Flow rate (ml/min)	Gas	Flow rate (ml/min)
Anode	H <sub>2</sub>	285	H <sub>2</sub>	190
	CO <sub>2</sub>	71	CO <sub>2</sub>	48
	H <sub>2</sub> O	40	H <sub>2</sub> O	26
Cathode	Air	665		
	CO <sub>2</sub>	285		
	H <sub>2</sub> O	31		

**Table 2. The gas utilization at each electrode for the additional H<sub>2</sub>S condition**

$u_f$	0.4		0.6	
	Gas	Flow rate (ml/min)	Gas	Flow rate (ml/min)
Anode	H <sub>2</sub>	285	H <sub>2</sub>	190
	CO <sub>2</sub>	71	CO <sub>2</sub>	48
	H <sub>2</sub> O	40	H <sub>2</sub> O	26
	H <sub>2</sub> S (50 ppm)	30	H <sub>2</sub> S (50 ppm)	30
Cathode	Air	665		
	CO <sub>2</sub>	285		
	H <sub>2</sub> O	31		

MCFCs [14]. All materials were made by MTFC Co. in Korea and Korea Institute of Science and Technology (KIST).

The cell was operated at 620 °C under atmospheric pressure. The anode was supplied with H<sub>2</sub>:CO<sub>2</sub>:H<sub>2</sub>O in the ratio of 72:18:10 mol% and the cathode was fed with Air, CO<sub>2</sub>, and H<sub>2</sub>O in the ratio of 68:29:3 mol%. The gases were supplied according to specific utilization ( $u_f$ ). The gas utilization was calculated based on Faraday's law for molar flows for the reactions of a cell. The utilization was calculated using Eq. (5):

$$u_f = \frac{\text{Required amount of reactant gas}}{\text{Amount of fed gas}} \quad (5)$$

Tables 1 and 2 show each operation gas condition used as computed from Eq. (5). For the additional H<sub>2</sub>S condition, the total flow rate was increased due to the addition of 30 ml/min of 50 ppm H<sub>2</sub>S/Balanced N<sub>2</sub> gas mixture. The concentration of H<sub>2</sub>S in the anode gas stream was 3.5 ppm and 5.0 ppm for utilizations 0.4 and 0.6, respectively.

Steady-state polarization (SSP) and ISA were used for the cell performance analysis. The SSP measures the relationship between current and voltage for a current density range of 0 to 150 mA/cm<sup>2</sup>. The ISA measures the overpotential at an electrode according to the mass transfer resistance by adding an inert gas, e.g., N<sub>2</sub> gas, at various flow rates to the electrode [15]. In this experiment, only the overpotential change in the anode was measured.

In a fuel cell, the open circuit voltage ( $E_{OCV}$ ) is determined by the partial pressure of reactant gas due to the following equation (6):

$$E_{OCV} = E^0 + \frac{RT}{2F} \ln \left( \frac{p(\text{H}_2)p(\text{CO}_2)_{ca}p(\text{O}_2)_{ca}^{0.5}}{p(\text{H}_2\text{O})p(\text{CO}_2)_{an}} \right) \quad (6)$$

where  $E^0$  is the standard voltage;  $T$  is the temperature of operation;  $F$  is Faraday's constant; and the subscripts *an* and *ca* denote the anode and cathode, respectively. Therefore, the theoretical voltage is determined only by the reactant gas partial pressure and the temperature of operation of the cell. However, the actual voltage is lower than expected due to the influence of the resistance existing in each electrode and other cell components.

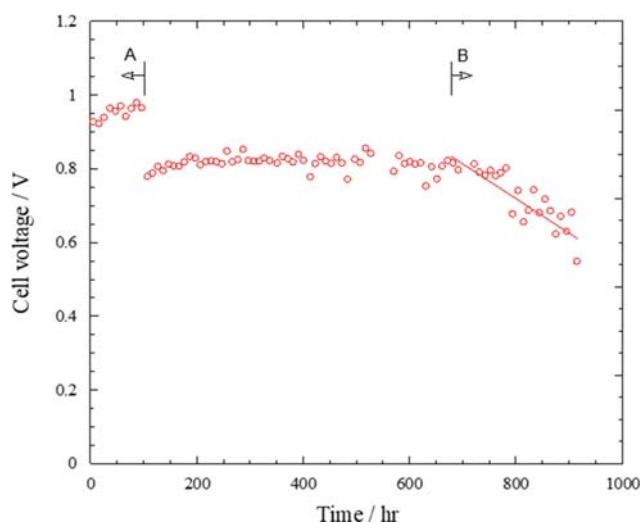
$$V = E_{OCV} - \eta_{IR} - (\eta_{an} + \eta_{ca}) \quad (7)$$

Eq. (7) represents the actual output voltage ( $V$ ). The  $E_{OCV}$  is the open circuit voltage;  $\eta_{IR}$  is the internal resistance due to the cell components,  $\eta_{an}$  and  $\eta_{ca}$  are the overpotential due to the chemical and physical reaction at the anode and cathode, respectively. Therefore, a change in cell performance can be seen through changes in the overpotential of  $\eta_{an}$  and  $\eta_{ca}$ .

## RESULTS AND DISCUSSION

Fig. 1 shows the voltage behavior of the cell with time. The section labeled "A" was the preconditioning process. The starting point of section "B" is the 0 hr of the H<sub>2</sub>S gas addition. A 150 mA/cm<sup>2</sup> current density was connected to the cell and the voltages measured are shown between the sections "A" and "B". After the preconditioning process, the  $E_{OCV}$  and the polarization voltage (at a current density of 150 mA/cm<sup>2</sup>) recorded at  $u_f=0.4$  was 1.086 V and 801 mV, respectively. To evaluate the stability of the cell performance, the cell was operated continuously for about 500 hours at  $u_f$  of 0.4 and a current density of 150 mA/cm<sup>2</sup> (section A-B).

The performance characteristics of the cell over a period of 240 hrs after the addition of 3.5 ppm H<sub>2</sub>S gas to the fuel gas are also shown in Fig. 1 as section "B". There were no significant changes in voltage when H<sub>2</sub>S was initially added; however, the cell performance dropped drastically after 100 hours from the injection of



**Fig. 1. Voltage behaviors with time at 620 °C,  $u_f=0.4$ , current density=150 mA/cm<sup>2</sup>.**

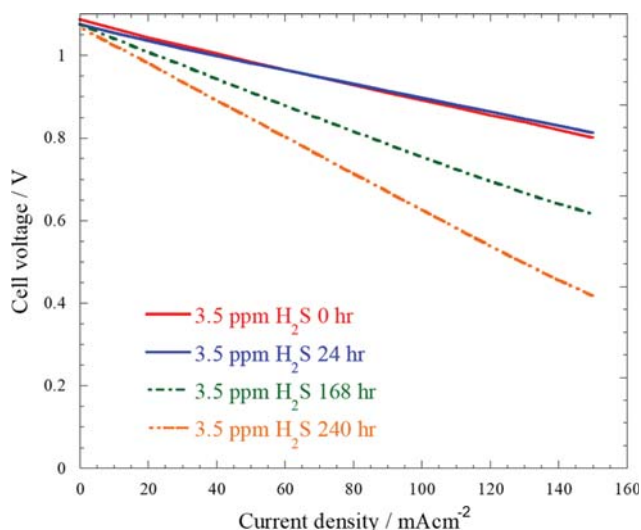


Fig. 2. Steady-state polarization behavior with time at 620 °C,  $u_f=0.4$ .

H<sub>2</sub>S gas. This showed that the poisoning reactions (1), (2), (3), and (4) caused by H<sub>2</sub>S gas proceeded slowly. After about 170 hours, the polarization voltage tended to decrease sharply because the reaction surface area was reduced due to the decrease in the electrolyte amount and corrosion of the cell components due to the S poisoning reaction. This result suggests that even a small amount of sulfur gas can have a significant effect on the cell performance. Also, the slope of the polarization voltages after the injection of 3.5 ppm H<sub>2</sub>S gas showed a voltage reduction rate of  $-2.62 \times 10^{-4}$  mV/s. This indicates that the poisoning reaction by sulfur was a very slow reaction, as stated in a previous report [2].

Fig. 2 shows the SSP behavior of cell voltages with time. All measurements were done at 620 °C and  $u_f=0.4$ . The SSP method helped in measuring the total overpotential of the cell. The total overpotential of the cell was computed from the difference between the open-circuit voltage and the polarization voltage at 150 mA/cm<sup>2</sup>. After a day of H<sub>2</sub>S gas injection, the total overpotential recorded at 150 mA/cm<sup>2</sup> was about 295 mV, which is not very different from the 285 mV recorded for the total overpotential at time 0 hr. However, after seven days of H<sub>2</sub>S gas injection, the total overpotential was 460 mV. It implies that the poisoning by sulfur seemed to increase the overpotential of the cell and could be attributed to the reaction between sulfur and the electrolyte as well as the electrode of the cell as shown in Eqs. (1) and (3). After ten days, the total overpotential recorded was 651 mV and was seen to have increased by 366 mV compared to the initial value. Therefore, it can be suggested that poisoning by the addition of a very small amount of sulfur had an influence on the reduction of cell life and performance.

In a previous work [15], the overpotential due to the gas phase mass-transfer resistance at the anode was suggested as follows:

$$\eta_{an} \cong q u_f^{0.5} \quad (8)$$

where  $q = 1.51 \frac{R^2 T^2 (I \cdot S \cdot L)^{0.5} v_A^{1/6} \phi}{(n^3 F^3 a^2 p_{0,A})^{0.5} D_{G,A}^{2/3}}$ ,  $u_f$  is the gas utilization, subscript A is the reaction species, S is the cross sectional area of gas

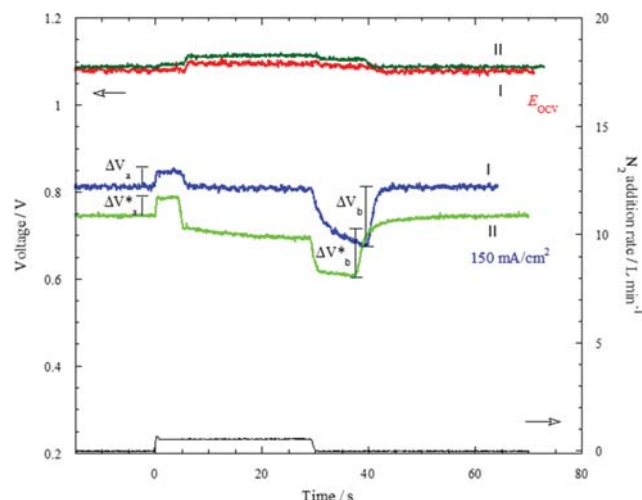


Fig. 3. ISA behavior of cell at 620 °C,  $u_f=0.4$ , N<sub>2</sub> flow=500 ml/min; I=normal gas condition, II=H<sub>2</sub>S 3.5 ppm additional condition.

channels,  $L$  is the electrode length,  $v_A$  is the kinematic viscosity of A,  $\phi$  is the Thiele modulus,  $p_{0,A}$  is the gas partial pressure in the bulk phase,  $a$  is the geometrical surface area,  $I$  is the current,  $D_{G,A}$  is the gas phase diffusivity of A,  $R$  is the molar gas constant,  $n$  is the number of reaction electrons,  $T$  is the temperature and  $F$  is the Faraday constant.

Therefore, if the partial pressure and the gas utilization are known, the overpotential at each electrode can be calculated. That is, when an inert gas is added to the anode, the partial pressure of the reactant gas and gas utilization is changed, which makes it possible to measure the overpotential caused by the added gas in the anode.

The height  $\Delta V_a$  in Fig. 3 was the overpotential recorded when N<sub>2</sub> gas was injected. Therefore, it is expected to possibly measure the overpotential quantitatively according to the flow rate of the reactant gas in the anode using the ISA method as shown in Eq. (9) [16].

$$\Delta V_a = m - q u_f^{0.5} \quad (9)$$

Fig. 3 shows the ISA result of the cell overpotential at the normal gas condition (I) and at H<sub>2</sub>S gas addition condition (II) under  $u_f$  of 0.4. The ISA measurement for condition (II) was done after about 100 hrs of H<sub>2</sub>S gas addition. N<sub>2</sub> gas was injected into the anode at 500 ml/min for 30 seconds to measure the overpotential change at open circuit voltage and at polarization voltage of 150 mA/cm<sup>2</sup> of current density. It was observed that the  $\Delta V_a$  was 35 mV when the inert gas was injected at the normal gas condition as shown in Fig. 3. This was because the addition of the inert gas instantaneously caused an overpotential reduction due to an increase in flow rate and a decrease in gas utilization at the anode. On the other hand, the overpotential change ( $\Delta V_a^*$ ) under the condition of 3.5 ppm H<sub>2</sub>S gas was about 45 mV as shown in Fig. 3, which is 10 mV higher than the overpotential observed at the normal gas condition. This increase in overpotential was suggested to be due to sulfur poisoning effect. Thus, it can be said that the H<sub>2</sub>S gas reacted with the electrolyte or the cell components, thereby causing a decrease in electrolyte amount or a reduction in the active surface area of the

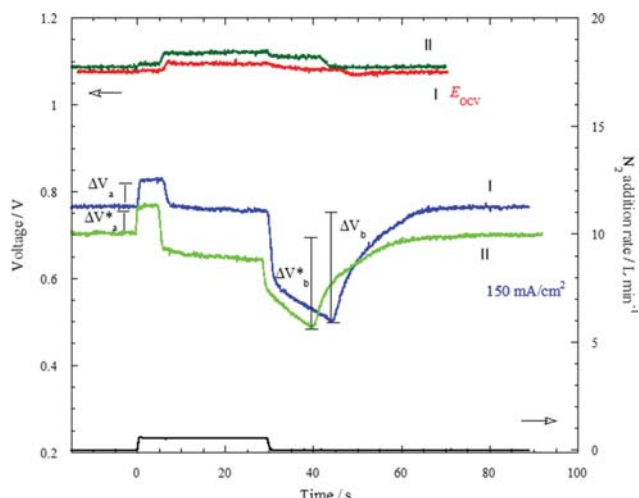


Fig. 4. ISA behavior of cell at 620 °C,  $u_f=0.6$ ,  $N_2$  flow=500 ml/min; I= normal gas condition, II=H<sub>2</sub>S 5.0 ppm additional condition.

electrode and hence increasing the mass transfer resistance, which was observed as an increase in overpotential.

Fig. 4 shows the ISA result of the cell overpotential at the normal gas condition (I) and at H<sub>2</sub>S gas addition condition (II) under  $u_f=0.6$ . It was observed that the overpotential change ( $\Delta V_a$ ) for the normal gas condition was about 62 mV, which is much bigger than the overpotential obtained at  $u_f=0.4$ . Larger overpotential at higher utilization is acceptable according to Eq. (8). When 5 ppm H<sub>2</sub>S gas was added, the overpotential ( $\Delta V_a^*$ ) was 65 mV. It can be suggested that the reactant gas partial pressure change by H<sub>2</sub>S gas addition did not become very large due to excessive N<sub>2</sub> gas at  $u_f=0.6$ .

In Figs. 3 and 4, a faster recovery behavior was observed in the

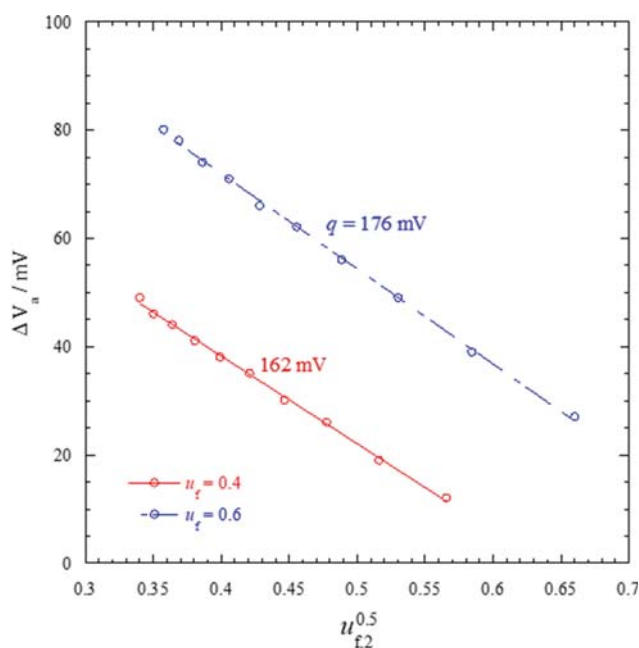


Fig. 5. The  $q$  value of the anode for the normal gas condition at 620 °C, current density=150 mA/cm<sup>2</sup>.

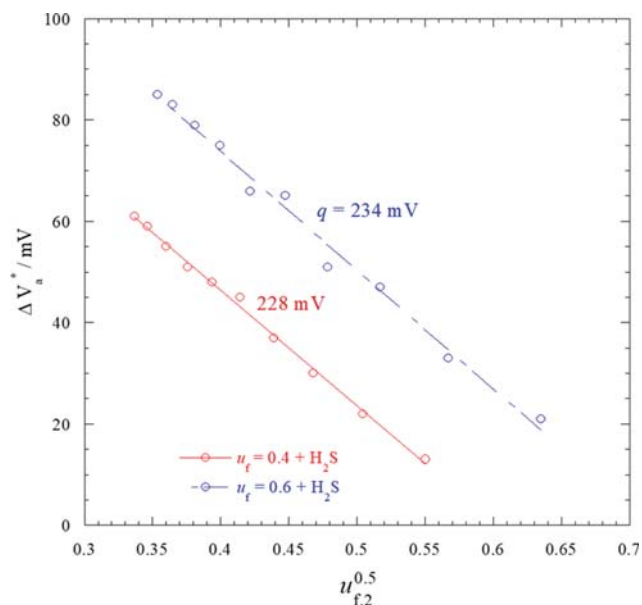


Fig. 6. The  $q$  value of the anode for H<sub>2</sub>S additional gas condition (3.5 ppm at  $u_f=0.4$  and 5.0 ppm at  $u_f=0.6$ ) at 620 °C, current density=150 mA/cm<sup>2</sup>.

case of additional H<sub>2</sub>S condition than the normal condition. This was due to the different total flow rate in both cases. The total flow rate increased by 30 ml/min due to the addition of 50 ppm of H<sub>2</sub>S/Balanced N<sub>2</sub> gas mixture as mentioned in Table 2. In addition, the starting point for the relaxation in the additional H<sub>2</sub>S condition ( $\Delta V_b^*$ ) was faster than in the normal condition ( $\Delta V_b$ ), but it can be confirmed that the return to steady state occurred at similar times. This observation can be attributed to the relatively small reaction surface area due to the sulfur poisoning. The width of the peak  $\Delta V_a^*$  is smaller than peak  $\Delta V_a$  due to the dilution of the nitrogen gas by the 5 ppm H<sub>2</sub>S gas in both Figs. 3 and 4.

Figs. 5 and 6 show the change in overpotential ( $\Delta V$ ) against gas utilization obtained via the ISA method and Eq. (9) at normal gas condition (Fig. 5) and at sulfur added condition (Fig. 6). The inert gas (N<sub>2</sub>) was added to the anode in a range of 100 to 1,000 ml/min at 100 ml/min interval. The overpotential changes and gas utilizations obtained from Figs. 3 and 4 were used in plotting Figs. 5 and 6. According to the results from Fig. 5, the slopes were almost similar to values of 162 and 176 mV at gas utilizations of 0.4 and 0.6, respectively. The average of the two values gave a  $q$  value of 169 mV at normal condition. As mentioned, the slope expresses the quantitative changes in anodic overpotential by the mass transfer resistance in fuel gas. When we use Eq. (8), the anodic overpotential at  $u_f=0.4$  and 0.6 is 107 and 130 mV, respectively. In Fig. 6, the slopes at gas utilizations of 0.4 and 0.6 were 228 and 234 mV, respectively. Thus, an average of the two gave a  $q$  value of 231 mV at H<sub>2</sub>S present condition. This shows an increase of 62 mV in the  $q$  value by the sulfur poisoning. The anodic overpotential at sulfur present condition was 146 mV and 179 mV at  $u_f=0.4$  and 0.6, respectively. Thus, the sulfur addition increases anodic overpotential by 39 mV at  $u_f=0.4$  and 49 mV at  $u_f=0.6$ . Therefore, the reaction of sulfur with the electrolyte or electrode reduces the active surface area of the anode, which

in turn increases the mass transfer resistance and hence increases the overpotential. Thus, it can be deduced from the results that sulfur poisoning caused ca. 40% additional overpotential at the anode and that was measured and compared quantitatively by the ISA method.

## CONCLUSION

Performance degradation by sulfur poisoning was evaluated for a bench-scale MCFC. In the normal gas condition of  $u_f=0.4$ , the  $E_{OCV}$  was 1.086 V, and the polarization voltage at 150 mA/cm<sup>2</sup> was about 801 mV. After a 500 hour performance stabilization test, 3.5 ppm of H<sub>2</sub>S gas was injected into the anode to investigate the sulfur poisoning effect. The voltage degradation rate by sulfur poisoning after 240 hours from the point of H<sub>2</sub>S gas addition was  $-2.62 \times 10^{-4}$  mV/s, indicating that the sulfur poisoning reaction was a slow reaction. Also, the overpotential remained unchanged after the sulfur gas was immediately injected, but after ten days, the overpotential increased by 366 mV compared to the initial overpotential.

According to the ISA results, when H<sub>2</sub>S gas was added, an additional overpotential was introduced for the utilization ratios of 0.4 and 0.6, respectively. It was suggested that the sulfur gas caused additional overpotential due to the poisoning. Also, the  $q$  value, which is the overpotential change according to changes in gas utilization, was obtained via Eq. (14). As a result, it was confirmed that the overpotential changes were 39 and 49 mV larger than that of the normal gas condition at utilization ratios of 0.4 and 0.6, respectively. This corresponded to ca. 40% increase in the anodic overpotential. It can therefore be concluded that, sulfur poisoning in the anode can reduce the cell performance and the cell life. In addition, the use of the ISA method for quantitative measurement of overpotential at each electrode is feasible.

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