Influence of Impurities in Hydrogen on Fuel Cell Performance

Japan Automobile Research Institute

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Objective

H_2 purity

- Increase of H_2 fuel cost
- High purity
- Poor purity
- Influence on fuel cell performance

Existing standards of H_2 quality

JIS K0512

No regulation for fuel cell vehicles

ISO 14687

Common regulation with internal combustion engine vehicles

JARI's study

Evaluation of impurities influence on the FC performance

Establishment of H_2 quality standard for fuel cell vehicles

Result of impurities analysis in commercial hydrogen

Impurities		Conc.	Naphtha reformation		Hydrocarbon decomposition		Methanol reformation		LNG reformation	
			Before purification	After purification	Before purification	After purification	Before purification	After purification	Before purification	After purification
CO		[ppb-vol.]	0.11%	< 10[1)]	< 10[1)]	< 10[1)]	0.48%	< 10[1)]	0.98%	< 10[1)]
CO_2		[ppb-vol.]	210	< 10[1)]	190	< 10[1)]	23%	< 10[1)]	13%	28
HC	CH_4	[ppbC]	16.0%	1,700	2.9%	3,400	1,400	1,900	<0.5[1)]	1,600
	C_2H_6		18,000	<0.5[1)]	1,400	<0.5[1)]	42	5	<0.5[1)]	<0.5[1)]
	C_2H_4		95,000	<0.5[1)]	<0.5[1)]	<0.5[1)]	<0.5[1)]	<0.5[1)]	<0.5[1)]	<0.5[1)]
	C_6H_6		9	<0.5[1)]	<0.5[1)]	<0.5[1)]	2	2	<0.5[1)]	<0.5[1)]
	Others		1,425	12	65	9	42	18	-	10
Sulfur		[nmol/mol.]	-	-	-	-	-	N.D.	-	N.D.

Impurities		Conc.	Coke oven gas	Butane reformation	Converter gas	Electrosis of saltwater		
			After purification	After purification	After purification	After purification		
CO		[ppb-vol.]	< 10[1)]	< 10[1)]	< 10[1)]	< 10[1)]	< 10[1)]	< 10[1)]
CO_2		[ppb-vol.]	600	< 10[1)]	< 10[1)]	24	21	21
HC	CH_4	[ppbC]	<0.5[1)]	1,800	<0.5[1)]	2,400	1,600	1,700
	C_2H_6		<0.5[1)]	<0.5[1)]	<0.5[1)]	<0.5[1)]	<0.5[1)]	<0.5[1)]
	C_2H_4		<0.5[1)]	<0.5[1)]	<0.5[1)]	<0.5[1)]	<0.5[1)]	<0.5[1)]
	C_6H_6		<0.5[1)]	<0.5[1)]	<0.5[1)]	<0.5[1)]	<0.5[1)]	<0.5[1)]
	Others		-	19	13	9	12	14
Sulfur		[nmol/mol.]	N.D.	N.D.	-	N.D.	< 18.7	N.D.

1) <: Minimum limit of determination

2) N.D.: Not detected

- O-containing organic compounds -

Impurities	Methanol reformation		Detect limit
	Before purification	After purification	
CH_3OH	393 ppm	N.D.	0.1 ppm
HCHO	31 ppb	5 ppb	1.8 ppb
CH_3CHO	37 ppb	N.D.	1.2 ppb
CH_3COCH_3	14 ppb	4 ppb	2.1 ppb
C_2H_5CHO	6 ppb	N.D.	1.9 ppb
$CH_3COC_2H_5$	17 ppb	N.D.	9.2 ppb

N.D.: Not detected

Examples of product standard of hydrogen production companies in Japan

Grade	4N			5N			
Production company	A	B	C	A	C	D	A
Purity [%]	>99.998	99.99%	99.99%	>99.9995	>99.9995	>99.999	>99.9998
Water [ppm]	<5	-	-	<2	-	-	<1
Dew-point [℃]	—	<-60.0	<-55.0	-	<-70	<-70	-
THC [ppm]	<1	<1.0	-	<0.5	-	-	<0.1
CH_4 [ppm]	—	-	<1.0	-	<0.1	-	-
O_2 [ppm]	<1	<4.0	<3.0	<1	<0.1	<1	<0.1
N_2 [ppm]	<10	<25.0	<100.0	<2	<0.5	-	<0.5
CO_2 [ppm]	<1	<1.0	<1.0	<0.5	<0.1	-	<0.1
CO [ppm]	<1	<1.0	<1.0	<0.5	<0.1	-	<0.1
Ar [ppm]	-	-	-	-	-	-	-

Grade	6N					7N		
Production company	A	C	D	E	F	C	G	H
Purity [%]	>99.9999	>99.9999	>99.9999	>99.9999	>99.99995	>99.99999	>99.99999	>99.99999
Water [ppm]	<0.5	-	-	<0.5	<1	-	-	<0.01
Dew-point [℃]	-	<-76	<-80	-	-	<-76	<-80	-
THC [ppm]	-	-	-	<0.1	<0.1	-	-	<0.02
CH_4 [ppm]	<0.05	<0.1	<0.05	-	-	<0.05	N.D	-
O_2 [ppm]	<0.1	<0.1	<0.05	<0.1	<0.1	<0.05	<0.05	<0.01
N_2 [ppm]	<0.5	<0.2	<0.05	<0.1	<0.1	<0.1	N.D	<0.02
CO_2 [ppm]	<0.05	<0.1	<0.01	<0.1	<0.1	<0.05	N.D	<0.02
CO [ppm]	<0.05	<0.1	-	<0.1	<0.1	<0.05	N.D	<0.02
Ar [ppm]	-	-	<0.05	-	-	-	-	-

Existing H_2 fuel quality standards

- Japanese Industrial Standard (JIS) and ISO -

Characteristics	Standards								
	JIS K 0512[a]					ISO 14687, Type I			
	Grade 1	Grade 2	Grade 3	Grade 4	unit	Grade A[c]	Grade B[d]	Grade C[e]	unit
Hydrogen purity (minimum fraction)	99.9999	99.999	99.99	99.9	%	98.0	99.9	99.995	mol %
Impurities (maximum content)									
Total hydrocarbon	0.3[b]	5.0[b]	10.0[b]	-[b]	ppm	100	NC	g	μmol/mol
Oxygen	0.3	0.5	4.0	100	ppm	f	100	h	μmol/mol
Nitrogen	0.2	5.0	25	40	ppm	f	400	g	μmol/mol
Carbon dioxide	0.1	1.0	10	-	ppm	-	-	i	μmol/mol
Carbon monoxide	0.1	1.0	10	-	ppm	1	-	i	μmol/mol
Sulfur compounds	0.00	0.00	2.0	10	ppm	2	10	-	μmol/mol

Note NC: Not to be condensed

a: % and ppm mean volume ratio
b: Not to be condensed
c: For the fuel of internal combustion engines and fuel cells for transportation, electrical equipment of residential and stationary
d: Industrial fuel, for use e.g. in power generation or as a heat energy source
e: Aircraft and space-vehicle ground support systems
f: Mixture of water, oxygen, nitrogen and argon is less than 1,900 μmol/mol
g: Mixture of nitrogen, water and hydrocarbon is less than 9 μmol/mol
h: Mixture of oxygen and argon is less than 1 μmol/mol
i: Total of carbon dioxide and carbon monoxide is less than 1 μmol/mol

Existing H_2 fuel quality standards

Characteristics	Standards			
	JIS K 0512[a] Grade 3		ISO 14687 Type I, Grade A[b]	
Hydrogen purity (minimum fraction)	99.99	%	98.0	mol %
Impurities (maximum content)				
Total hydrocarbon	10.0[c]	ppm	100	µmol/mol
Oxygen	4.0	ppm	d	µmol/mol
Nitrogen	25	ppm	d	µmol/mol
Carbon dioxide	10	ppm	-	µmol/mol
Carbon monoxide	10	ppm	1	µmol/mol
Sulfur compounds	2.0	ppm	2	µmol/mol

a: % and ppm mean volume ratio
b: For the fuel of internal combustion engines and fuel cells for transportation, electrical equipment of residential and stationary
c: Not to be condensed
d: Mixture of water, oxygen, nitrogen and argon is less than 1,900 µmol/mol

Some of limiting characteristics (yellow colored portions) should be reconsidered for fuel cell vehicles.

Selection of impurity species

- Existing standards of H_2 quality
- Analysis of impurities in commercial H_2

→ 12 kinds of impurity species are selected.

Impurities	Maximum content
CH_4	1%
C_2H_6	100 ppm
C_2H_4	100 ppm
C_6H_6	100 ppm
CO_2	1%
CO	10 ppm

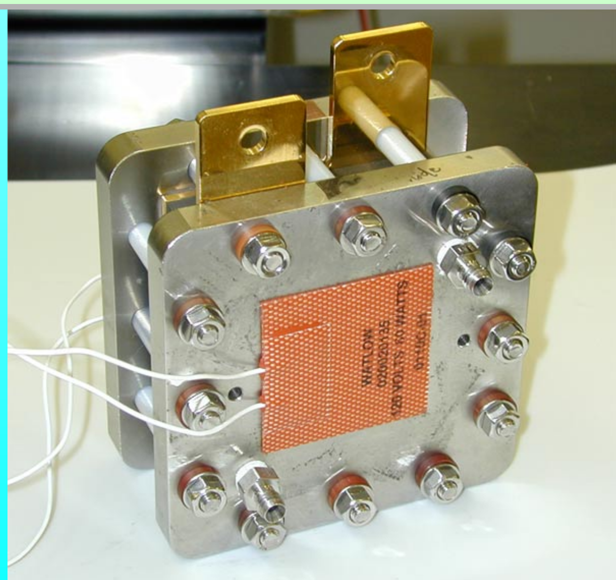
Impurities	Maximum content
SO_2	2 ppm
H_2S	2 ppm
CH_3OH	500 ppm
HCHO	20 ppm
HCOOH	100 ppm
CH_3COCH_3	100 ppm

Reason of selecting GORE and Nafion

- Availability and reliable quality of the products.
- Test data can be disclosed.
- Typical characteristics can be obtained by testing the products of the leading manufactures.

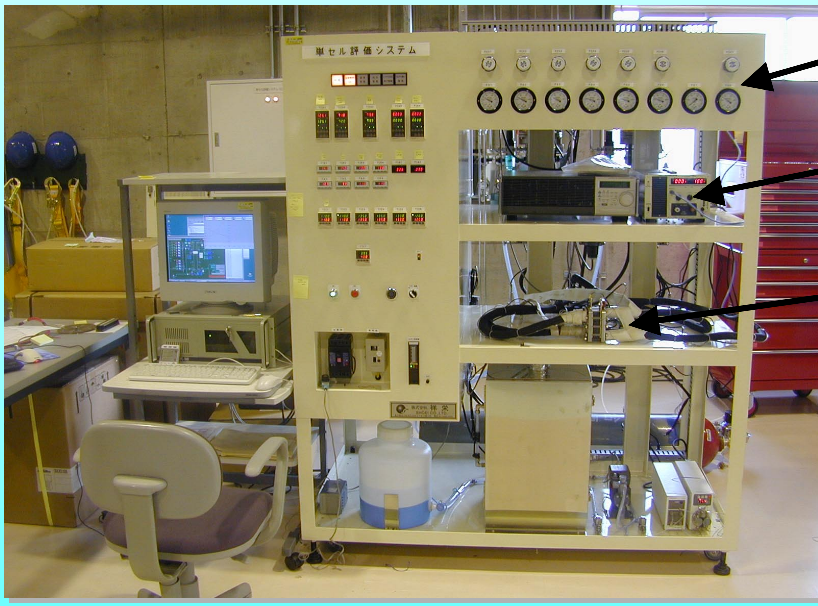
Membrane & Electrode Assembly	JAPAN GORE-TEX		Electrochem	
Electrolyte	GORE-SELECT		Nafion 115	
Electrode catalyst (Anode/Cathode)	Pt / Pt	Pt-Ru / Pt	Pt / Pt	Pt-Ru / Pt
Catalyst loading (Anode/Cathode) [mg/cm^2]	0.3 / 0.3	0.45 / 0.3	1.0 / 1.0	1.0 / 1.0
Electrode area [cm^2]	25 (5cm*5cm)		25 (5cm*5cm)	

JARI's standard single cell

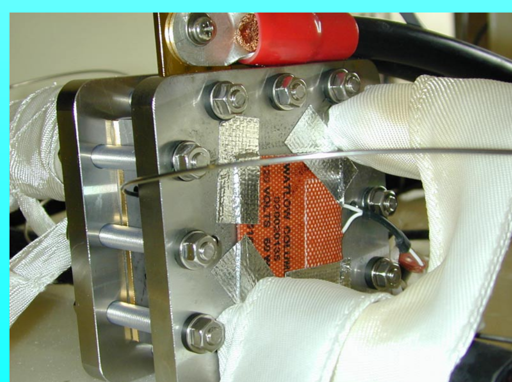


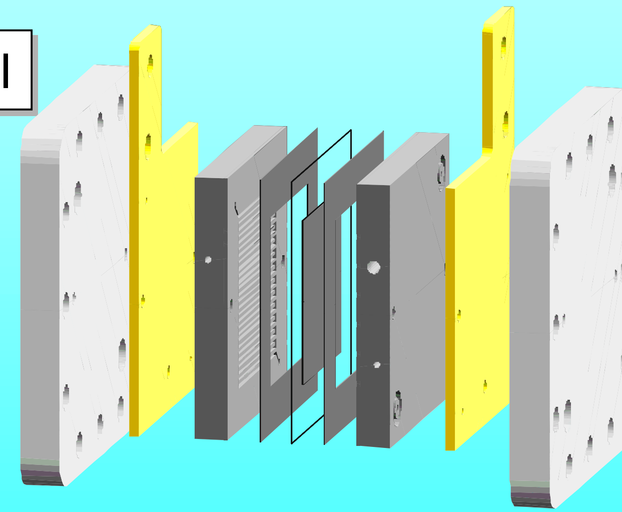
Separator
(one channel, serpentine)

Outward of the test equipment



Single cell test equipment

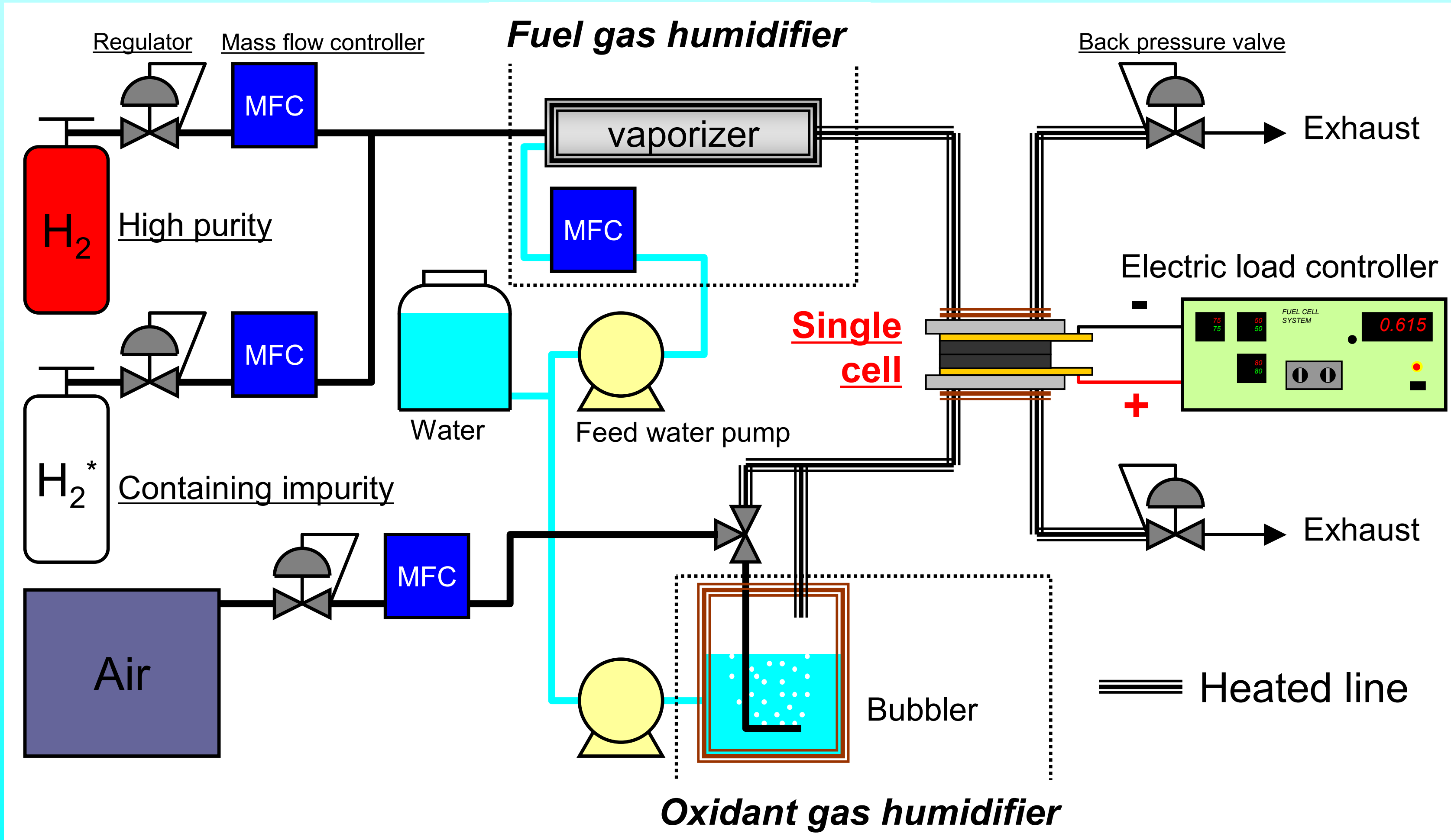




Structure of JARI's standard single cell

Outline of the test equipment

Humidification technique;
Mass flow controller and vaporizer system is used as a fuel humidifier to prevent the trap of soluble impurities.



Evaluation test approach

1st step evaluation test

Measurement of I-V characteristics
to investigate influence of impurities
on the fuel cell performance
(5 minutes operation for each current density)

Test condition

Flow rate of fuel gas	249mL/min (Uf=70%@1000mA/cm^2)
Flow rate of oxidant gas	1037mL/min (Ua=40%@1000mA/cm^2)
Pressure of fuel/oxidant gas	Atmospheric pressure (cell outlet)
Dew point of fuel/oxidant gas	77℃/70℃
Cell temperature	80℃

2nd step evaluation test

Measurement of voltage drop
under constant current density
for 10 hours operation

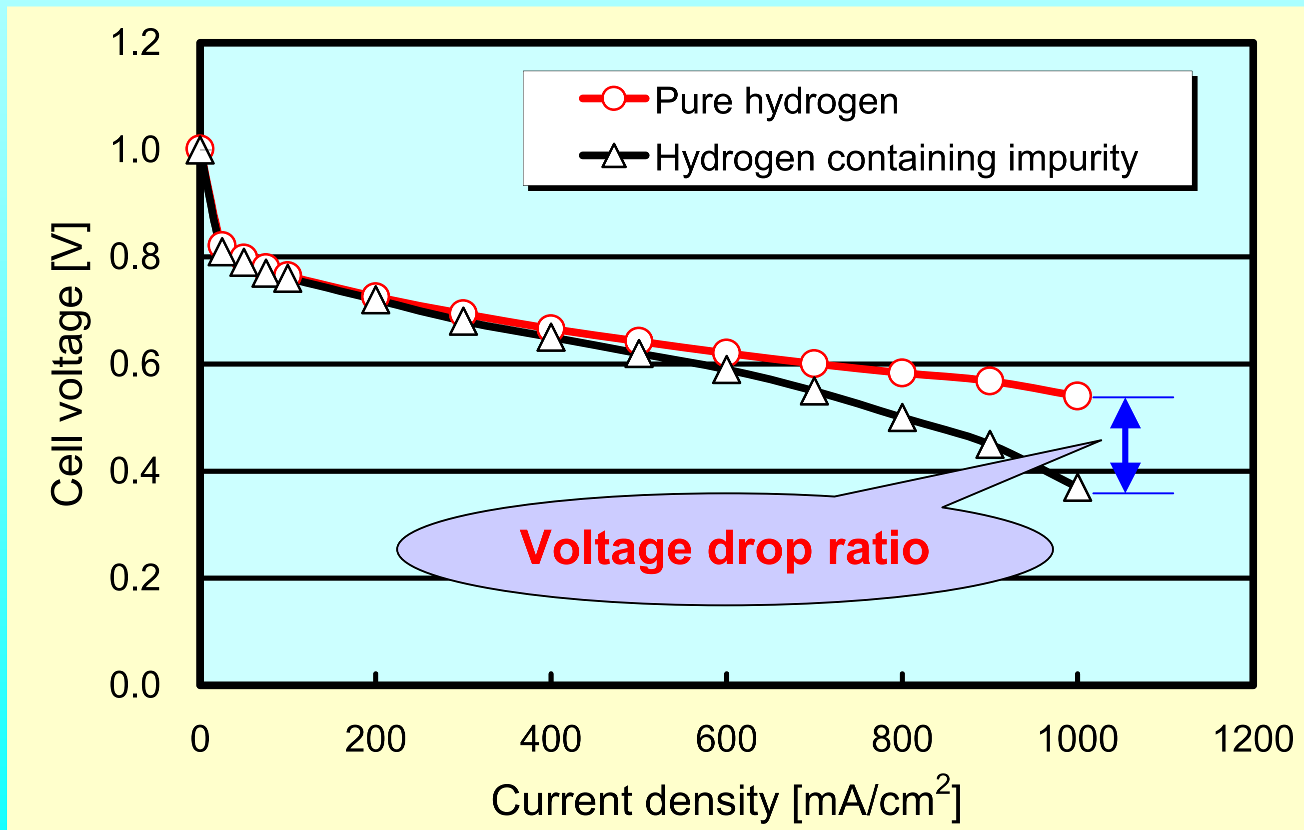
Test condition

Current density	1000mA/cm^2
Flow rate of fuel gas	1000mL/min (Uf=17%)
Flow rate of oxidant gas	1037mL/min (Ua=40%)
Pressure of fuel/oxidant gas	0.1MPaG/0.1MPaG (inlet pressure control)
Dew point of fuel/oxidant gas	77℃/50℃
Cell temperature	80℃

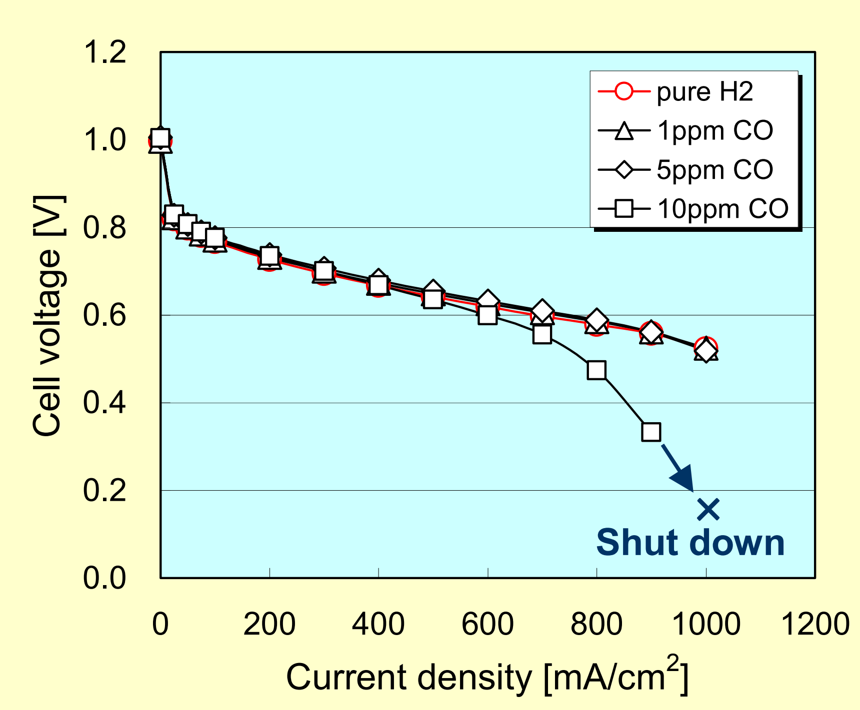
Allowable impurity limit

Method of 1st step evaluation test

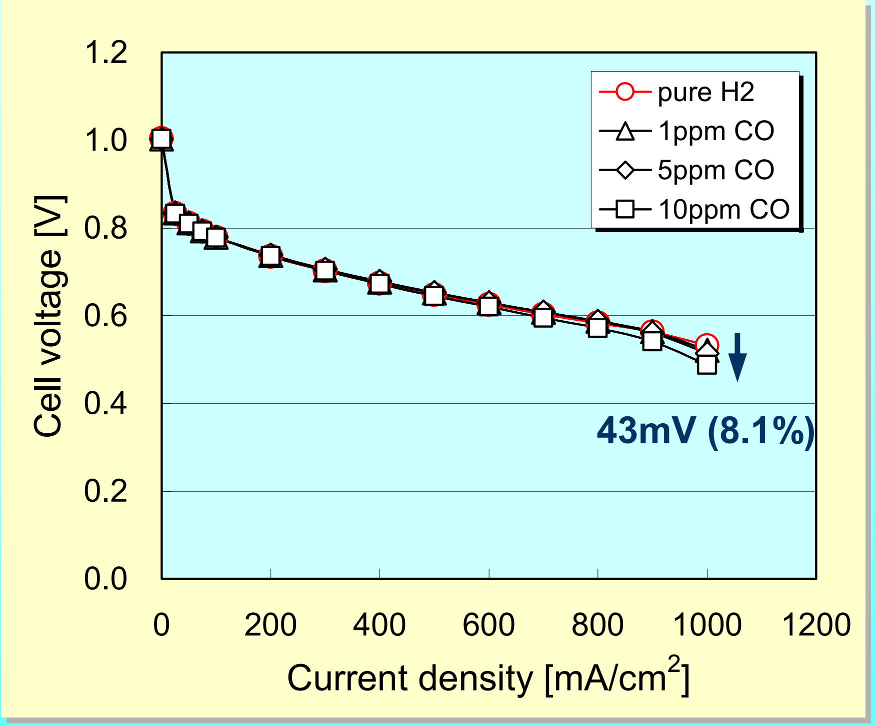
- The **voltage drop ratio** under the current density of 1,000 mA/cm^2 is measured and compared with the performance of reference hydrogen. (purity; 99.99999%)
- As repeatability of the test is within 2%, more than 2% of voltage drop ratio is judged that there is influence of impurities.



Examples of 1st step evaluation test (CO)



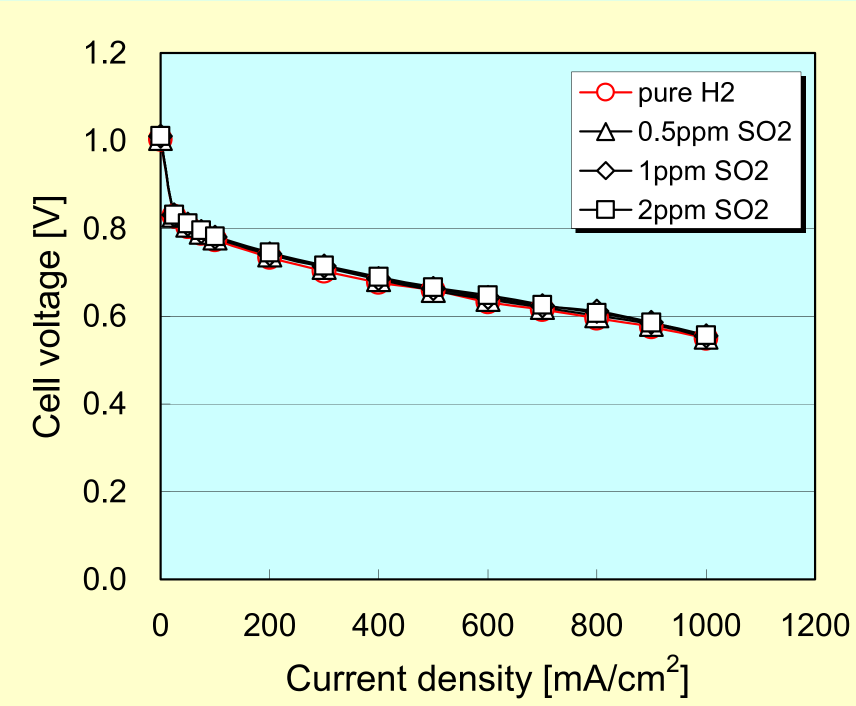
Electrolyte: GORE-SELECT
Electrode catalyst (Anode/Cathode): Pt/Pt



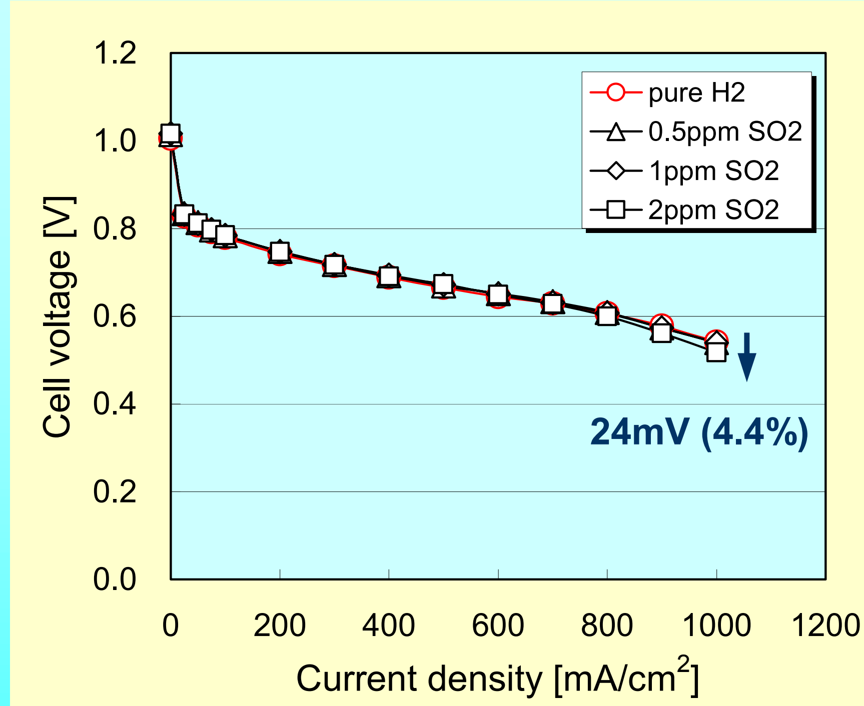
Electrolyte: GORE-SELECT
Electrode catalyst (Anode/Cathode): Pt-Ru/Pt

- If 10ppm CO is contained, the voltage drop ratio is more than 2%.
- Pt-Ru catalyst has the tendency of preventing CO poisoning.

Examples of 1st step evaluation test (SO_2)



Electrolyte: GORE-SELECT
Electrode catalyst (Anode/Cathode): Pt/Pt



Electrolyte: GORE-SELECT
Electrode catalyst (Anode/Cathode): Pt-Ru/Pt

- **If 2ppm SO_2 is contained, the voltage drop ratio is more than 2% in case of Pt-Ru catalyst.**

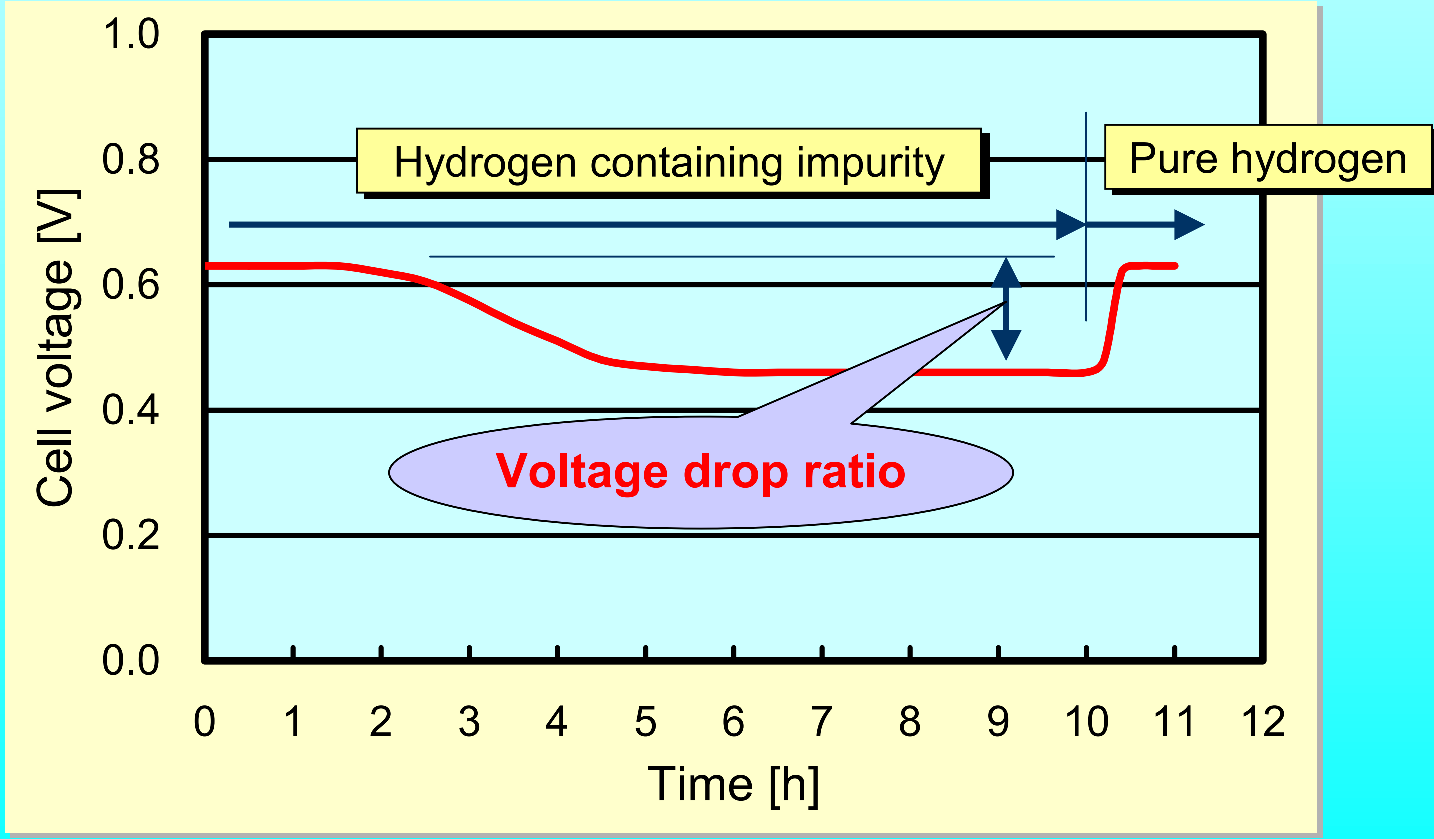
Results of 1st step evaluation test

Impurities	Concentration	GORE, Pt/Pt		GORE, Pt-Ru/Pt		Nafion115, Pt/Pt	Nafion115, Pt-Ru/Pt
		$500mA/cm^2$	$1000mA/cm^2$	$500mA/cm^2$	$1000mA/cm^2$	$500mA/cm^2$	$500mA/cm^2$
CH_4	10 ppm	0%	0%	0%	0%	0%	0%
	100 ppm	0%	0%	0%	0%	0%	0%
	1 %	0%	0%	0%	0%	0%	0%
C_2H_6	10 ppm	0%	0%	0%	0.7% (3mV)	0%	0%
	100 ppm	0%	0%	0%	0%	0%	0%
C_2H_4	10 ppm	0%	0%	0%	0%	0%	0%
	100 ppm	0%	0.6% (3mV)	0%	0%	1.1% (4mV)	0%
C_6H_6	10 ppm	0%	0%	0%	0%	0%	0%
	100 ppm	0%	0%	0%	0%	0%	0%
CO_2	10 ppm	0%	2.2% (11mV)	0%	0.6% (3mV)	0%	0%
	100 ppm	0%	2.1% (11mV)	0%	0.8% (4mV)	0%	0%
	1 %	0%	2.4% (12mV)	0%	1.2% (7mV)	0%	0%
	(1% N_2)	0%	1.9% (10mV)	0%	0.8% (4mV)	0%	—
CO	1 ppm	0%	0%	0%	1.9% (11mV)	0.6% (2mV)	0%
	5 ppm	0%	0.9% (5mV)	0%	**3.3% (18mV)**	0%	0%
	10 ppm	1.1% (7mV)	**Breakdown**	0.5% (3mV)	**8.1% (43mV)**	**6.2% (23mV)**	0%
SO_2	0.5 ppm	0%	0%	0%	0%	0%	0%
	1 ppm	0%	0%	0%	0%	0%	0.6% (3mV)
	2 ppm	0%	0%	0%	**4.4% (24mV)**	0%	0%
H_2S	0.5 ppm	0%	0%	0%	0%	0%	1.7% (8mV)
	1 ppm	0%	0%	0%	0%	0%	**2.7% (14mV)**
	2 ppm	0%	0%	0%	**4.6% (25mV)**	0%	**4.2% (25mV)**
CH_3OH	100 ppm	0%	0%	0%	0%	0%	0%
	200 ppm	0%	0%	0%	0%	0%	0%
	500 ppm	0%	0.8% (5mV)	0%	0%	0%	0%
HCHO	5 ppm	0%	0%	0%	0.4% (2mV)	0%	0.5%(2mV)
	10 ppm	0%	0%	0.3% (2mV)	**2.5% (14mV)**	0.9% (4mV)	**4.8% (24mV)**
	20 ppm	0%	**2.2% (12mV)**	**2.9% (19mV)**	**8.5% (48mV)**	0%	**6.5% (32mV)**
HCOOH	10 ppm	0%	0%	0%	0.4% (2mV)	0%	1.0%(5mV)
	50 ppm	0%	0%	1.1% (8mV)	**4.0% (22mV)**	0.5% (2mV)	**7.6% (38mV)**
	100 ppm	0%	0%	**2.6% (17mV)**	**6.3% (35mV)**	0%	**24.1% (121mV)**
CH_3COCH_3	10 ppm	0%	0%	0%	0%	0%	0.2% (1mV)
	50 ppm	0%	0%	0%	0%	0.9% (4mV)	0%
	100 ppm	0%	0%	0%	0%	0.5% (2mV)	0.3% (2mV)

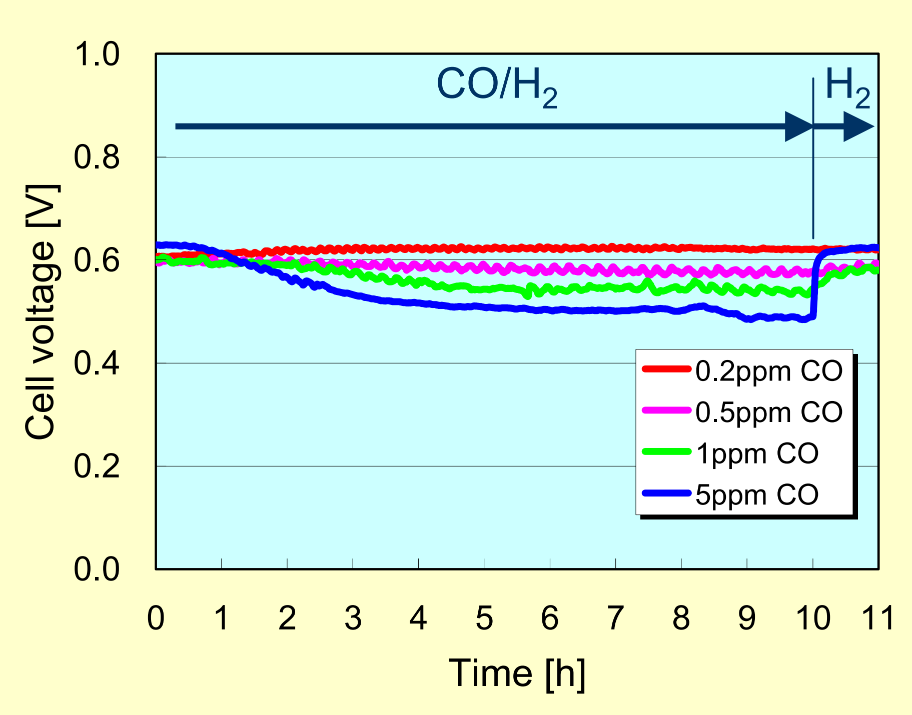
GORE and Nafion have the same tendency of poisoning.

Method of 2nd step evaluation test

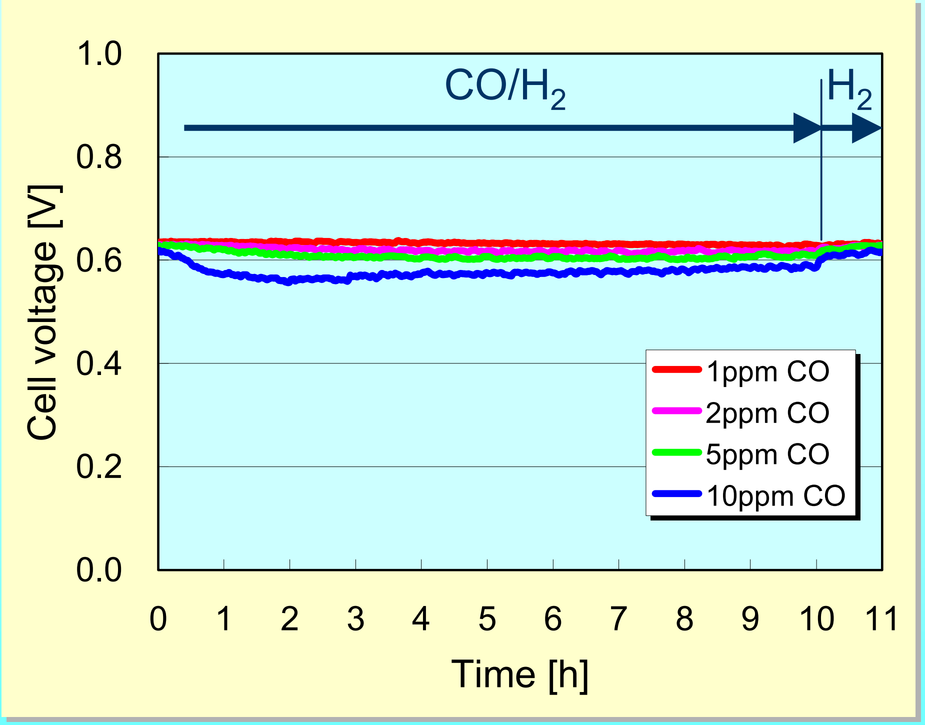
- The **voltage drop ratio** under the current density of 1,000 mA/cm^2 for **10 hours** is measured.
- After 10 hours test, to check the cell voltage recovery, pure hydrogen (purity; 99.99999%) is supplied.



Examples of 2nd step evaluation test (CO)



Electrolyte: GORE-SELECT
Electrode catalyst (Anode/Cathode): Pt/Pt

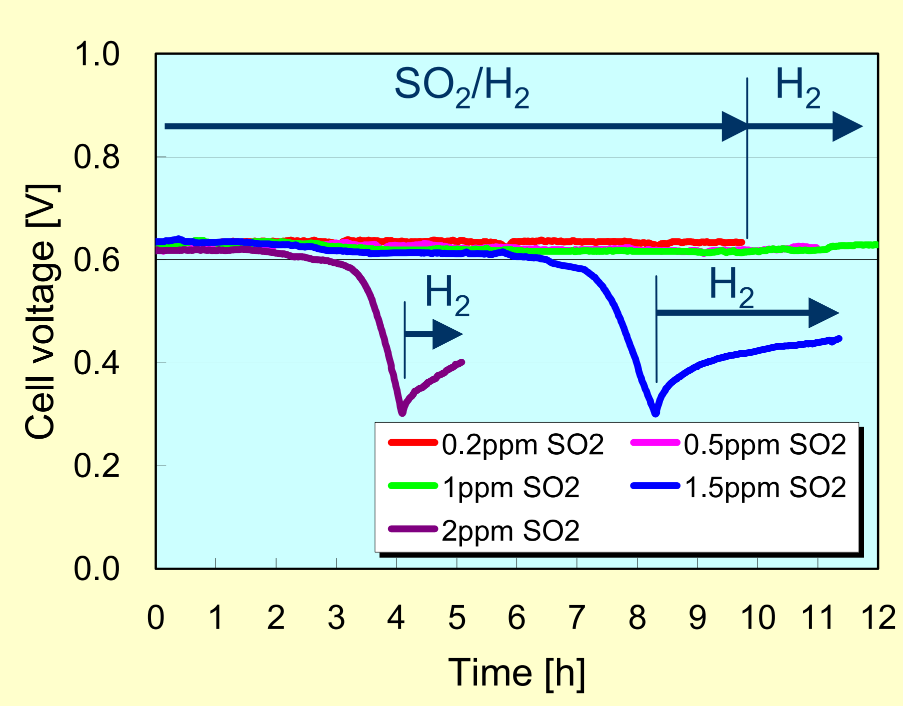


Electrolyte: GORE-SELECT
Electrode catalyst (Anode/Cathode): Pt-Ru/Pt

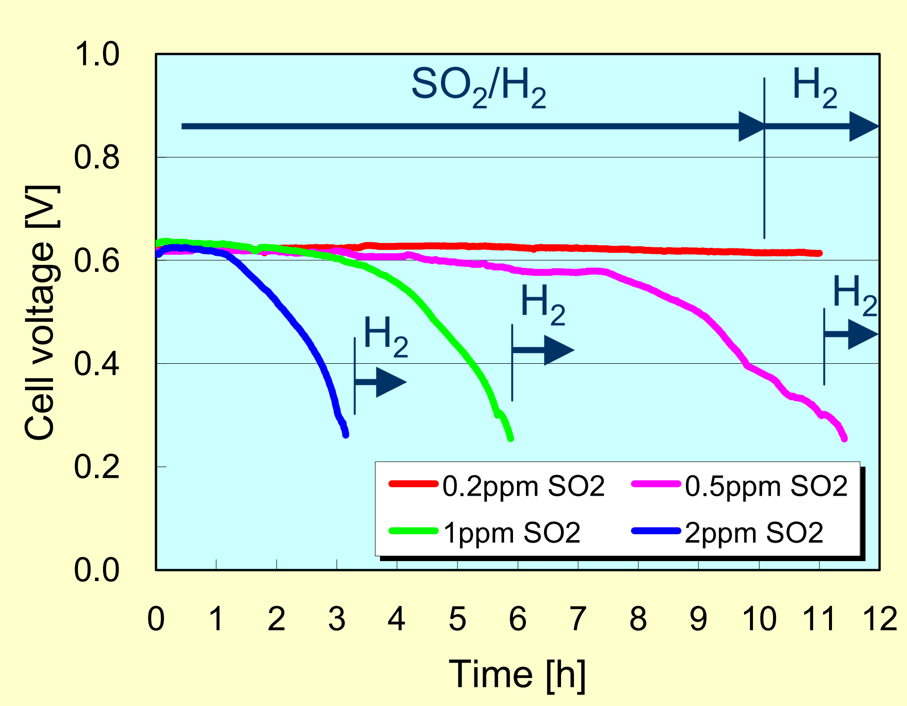
- Compared with 1st evaluation test, lower impurity concentration have influence on the fuel cell performance.
-After 10 hours test, the cell voltage is recovered by supplying pure hydrogen.

CO poisoning is reversible

Examples of 2nd step evaluation test (SO_2)



Electrolyte: GORE-SELECT
Electrode catalyst (Anode/Cathode): Pt/Pt

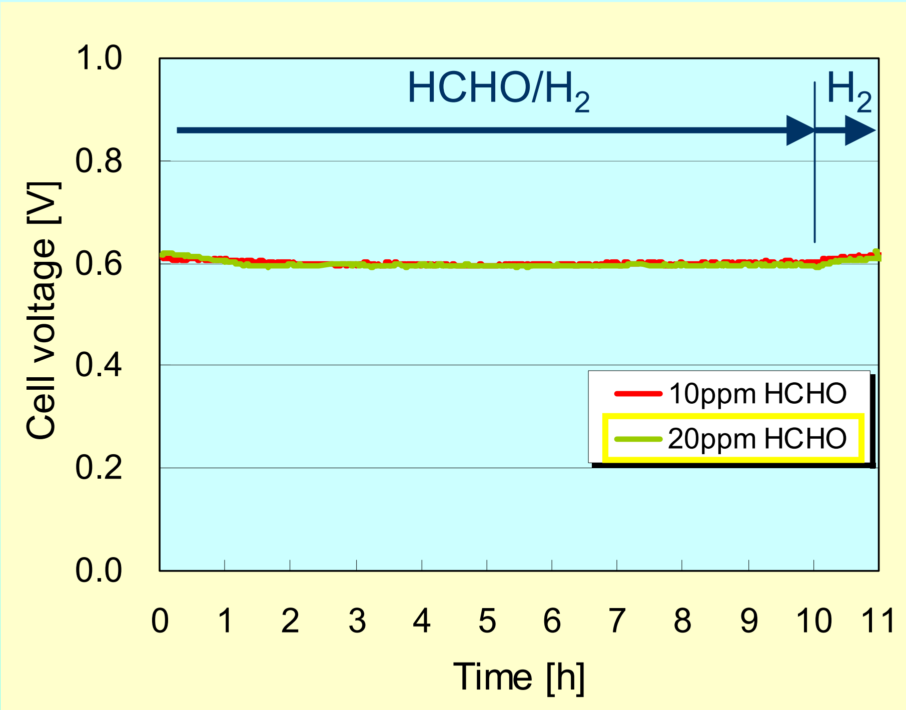


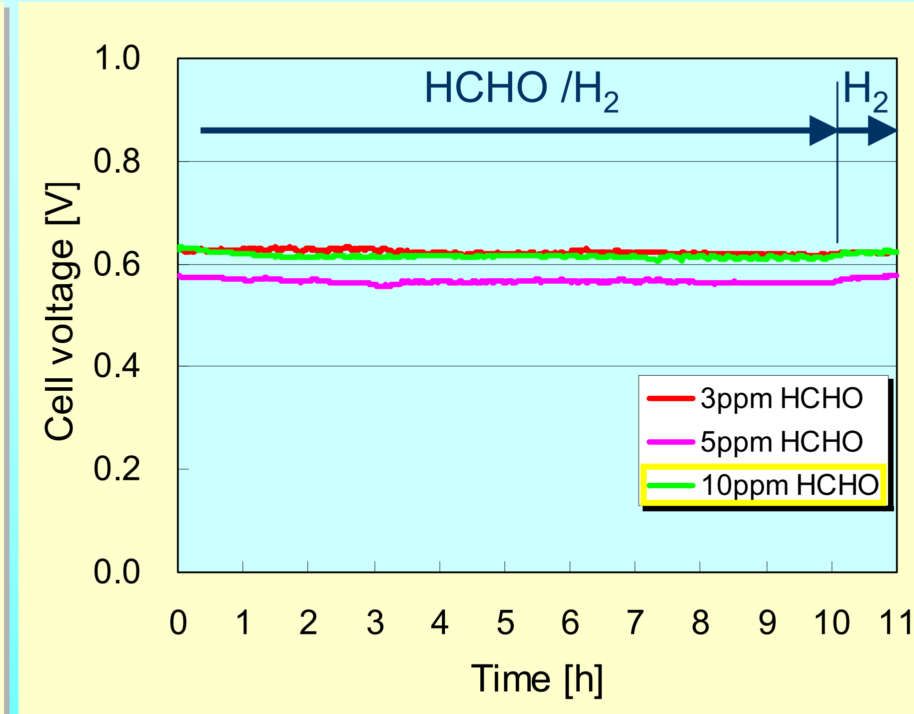
Electrolyte: GORE-SELECT
Electrode catalyst (Anode/Cathode): Pt-Ru/Pt

- Compared with 1st evaluation test, lower impurity concentration have influence on the fuel cell performance.

-After 10 hours test, the cell voltage is not recovered by supplying pure hydrogen.

SO_2 poisoning is irreversible





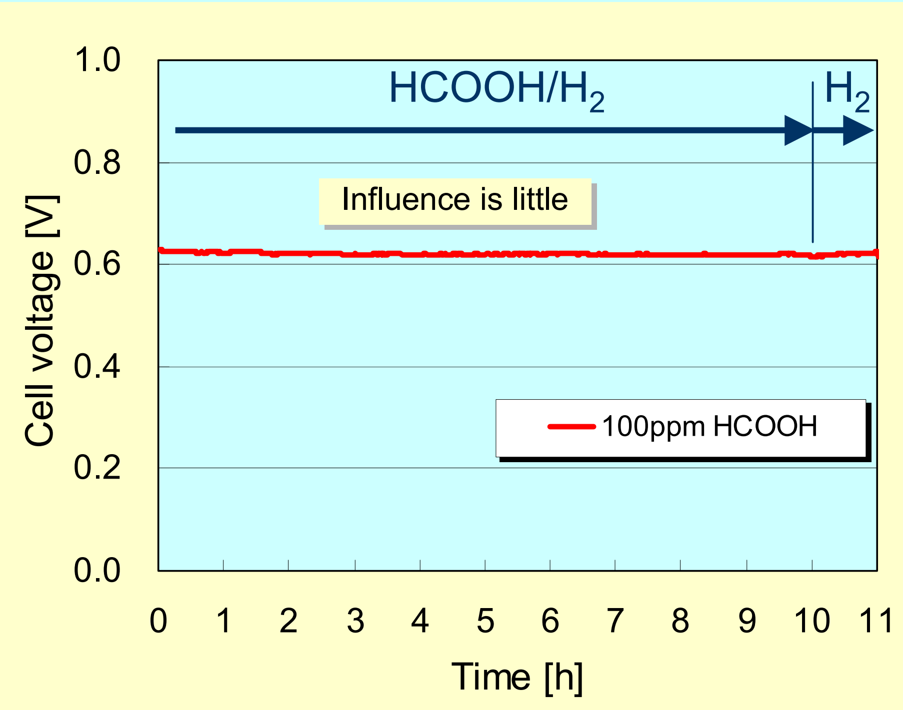
Electrolyte: GORE-SELECT
Electrode catalyst (Anode/Cathode): Pt/Pt

Electrolyte: GORE-SELECT
Electrode catalyst (Anode/Cathode): Pt-Ru/Pt

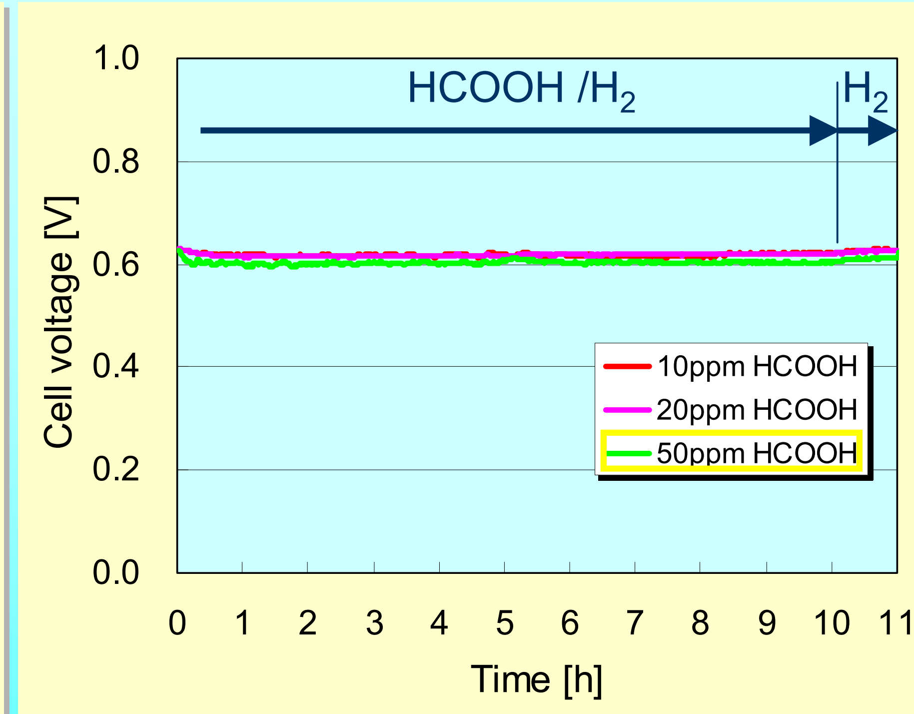
- After 10 hours test, the cell voltage is recovered by supplying pure hydrogen.

↓

HCHO poisoning is reversible



Electrolyte: GORE-SELECT
Electrode catalyst (Anode/Cathode): Pt/Pt



Electrolyte: GORE-SELECT
Electrode catalyst (Anode/Cathode): Pt-Ru/Pt

- After 10 hours test, the cell voltage is recovered by supplying pure hydrogen.

↓

HCOOH poisoning is reversible

New results of 2nd step evaluation test

The influence of impurities in hydrogen on the FC performance

Impurities	Concentration	GORE, Pt/Pt	GORE, Pt-Ru/Pt
CH_4	1 %	0%	0%
	5 %	0%	0%
C_2H_6	100 ppm	0%	0%
	5 %	0%	0%
C_2H_4	100 ppm	0%	0%
	5 %	0%	1.9% (12mV)
C_6H_6*	100 ppm	0%	0%
	1000 ppm	3.5% (22mV)	4.8% (30mV)
CO_2	5 %	0%	0%
CO	0.2 ppm	0%	–
	0.5 ppm	3.5% (21mV)	–
	1 ppm	9.6% (57mV)	1.1% (7mV)
	2 ppm	–	2.0% (12mV)
	3 ppm	–	2.0% (12mV)
	5 ppm	22% (141mV)	3.1% (20mV)
	10 ppm	–	5.0% (31mV)
SO_2	0.1 ppm	–	0.8% (5mV)
	0.2 ppm	0.6% (4mV)	1.9% (12mV)
	0.5 ppm	2.4% (15mV)	36% (222mV)
	1 ppm	3.1% (20mV)	> 50%
	1.5 ppm	> 50%	–
	2 ppm	> 50%	> 50%

Impurities	Concentration	GORE, Pt/Pt	GORE, Pt-Ru/Pt
H_2S	0.1 ppm	–	0.6% (4mV)
	0.2 ppm	0.5% (3mV)	3.3% (21mV)
	0.5 ppm	2.6% (16mV)	> 50%
	1 ppm	3.4% (21mV)	> 50%
	2 ppm	> 50%	> 50%
CH_3OH*	500 ppm	0%	0%
	2500 ppm	0%	2.7% (17mV)
HCHO	3 ppm	–	1.4% (9mV)
	5 ppm	–	1.9% (11mV)
	10 ppm	1.1% (7mV)	2.6% (17mV)
	20 ppm	3.5% (21mV)	–
HCOOH	10 ppm	–	0.8% (5mV)
	20 ppm	–	1.5% (9mV)
	50 ppm	–	2.5% (15mV)
	100 ppm	1.0% (6mV)	–
	500 ppm	2.5% (16mV)	–
CH_3COCH_3*	100 ppm	0%	0%
	250 ppm	1.8% (11mV)	–
	500 ppm	2.4% (15mV)	0%
NH_3*	0.3 ppm	0.5% (3mV)	1.3% (8mV)
	0.5 ppm	3.1% (18mV)	2.2% (14mV)
	1.0 ppm	4.0% (24mV)	5.2% (32mV)

*) New test results are not reflected to the NWIP from Japan. The results indicate that new limits should be introduced into the ISO standard.

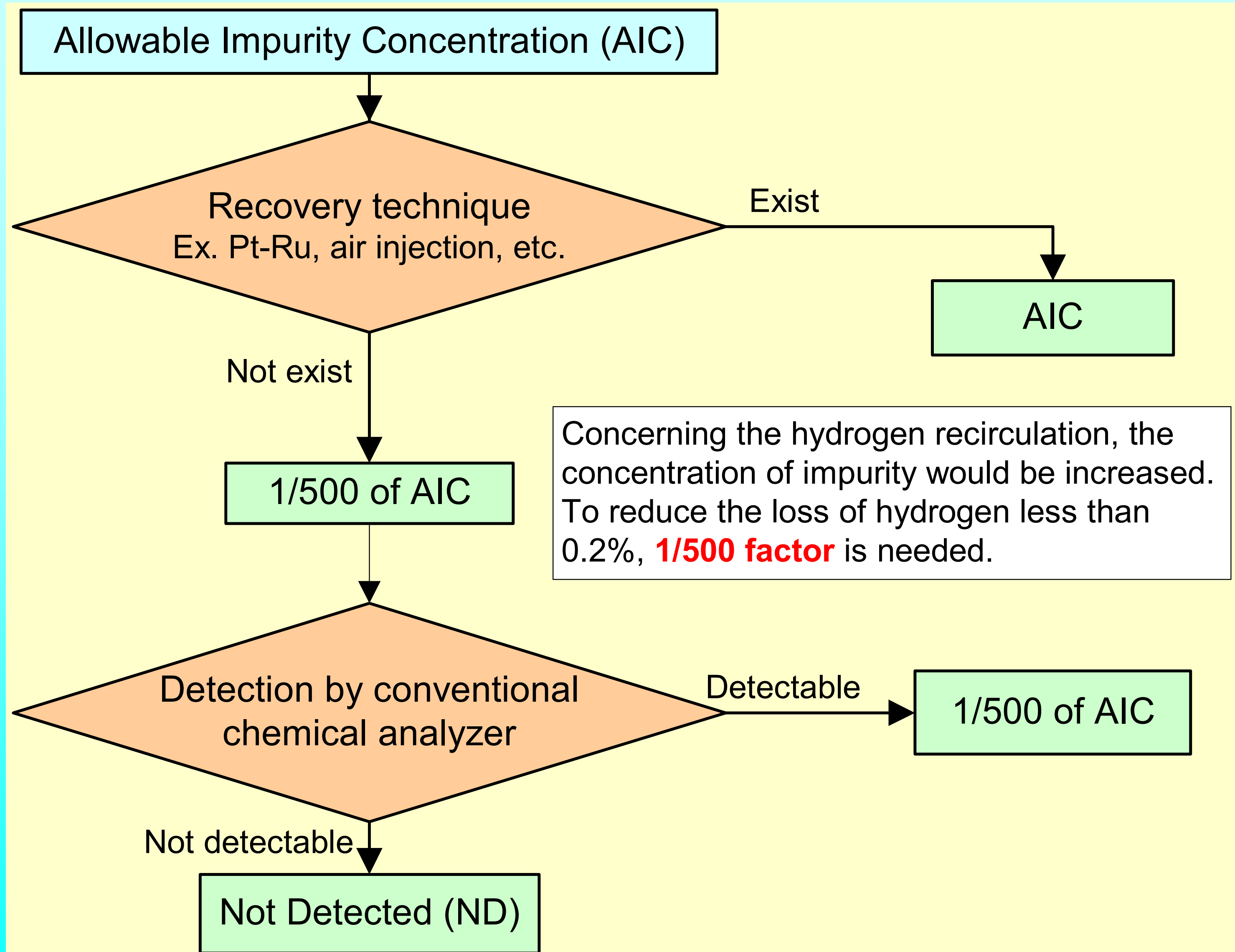
Allowable impurity limit from the 2nd step evaluation test results

Impurities		Tentative allowable limit Fuel electrode catalyst Pt/Pt	Tentative allowable limit Fuel electrode catalyst Pt-Ru/Pt	JIS K 0512 Grade 3 (max. content)	ISO 14687 Type I, Grade A (max. content)
Hydrocarbon	CH_4	5%	5 %	10.0 ppm	100 ppm
	C_2H_6	5%	5 %		
	C_2H_4	5%	5 %		
	C_6H_6*	100 ppm	100 ppm		
CO_2		5%	5 %	10 ppm	No regulation
CO		0.2 ppm	1 ppm	10 ppm	1 ppm
Sulfur	SO_2	0.2 ppm	0.2 ppm	2.0 ppm	2 ppm
	H_2S	0.2 ppm	0.1 ppm		
CH_3OH*		2500 ppm	500 ppm	No regulation	No regulation
HCHO		10 ppm	5 ppm		
HCOOH		100 ppm	20 ppm		
CH_3COCH_3*		250 ppm	500 ppm		
NH_3*		0.3 ppm	0.3 ppm		

*) New test results are not reflected to the NWIP from Japan. The results indicate that new limits should be introduced into the ISO standard.

Reconsideration of H_2 quality standards is necessary.

Flowchart of the impurity limit consideration



Concept of 1/500 factor

- Allowable concentration must guarantee 98% of electric generation capacity of the fuel cell.

- Hydrogen utilization is 99.8%.

- Impurity concentration of hydrogen is 1/500 of the allowable concentration to meet the allowable concentration when utilizing 99.8% of hydrogen.

Because after utilizing 99.8% of hydrogen, concentration of impurities increases by x500 (1 / 0.002 = 500).

NWIP to ISO/TC197 ISO14687 amendment

Dimensions in micromoles per mole unless otherwise stated

Subclause	Characteristics (Assay)	Proposal specifications	ISO 14687 (Type 1, Grade A)
6.2	Hydrogen purity (minimum mole fraction, %)	99.99	98.0
6.3	Para-hydrogen (minimum mole fraction, %)	NS	NS
	Impurities (Max. content)		
	Total gases		
6.4	Water (cm^3/m^3)	NC	NC[a]
6.5	Total hydrocarbon	NS	100
6.6	Oxygen	NS	a
6.7	Argon	NS	a
6.7	Nitrogen	NS	a
6.7	Helium		
6.8	CO_2	NS	
6.9	CO	0.2	1
6.10	Mercury		
6.11	Sulfur	ND[*1]	2.0
6.12	Permanent particulates	f	f
6.13	HCHO	ND[*2]	
6.14	HCOOH	ND[*3]	

NOTE 1 NS: Not specified
NOTE 2 NC: Not to be condensed
NOTE 3 ND: Not detected

a Combined water, oxygen, nitrogen and argon: max. 1900×10^{-6} mol/mol
f The hydrogen shall not contain dust, sand, dirt, gums, oils, or other substancesin an amount sufficient to damage the fueling station equipment or the vehicle (engine, fuel cell) being fuelled.

*1) Recommended value is 0.0002×10^{-6} mol/mol, however it is beyond the lower limit of detection, 0.02×10^{-6} mol/mol by means of a flame photometer-type detector for gas chromatograph.
*2) Recommended value is 0.01×10^{-6} mol/mol, however it is beyond the lower limit of detection, 0.05×10^{-6} mol/mol by means of a detector tube.
*3) Recommended value is 0.04×10^{-6} mol/mol, however it is beyond the lower limit of detection, 0.5×10^{-6} mol/mol by means of a detector tube.

Future plans

Need considerations on the allowable impurity concentration from the following viewpoints:

- **Influence of impurities for longer duration**
- **Influence of impurity accumulation in H_2 circulation system**
- **Measures against impurity poisoning**
- **Cost effect in H_2 production**
- **Methods of monitoring impurity concentration during H_2 production process**

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Japan Automobile Research Institute (JARI)

Thank you for your attention !