

# Exploration of hydrogen odorants for fuel cell vehicles<sup>☆</sup>

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## Abstract

The suitability of sulfur compounds (e.g., mercaptan and sulfide) and various sulfur-free smelling compounds for hydrogen odorants were evaluated. The influence of each smelling compound on fuel cell performance was evaluated through the measurement of  $I$ - $V$  curves and voltage decline under constant current density, and their condensation properties under high-pressure condition were evaluated by measuring their vapor pressures. The results indicated that all the sulfur compounds evaluated in this study were not suitable as hydrogen odorants since their addition to the hydrogen caused serious degradation of fuel cell performance. Among the sulfur-free compounds, however, some oxygen-containing compounds (2,3-butanedione, ethyl isobutyrate and ethyl sugar lactone) and an unsaturated hydrocarbon (5-ethylidene-2-norbornene) proved to be promising candidates since their adverse effects on the fuel cell performance were minimal and their vapor pressures were adequate.

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**Keywords:** Odorant; Hydrogen leakage; Detection threshold; Electrode catalyst; Poisoning

## 1. Introduction

To pave the way for the widespread use of fuel cell vehicles, a standard concerning their safety and reliability needs to be established. While a wide variety of compounds can be employed as fuels for fuel cell vehicles, currently, at the most advanced stage of development is the polymer electrolyte fuel cell system fueled by hydrogen. To use hydrogen in large quantities for fuel cell vehicles, the safety of handling hydrogen must be achieved. Hydrogen is a flammable gas, which has no color or smell, so it is very important to establish a reliable and practical method of detecting hydrogen leakage.

Although there are several types of hydrogen sensors, they have some demerits. For example, they can be affected by other gases, ambient temperature and humidity. Furthermore, the sensors cannot detect without electricity and the cost will be high since many will be needed if only sensors are used to detect hydrogen.

On the other hand, regulations concerning city gas and LPG require an odorant to be added to these gases for leak

detection. This leak detection method using human olfactory sense has been spreading and has worked effectively as a safety measure for many years. Although there is no such requirement for hydrogen, the development of a hydrogen odorant is in demand as a promising means of leak detection. Currently, mercaptan and sulfide additives among sulfur compounds are mixed into city gas and LPG as odorants. However, since sulfur compounds, for example, hydrogen sulfide, is known to poison the electrode catalysts of fuel cells [1,2] and thereby seriously impair their electric generation performance, sulfur compounds may not be suitable odorants for hydrogen.

This paper reports evaluation results concerning the suitability of sulfur compounds (e.g., mercaptan and sulfide) and various sulfur-free compounds as hydrogen odorants.

## 2. Experimental

### 2.1. Candidate compounds evaluated in this study

The sulfur compounds evaluated in this study are listed in [Table 1](#). Their detection thresholds listed in [Table 1](#) is the data reported by Japan Environmental Sanitation Center [3], and

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Table 1  
Sulfur-containing smelling compounds

Functionality	Compounds (abbreviation)	Formula	Detection threshold (ppm)
Mercaptans	Ethyl mercaptan (EM)	C <sub>2</sub> H <sub>5</sub> SH	8.7 × 10 <sup>-6</sup> [3]
	Allyl mercaptan (AM)	CH <sub>2</sub> =CHCH <sub>2</sub> SH	N/A
	Isopropyl mercaptan (IPM)	(CH <sub>3</sub> ) <sub>2</sub> CHSH	6.0 × 10 <sup>-6</sup> [3]
	<i>tert</i> -Butyl mercaptan (TBM)	(CH <sub>3</sub> ) <sub>3</sub> CSH	2.9 × 10 <sup>-5</sup> [3]
Sulfides	Dimethyl sulfide (DMS)	CH <sub>3</sub> SCH <sub>3</sub>	3.0 × 10 <sup>-3</sup> [3]
	Ethylmethyl sulfide (EMS)	C <sub>2</sub> H <sub>5</sub> SCH <sub>3</sub>	N/A
	Allylmethyl sulfide (AMS)	CH <sub>2</sub> =CHCH <sub>2</sub> SCH <sub>3</sub>	1.4 × 10 <sup>-4</sup> [3]
	Tetrahydrothiophene (THT)	C <sub>4</sub> H <sub>8</sub> S	6.2 × 10 <sup>-4</sup> [3]
	Diethyl sulfide (DES)	C <sub>2</sub> H <sub>5</sub> SC <sub>2</sub> H <sub>5</sub>	3.3 × 10 <sup>-5</sup> [3]
	<i>tert</i> -Butyl methyl sulfide (TBMS)	(CH <sub>3</sub> ) <sub>3</sub> CSCH <sub>3</sub>	N/A

they had been measured by the triangle odor bag method [4]. These 10 compounds were selected from among the compounds currently in use as odorants for city gas and LPG and among the smelling compounds that are yet to be used as odorants. The sulfur-free compounds shown in Table 2 were selected from among smelling compounds on the basis of the boiling point and toxicity data retrieved from the Online Reagent Catalog [5] or with the cooperation of the Japan Flavor and Fragrance Materials Association. Some of their detection thresholds were found in the reference [3], and others were measured by the triangle odor bag method.

## 2.2. Estimation of the appropriate concentration of hydrogen odorants

Japanese regulations require that when city gas or LPG leaks into the air, the gas must be noticed by its smell when the mixture ratio of gas to the air becomes more than 1/1000. The lower flammable limit of hydrogen is 4 vol%, which is much higher than the ratio of 1/1000 (=0.1 vol%). Assuming the same ratio is applied to hydrogen, the concentration of an odorant in hydrogen should be at least 1000 times the recognition threshold (concentration at which the odor becomes discernible). Since available data indicate that the recognition threshold can be roughly approximated to 10× detection threshold and a safety factor of 10 times is deemed reasonable to account for individual differences in olfactory sensitivity, the necessary concentration of an odorant additive in hydrogen was assumed to be 10<sup>5</sup> times the detection threshold (hereafter “estimated legal concentration”).

## 2.3. Electrochemical measurements

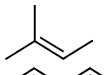
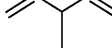
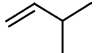
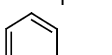
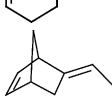

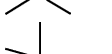
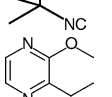
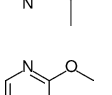
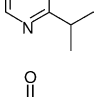
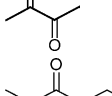
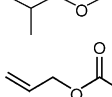
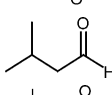
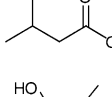
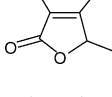
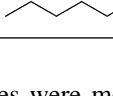
A JARI standard single cell [6] was employed as single cell to evaluate fuel cell performance, and a PRIMEA<sup>®</sup> with a GORE-SELECT<sup>®</sup> membrane, a Pt/Pt (anode/cathode) catalyst and an electrode area of 25 cm<sup>2</sup> was used as membrane electrode assembly. As anode gas, pure hydrogen (purity > 99.99999%) and hydrogen mixed with a smelling compound were used. They were mixed to adjust the concentration of odorant by regulating the flow rate of these gases.

As cathode gas, compressed air was employed. A mass flow controller was applied to regulate the flow rate of each gas. To humidify anode gas, a vaporizer system was used to prevent the soluble compounds from being trapped in water. In the vaporizer system, water, whose flow rate was regulated by a liquid mass flow controller, was mixed into the heated container with anode gas. Cathode gas was humidified with the bubbling method. The cell temperature was set at 80 °C, anode dew point at 77 °C, cathode dew point at 70 °C and cell exit at the atmospheric pressure for both anode and cathode. For the electrochemical measurement, the As-510 fuel cell measurement system (NF Corporation) was used, which consisted of the TYO30830 electric load and FRA5095 frequency response analyzer.

For the primary evaluation of the influence of smelling compounds on fuel cell performance, the current density was varied up to 1000 mA/cm<sup>2</sup> and *I*-*V* curves were measured for each 5-min period at various current densities. The flow rates of anode gas and cathode gas were set at 249 mL/min (*U*<sub>f</sub> = 70% per 1000 mA/cm<sup>2</sup>) and 1037 mL/min (*U*<sub>a</sub> = 40% per 1000 mA/cm<sup>2</sup>), respectively. For the secondary evaluation, those smelling compounds whose voltage drop ratio recorded at 1000 mA/cm<sup>2</sup> was less than 2% underwent a 10-h continuous electric generation test at a constant current density of 1000 mA/cm<sup>2</sup>.

The concentration of each smelling compound additive in hydrogen was set at the estimated legal concentration. In the case that the vapor pressure of a compound was too low to refill at the estimated legal concentration, it was tested at the maximum allowable concentration. The flow rate of anode gas was set at an excessive level of 1000 mL/min (*U*<sub>f</sub> = 17%) to obtain poisoning effects in a short time. The flow rate of cathode gas was set at 1037 mL/min (*U*<sub>a</sub> = 40%). AC impedance measurements were carried out within a frequency range between 0.1 and 1000 Hz during the continuous electric generation test to evaluate the poisoning effect on the electrode catalyst and electrolyte. All impedance spectra reported herein were measured between anode and cathode. For those compounds that had exhibited a voltage drop of less than 2% at the estimated legal concentration and could therefore be considered as promising candidates for hydrogen

Table 2  
Sulfur-Free Smelling Compounds

Functionality	Compounds (abbreviation)		Detection threshold (ppm)
Unsaturated hydrocarbons	2-Methyl-2-butene (2M2B)		[5] 1.4
	3-Methyl-1,4-pentadiene (3M14PD)		$2.8 \times 10^{-1}$
	3-Methyl-1-butene (3M1B)		$3.7 \times 10^{-1}$
	1,3-Cyclohexadiene (13CHD)		$1.2 \times 10^{-2}$
	5-Ethylidene-2-norbornene (5E2NB)		$1.7 \times 10^{-4}$
Amines	Trimethylamine (TMA)		$3.2 \times 10^{-5}$ [3]
Isocyanides	<i>tert</i> -Butyl isocyanide (TBIC)		$8.7 \times 10^{-4}$
Pyrazines	2-Isopropyl-3-methoxypyrazine (2iP3MP)		$3.7 \times 10^{-8}$
Ketones	2,3-Butanedione (23BD)		$5.0 \times 10^{-5}$ [3]
Esters	Ethyl isobutyrate (EIB)		$2.2 \times 10^{-5}$ [3]
	Allyl trifluoroacetate (ATFA)		$1.9 \times 10^{-1}$
Aldehydes	Isovaleraldehyde (IVAL)		$1.0 \times 10^{-4}$ [3]
Carboxylic acids	Isovaleric acid (IVAC)		$7.8 \times 10^{-5}$ [3]
Furanones	5-Ethyl-3-hydroxy-4-methyl-2(5 <i>H</i> )-furanone (ethyl sugar lactone) (ESL)		$1.0 \times 10^{-9}$
Lactones	$\gamma$ -Nonanoic lactone (GNL)		$2.5 \times 10^{-6}$
Ionones	$\beta$ -Ionone (BIO)		$1.1 \times 10^{-6}$

odorants, their concentrations were increased from the estimated legal concentration level and the continuous 10-h electric generation test was carried out under  $1000 \text{ mA/cm}^2$ , since odorant can accumulate in the hydrogen circulation system.

#### 2.4. Measurements of vapor pressure

When a container is filled with hydrogen at high pressure, the vapor pressure of the odorant needs to be such that the odorant will not condensate in order to maintain adequate odor intensity. Accordingly, for those compounds for which only a small poisoning effect had been recorded, their vapor

pressures were measured. The static measurement method was used for those compounds predicted from their boiling points to have a relatively high vapor pressure, and the transpiration method was used for those predicted to have a low vapor pressure.

### 3. Results and discussion

In the measurement of  $I$ - $V$  curves, all mercaptan compounds exhibited a major deterioration of electric generation performance. The case of *tert*-butyl mercaptan (TBM)

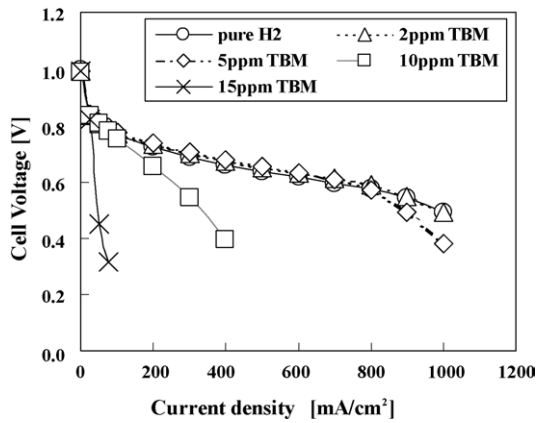


Fig. 1. Current–voltage polarization curves obtained at various concentrations of *tert*-butyl mercaptan (TBM).

is shown in Fig. 1 as an example, in which the concentration varies up to 15 ppm. The voltage dropped sharply with increase of concentration, thus suggesting a severe poisoning of the catalyst. On the other hand, the voltage drop was moderate with many of the sulfide compounds. *I*–*V* curves obtained by supplying diethyl sulfide (DES) containing hydrogen are shown in Fig. 2. Although the diethyl sulfide was added up to 20 ppm, the *I*–*V* curves almost overlapped those of pure hydrogen. Similarly, no marked voltage drop was recorded with many of the non-sulfur compounds tested.

Among the compounds that indicated only a moderate voltage drop (less than 2% at 1000 mA/cm<sup>2</sup>), those compounds that were considered suitable for hydrogen odorants due to their low detection threshold were selected and subjected to a continuous electric generation test at the current density of 1000 mA/cm<sup>2</sup> as the secondary evaluation. In this measurement, these compounds were mixed with hydrogen at their estimated legal concentrations. Among sulfur compounds, only diethyl sulfide was selected and subjected to secondary evaluation. The result is shown in Fig. 3(A). Be-

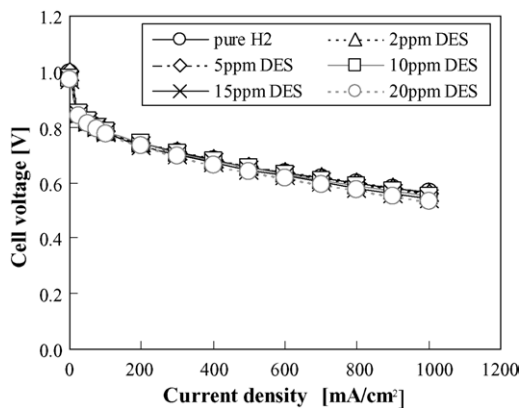


Fig. 2. Current–voltage polarization curves obtained at various concentrations of diethyl sulfide (DES).

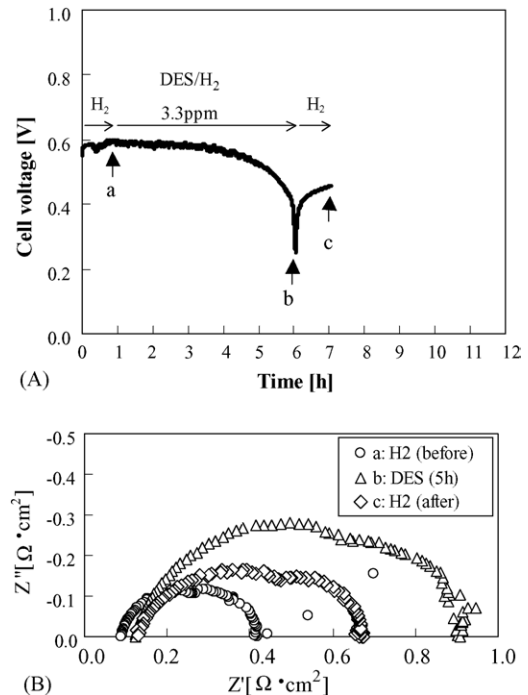


Fig. 3. (A) Deterioration of cell performance caused by 3.3 ppm of diethyl sulfide (DES). Current density = 1000 mA/cm<sup>2</sup>. The explanatory notes (a–c) show the points at which AC impedance spectra were measured; (B) changes of cell impedance caused by 3.3 ppm of diethyl sulfide (DES). The points (a–c) at which AC impedance spectra were measured are shown in (A).

fore supplying odorant-containing hydrogen, the cell was operated in pure hydrogen for 1 h. After supplying 3.3 ppm of diethyl sulfide for about 5 h, a rapid voltage drop was recorded. After that, the voltage recovered only partly even though pure hydrogen was supplied for 1 h. The AC impedance analysis was carried out before supplying diethyl sulfide, at 5 h after supplying diethyl sulfide, and after 1 h of recovery test with pure hydrogen. The Nyquist plot was as shown in Fig. 3(B). Since the diameter of the semicircle increased and the left edge of the semicircle moved to the right, it is thought that the electrode catalyst and electrolyte membrane were poisoned by diethyl sulfide. The increase of diameter of the semicircle recovered only partly, and the position of the left edge of the semicircle did not change by supplying pure hydrogen. These results indicate that degradation caused by diethyl sulfide is irreversible, similar to that by hydrogen sulfide [1].

Among sulfur-free smelling compounds, several compounds indicated virtually no voltage drop after 10 h of continuous electric generation at the estimated legal concentration. For example, the result with 2,3-butanedione (23BD) is shown in Fig. 4(A), and the Nyquist plot in Fig. 4(B). This compound hardly affected either the electrode catalyst or electrolyte membrane. The results of the electric generation test with other compounds are summarized in Table 3.

Table 3  
Influences of smelling compounds on fuel cell performance

Compound	Estimated legal concentration (ppm)	Concentration in test (ppm)	Voltage drop at 1000 mA/cm <sup>2</sup>		Cell AC impedance	Quality of odor
			%	mV		
DES	3.3	3.3	>50	>300	Increased	Garlic
TMA	3.2	3.2	44	259	Increased	Putrid fish
23BD	5.0	5.0	0.0	0	Not increased	Putrid butter
IVAL	10	10	4.0	22	Not increased	Ginkgo nut
ESL	0.00010	0.00010	0.0	0	Not increased	Caramel
GNL	0.25	0.25	0.0	0	Not increased	Sweet
BIO	0.11	0.11	0.3	2	Not increased	Woody
IVAC	7.8	2.3	0.3	2	Not increased	Sweaty
EIB	2.2	2.2	0.0	0	Not increased	Fruity
5E2NB	17	17	0.0	0	Not increased	Coal Gas
2iP3MP	0.0037	0.0050	1.3	7	Increased	Oily

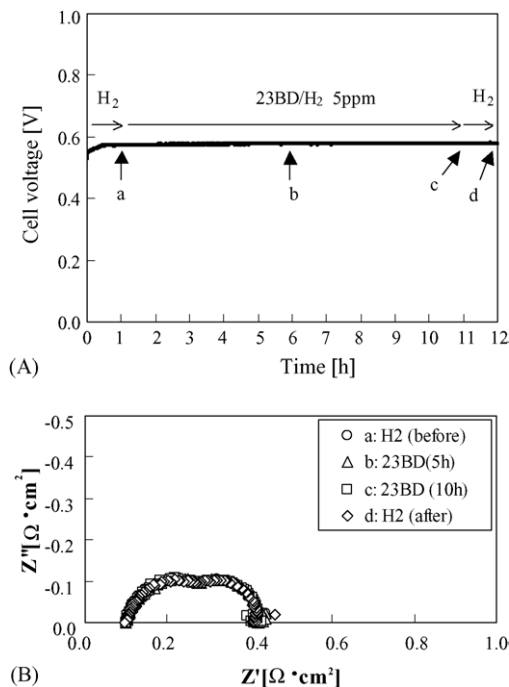


Fig. 4. (A) Deterioration of cell performance caused by 5 ppm of 2,3-butanedione (23BD). Current density = 1000 mA/cm<sup>2</sup>. The explanatory notes (a–d) show the points at which AC impedance spectra were measured; (B) changes of cell impedance caused by 5 ppm of 2,3-butanedione (23BD). The points (a–d) at which AC impedance spectra were measured are shown in (A).

Table 4  
Results of vapor pressure measurement

Compounds	Method	Vapor pressure (at 20 °C) (kPa)	Maximum filling pressure of H <sub>2</sub> (MPaG)
23BD	Static	5.2	>70
ESL	Transpiration	$8.5 \times 10^{-4}$ *	>70
EIB	Static	2.4	>70
5E2NB	Static	$5.8 \times 10^{-1}$	43
2iP3MP	Static	$6.0 \times 10^{-2}$	>70
GNL	Transpiration	$7.9 \times 10^{-4}$	3.2
BIO	Transpiration	$8.2 \times 10^{-4}$	7.8
IVAC	Static	$3.1 \times 10^{-2}$	4.1

\* At 23 °C.

The eight compounds that indicated only a small voltage drop (less than 2%) at the estimated legal concentration were subjected to the measurement of vapor pressure. From the result for each smelling compound at 20 °C (23 °C for ethyl sugar lactone), as shown in Table 4, the maximum hydrogen filling pressure was calculated for the case that it is added at the estimated legal concentration, applying the real gas value of hydrogen density at 25 °C. The filling pressure of hydrogen used in fuel cell vehicles today is 35 MPaG. The highest possible filling pressures for five compounds—2,3-butanedione, ethyl sugar lactone, ethyl isobutyrate (EIB), 5-ethylidene-2-norbornene (5E2NB) and 2-isopropyl-3-methoxypyrazine (2iP3MP)—proved to be 35 MPa or higher.

Impurities that are not oxidized at the electrode catalyst will be concentrated in the hydrogen circulation system. So, electric generation tests at higher concentration than the estimated legal concentration were carried out for those five compounds.

The result for 2,3-butanedione is shown in Fig. 5. Its concentration was 460 ppm, which is 93 times the estimated legal concentration. A few minutes after supplying 2,3-butanedione, a distinct voltage drop was observed, and the voltage drop ratio was 10.8%. After that, the voltage remained steady for 10 h, and then recovered upon decreasing the concentration to 4.2 ppm. The result for ethyl isobutyrate, which was tested at the concentration of 950 ppm (430 times the estimated legal concentration), is shown in Fig. 6; the tendency is about the same as for 2,3-butanedione. These re-

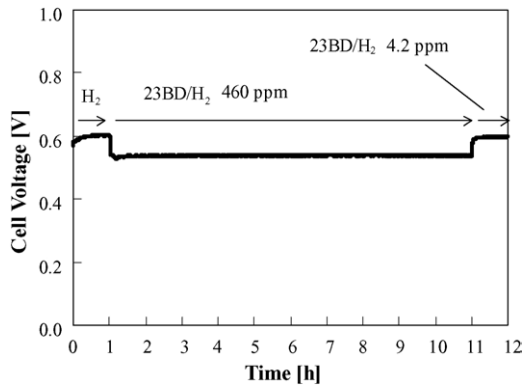


Fig. 5. Deterioration of cell performance caused by 460 ppm of 2,3-butanedione (23BD). Current density = 1000 mA/cm<sup>2</sup>.

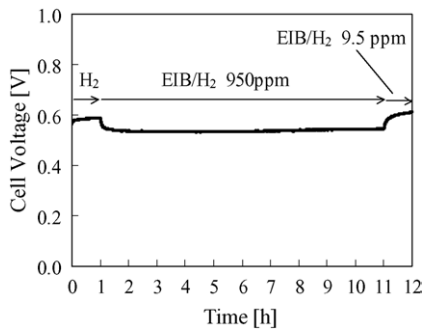


Fig. 6. Deterioration of cell performance caused by 950 ppm of ethyl isobutyrate (EIB). Current density = 1000 mA/cm<sup>2</sup>.

sults indicate that degradation of fuel cell performance caused by these oxygen-containing compounds is not so serious and can be recovered reversibly. The result for ethyl sugar lactone is shown in Fig. 7. Though it is also an oxygen-containing compound and it was tested at 500 times the estimated legal concentration, no degradation was observed. This seems to be because its detection threshold is extremely low. As a result, if the concentration increases 500 times, it becomes only 50 ppb, which is thought to be too low to poison the electrode catalyst.

The result for 5-ethylidene-2-norbornene, which is an unsaturated hydrocarbon, is shown in Fig. 8. The concentration is 120 ppm, which is seven times the estimated legal con-

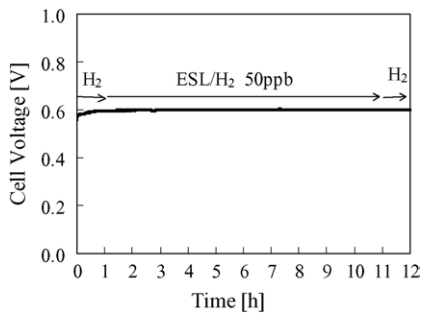


Fig. 7. Deterioration of cell performance caused by 50 ppb of ethyl sugar lactone (ESL). Current density = 1000 mA/cm<sup>2</sup>.

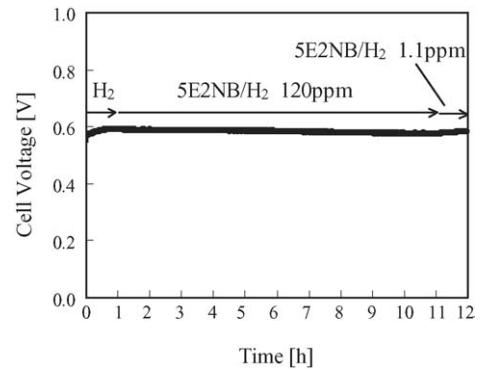
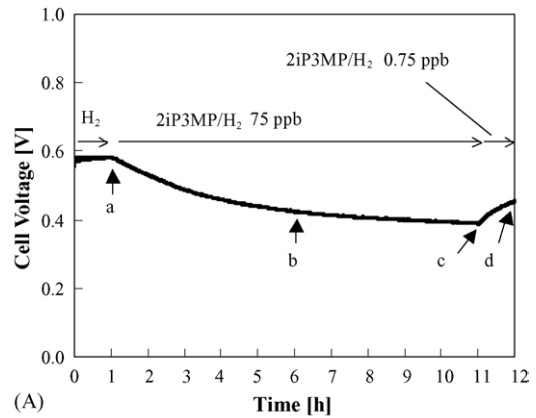


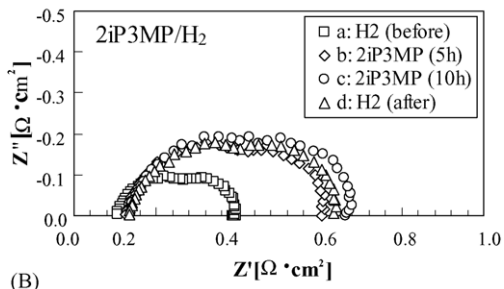
Fig. 8. Deterioration of cell performance caused by 120 ppm of 5-ethylidene-2-norbornene (5E2NB). Current density = 1000 mA/cm<sup>2</sup>.

centration. The voltage decreased gradually after the start of supply and the voltage drop ratio reached 2.4% after 10 h. This result is different from the case of the oxygen-containing compound, but this voltage drop recovered by diluting the concentration.

Fig. 9(A) shows the result when 75 ppb of 2-isopropyl-3-methoxy pyrazine, which corresponds to 20 times the estimated legal concentration, was supplied. This compound contains nitrogen and oxygen. In spite of the fact that its



(A)



(B)

Fig. 9. (A) Deterioration of cell performance caused by 75 ppb of 2-isopropyl-3-methoxy pyrazine (2iP3MP). Current density = 1000 mA/cm<sup>2</sup>. The explanatory notes (a–d) show the points at which AC impedance spectra were measured; (B) changes of cell impedance caused by 75 ppb of 2-isopropyl-3-methoxy pyrazine (2iP3MP). The points (a–d) at which AC impedance spectra were measured are shown in (A).

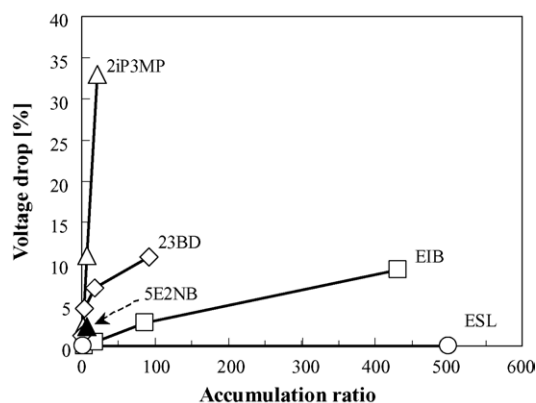


Fig. 10. Relationship between accumulation ratios vs. voltage drop.

concentration was very low, a relatively serious effect was observed. The voltage dropped with time and the voltage drop ratio reached 33%. The Nyquist plot, which is shown in Fig. 9(B), indicates that both the electrode catalyst and electrolyte membrane were affected by 2-isopropyl-3-methoxy-pyrazine, and recovered only partly when the concentration was diluted. This result indicates that degradation of fuel cell performance caused by 2-isopropyl-3-methoxy-pyrazine is serious.

The relationship between voltage drop and accumulation ratio for the estimated legal concentration is shown in Fig. 10. Ethyl sugar lactone indicated the best voltage stability against high accumulation factor values. Common to other compounds except for ethyl sugar lactone, the voltage drop accelerated as the concentration increased but, with 2,3-butanedione, ethyl isobutyrate and 5-ethylidene-2-norbornene, the voltage rebounded when the concentration was lowered.

Ethyl sugar lactone and ethyl isobutyrate, which have good stability against high accumulation factor values, have caramel-like and fruit-like odor, respectively. Since an offensive odor is preferred for an odorant that warns of danger, their odor may not be suitable as hydrogen odorants. Although slightly higher than ethyl isobutyrate in the effect on electric generation performance, 2,3-butanedione and 5-ethylidene-2-norbornene were considered suitable as hydrogen odorants because of their appropriate offensive odors and their voltage reversibility.

## 4. Conclusions

The suitability of various smelling compounds for hydrogen odorants was evaluated by measuring their effects on the electric generation performance of fuel cells and their condensation properties at high-pressure filling. It was found that sulfur compounds, such as mercaptans and sulfides, are not suitable for hydrogen odorants due to their adverse effects on electric generation performance. Among sulfur-free smelling compounds, 2,3-butanedione, ethyl isobutyrate, ethyl sugar lactone and 5-ethylidene-2-norbornene were found to be promising candidates for hydrogen odorants, thanks to their limited effects on electric generation and their high-pressure filling capability. Further studies will be necessary to evaluate their effects on the long-term performance of fuel cells, degradation of hydrogen storage materials, and diffusion properties.

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