Accumulation behavior of Impurities in Fuel Cell Hydrogen Circulation System

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- Conclusion

1-1. Hydrogen Specification for FCVs

Hydrogen for FCV

low — **hydrogen purity** — high

lower fuel cell performance | **high cost**

Evaluation the effects of impurities in hydrogen on fuel cell performance

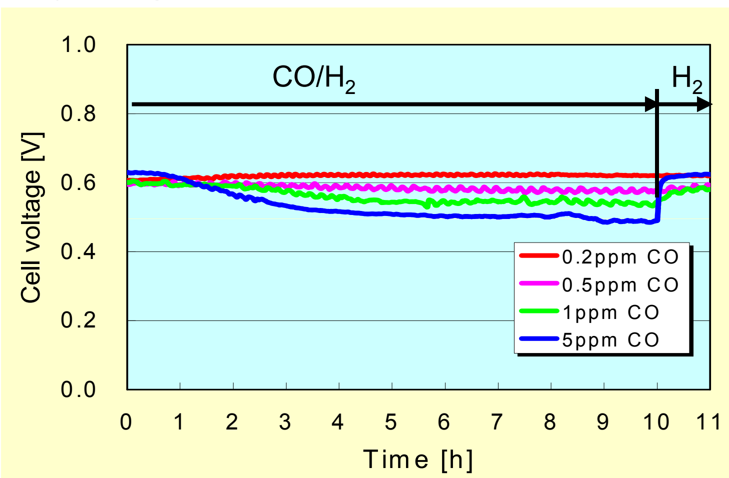


Fig. Example of impact evaluation of impurity (one way pass test).

- Hydrogen quality proposal for FCV
- Published as the TS（Technical Specification）

Table . Hydrogen specification
（ISO/TS 14687-2, March, 2008）

Characteristics	Type I Grade D
Hydrogen fuel index (minimum mole fraction)	99.99%
Non-hydrogen constituents(maximum content) [μmol/mol]	
Total gases	100
Water（H_2O）	5
Total hydrocarbons（C1 basis）	2
Oxygen（O_2）	5
Helium(He), Nitrogen(N_2), Argon(Ar)	100
Carbon dioxide（CO_2）	2
Carbon monoxide（CO）	0.2
Total sulfur compounds	0.004
Formaldehyde（HCHO）	0.01
Formic acid（HCOOH）	0.2
Ammonia（NH_3）	0.1
Total haloganated compounds	0.05
Maximum particles size	10μm
Maximum particles concentration	1μg/L at 20℃ and 101,325kPa

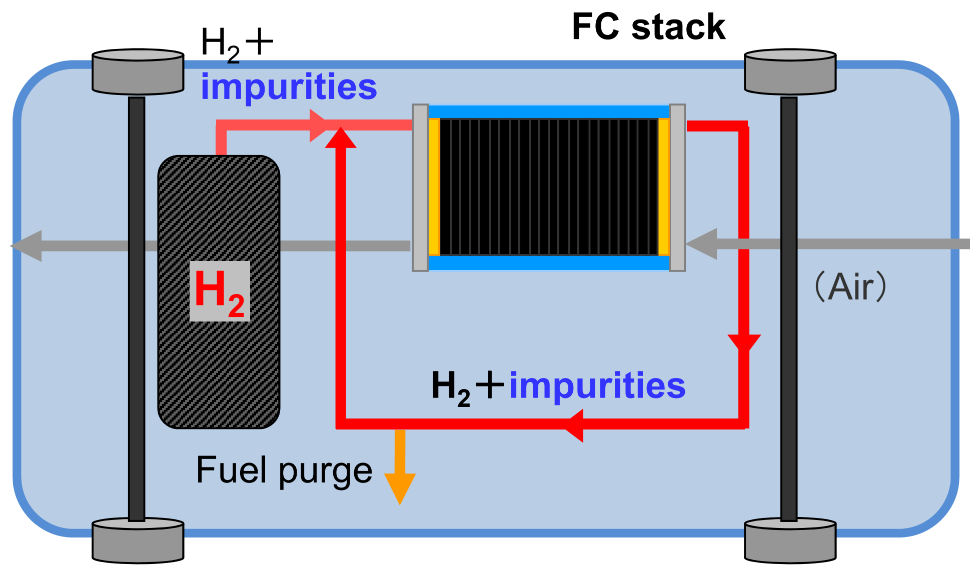
1-2. Purpose of this Study

In the single cell tests,

The unused hydrogen was released into the atmosphere.

In actual fuel cell systems,

The unused hydrogen is returned into the cell upstream by a hydrogen circulation system.



Accumulation behavior of impurities are examined in the fuel cell hydrogen circulation system.

2-1. Examined impurities

	Impurities	Factors to be present in the fuel	Analysis methods
(1)	He	･Exists in the natural gas ･May exceed TS limits, because separation of He from H_2 is difficult.	Direct Mass Spectroscopy
(2)	N_2	･Permeation from the cathode	GC-MS(mass spectroscopy)
(3)	CH_4	･Exists in natural gas	GC-FID (Flame Ionization Detector)
(4)	CO	･Exists in hydrogen reformed natural gas or liquefied petroleum gas ･Decreases fuel cell performance even few ppm	GC-FID (Flame Ionization Detector) for CO analysis, GC-MS for CO_2 analysis
(5)	H_2S		GC-SCD(Sulfur Chemiluminiscence Detector), GC-FPD(Flame Photometric Detector)
(6)	NH_3		GC-FTD(Flame Thermionic Detector) IC(Ion Chromatograph)

2-2. Experiment Methods

(1)Preconditioning

Fuel : High purity hydrogen
Until the cell voltage change ΔV≤1mV/h.

(2)Accumulation test

Fuel : Hydrogen + impurity

(3)Recovery test

Fuel : High purity hydrogen

The gas was sampled and analyzed every 2 hours.

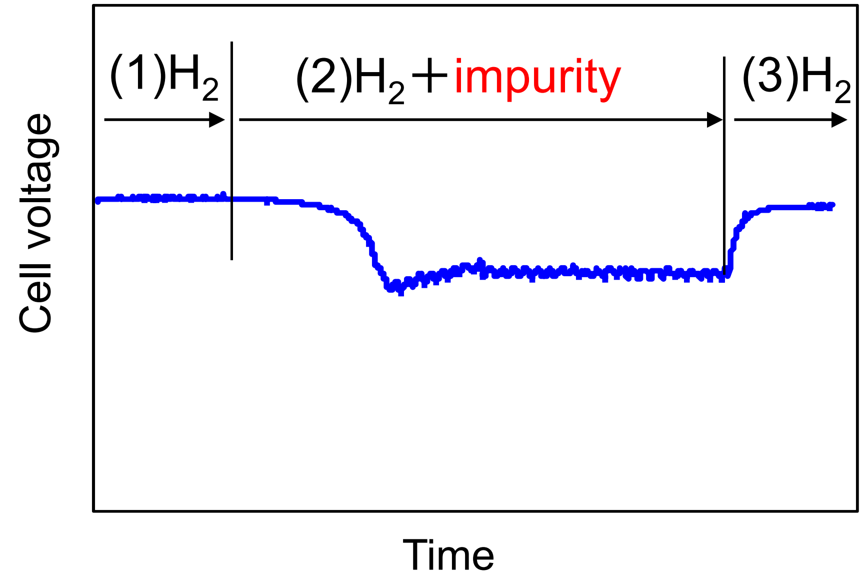


Table. Experiment conditions.

Current density	1000[mA/cm^2]
stoichiometry	4(fuel) / 2.5(air)
Cell temperature	80[℃]
Dew point	77 / 77[℃]
Pressure	0[MPaG](cell outlet)

2-3. Experimental apparatus

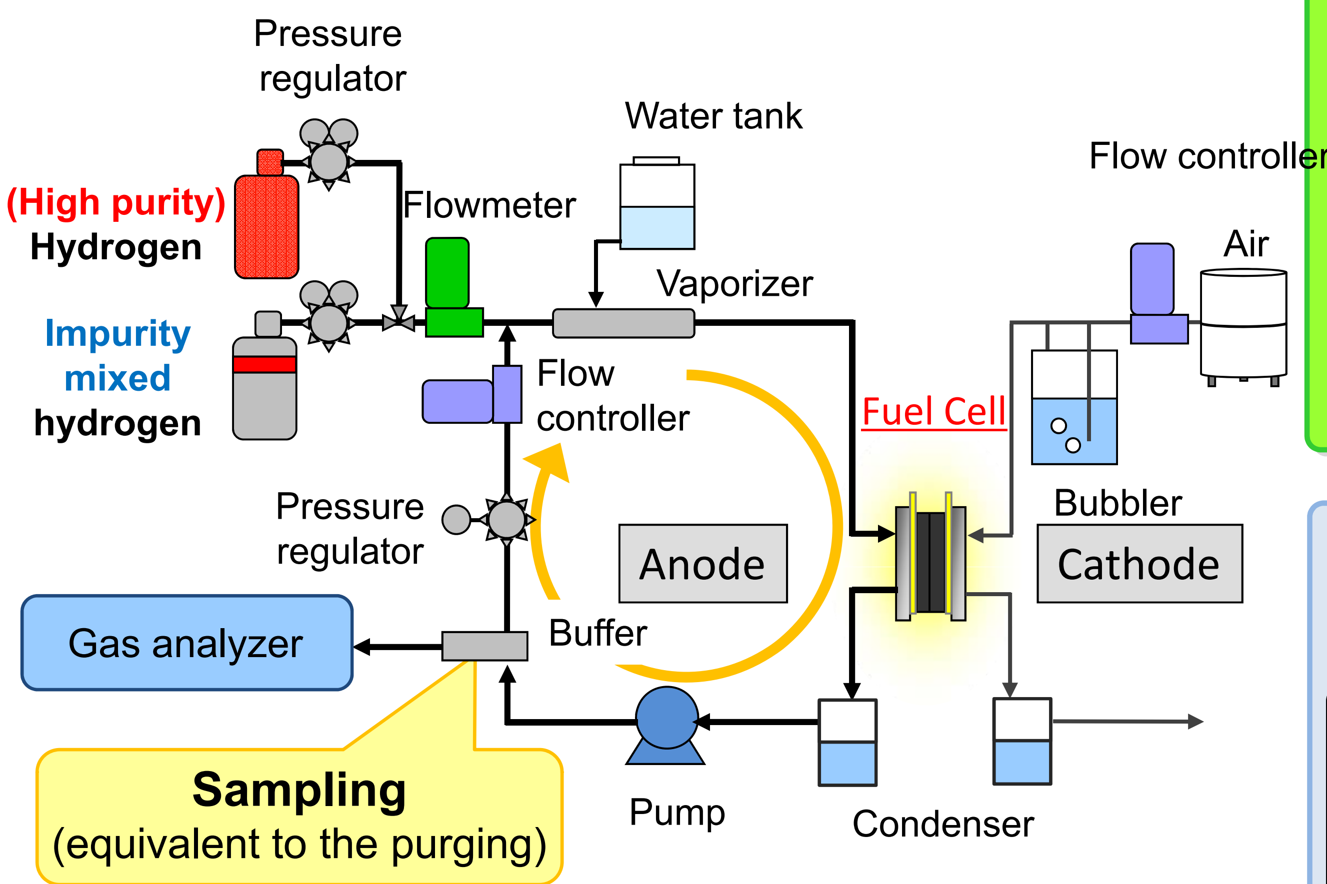


Fig. Experimental apparatus of hydrogen circulation system of fuel cell.

Cell :
JARI standard single cell

Membrane-Electrode Assembly (MEA):

catalyst : Pt / Pt (anode / cathode)

Loading : 0.4/0.4[mg/cm^2]

Electrode area :25[cm^2]

Membrane thickness :30[μm]

2-4. Influential factors on impurity accumulation

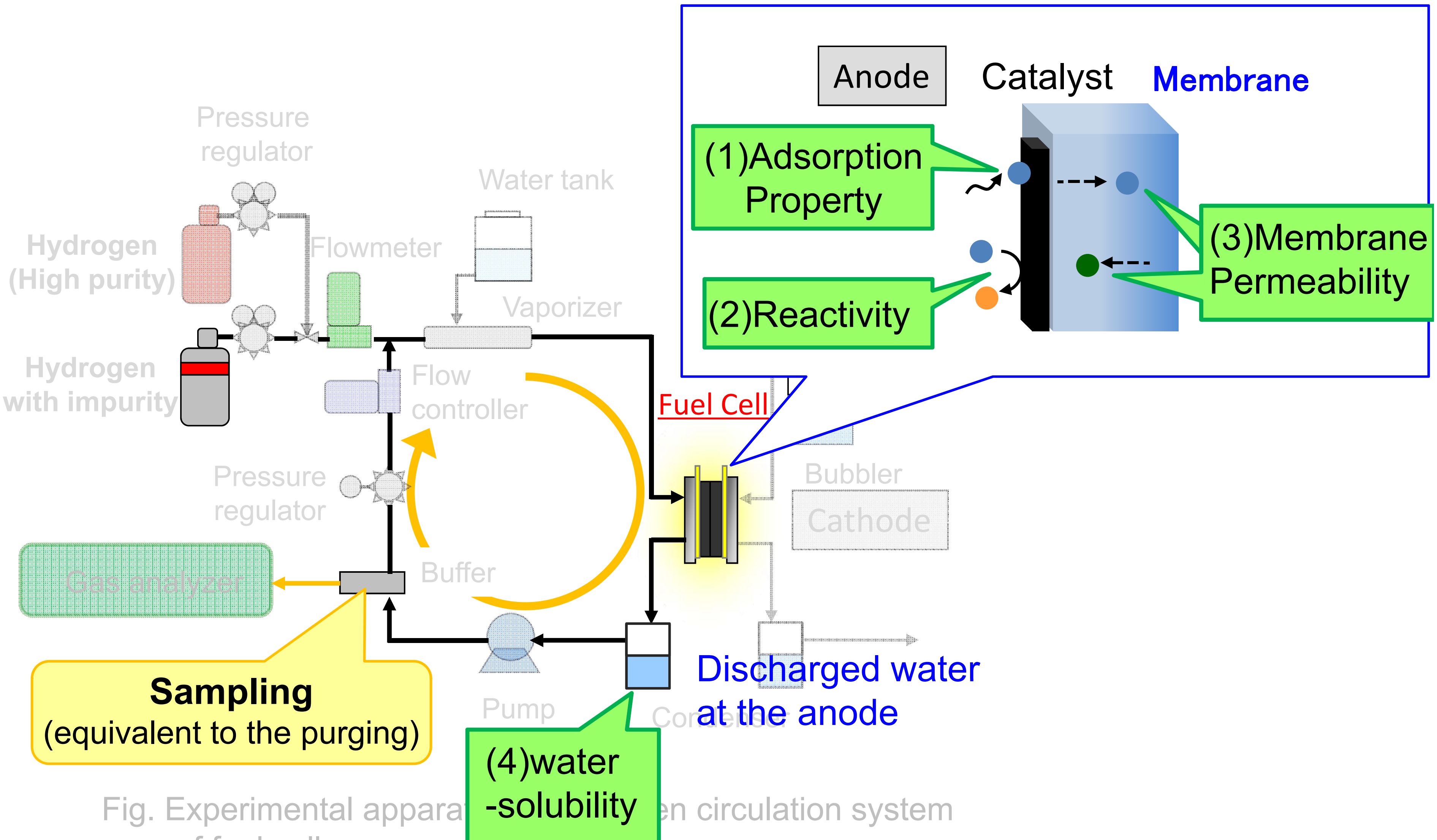
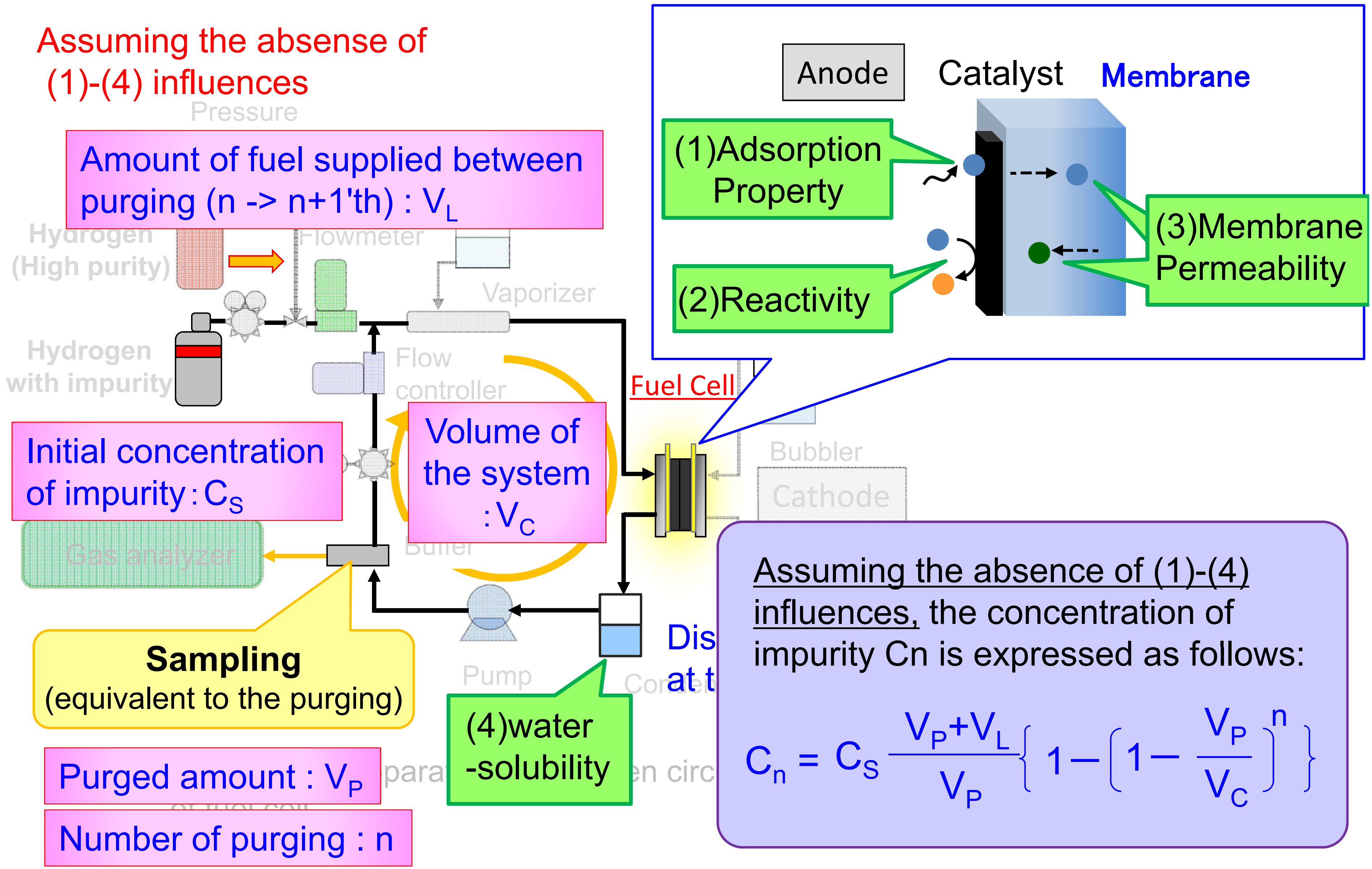


Fig. Experimental apparatus of hydrogen circulation system of fuel cell.

2-4. Influential factors on impurity accumulation behavior



<u>Assuming the absence of (1)-(4) influences,</u> the concentration of impurity Cn is expressed as follows:

$$C_n = C_S \frac{V_P+V_L}{V_P}\left\{1-\left(1-\frac{V_P}{V_C}\right)^n\right\}$$

3-1. Accumulation behavior of CH_4

・CH_4 is inert on the fuel cell reaction.

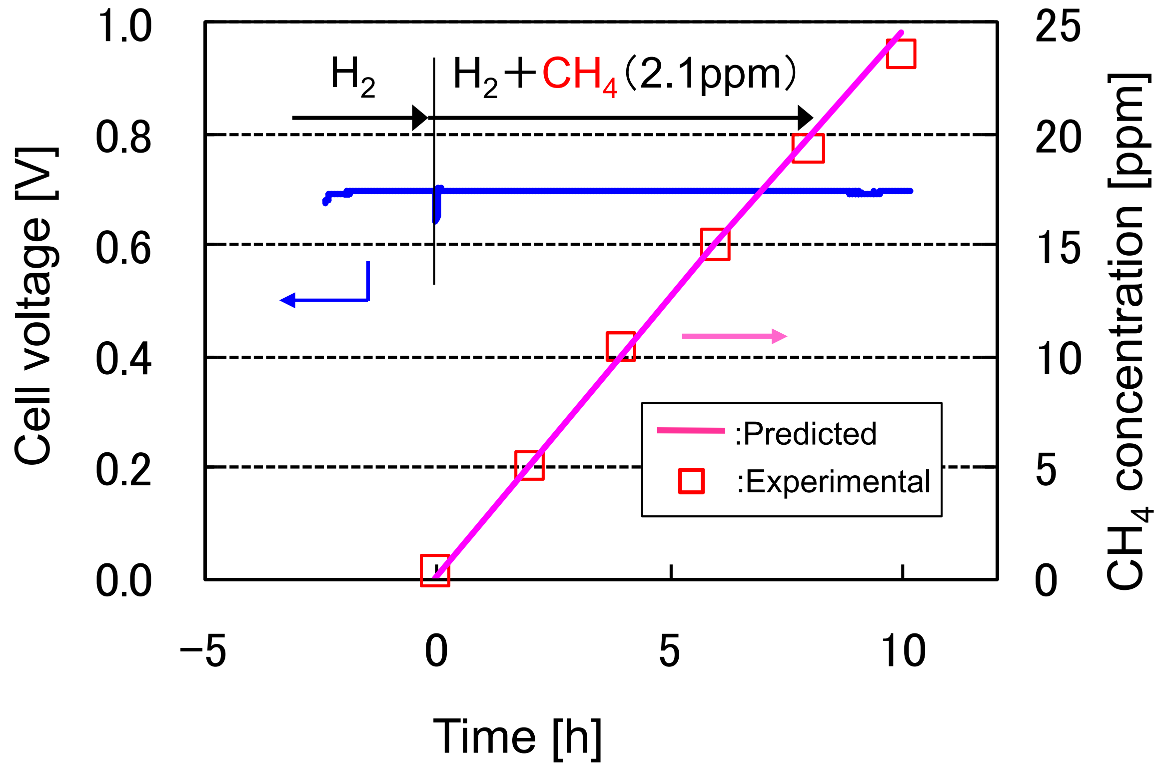


Fig. Accumulation behavior of CH_4 in hydrogen circulation system（500mA/cm^2, stoichi 1.4(fuel)/2.5(air), T=80℃, Dew Point=77℃）.

✓CH_4 concentration increased linearly
✓The measured values were equivalent to the predicted values

3-2. Accumulation behavior of helium (He)

- Separation of He from H_2 is difficult. (may exceed 100 ppm in the TS)
- If the He is easy to permeate, He accumulation may be suppressed.

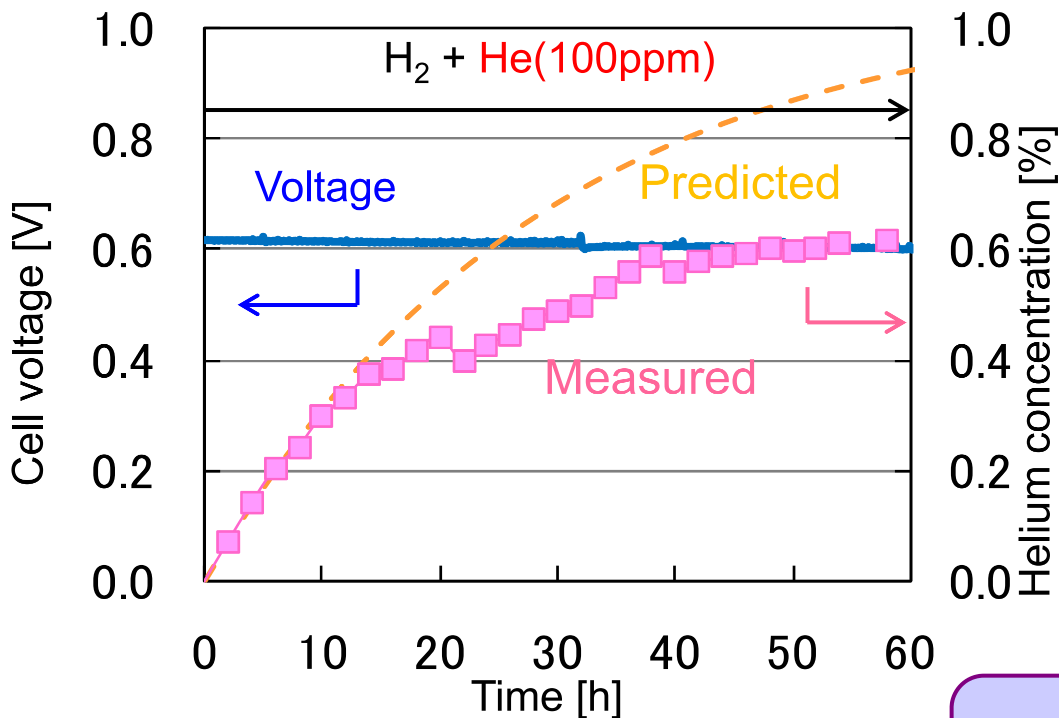


Fig. Cell voltage and helium concentration in the hydrogen circulation system.

Table. Permeability coefficients of hydrogen and helium（T=80℃, Dp=77℃）.

	Gas type	
	Hydrogen	**Helium**
Membrane permeability [mol・m/ m^2・s・Pa]	1.6×10^{-14}	2.4×10^{-14}

1.5 times

✓Helium accumulated, but the concentration became lower than the predicted values, because of the helium permeation.

3-3. Accumulation behavior of N_2

N_2 may permeate from the cathode to the anode

High purity hydrogen (N_2 < 0.05 ppm) was used, and then N_2 concentration was measured.

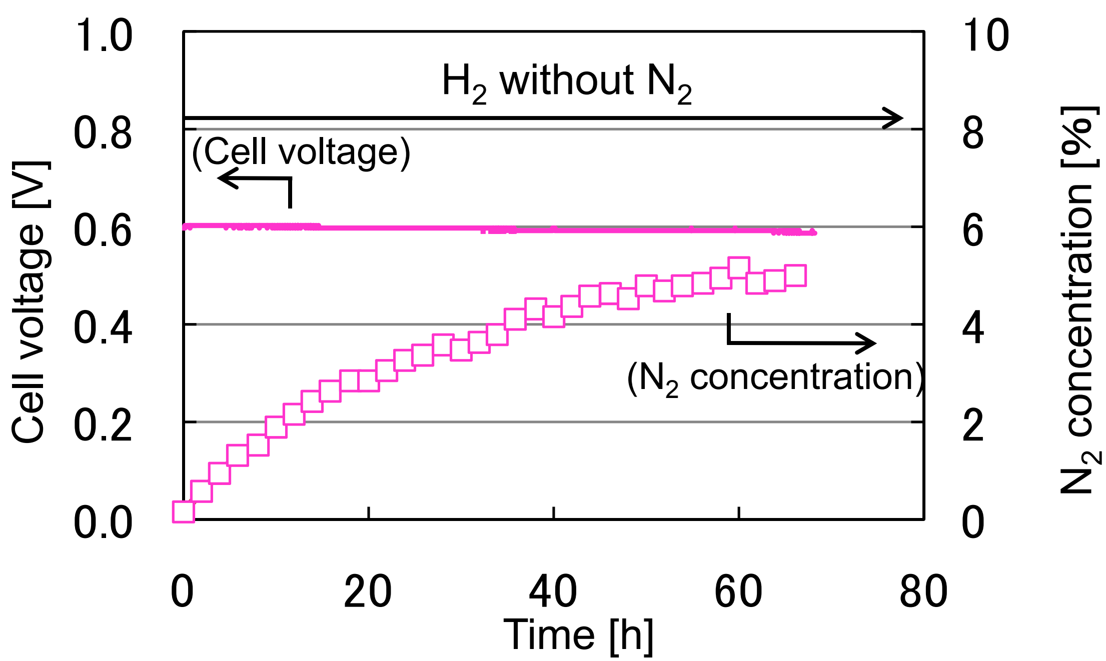
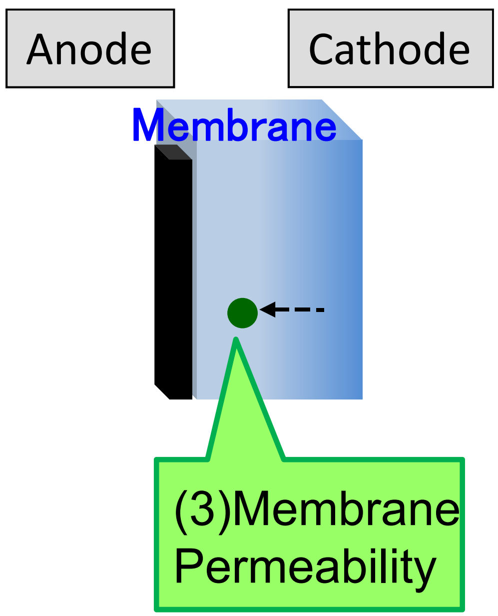


Fig. Cell voltage and N_2 concentration in the hydrogen circulation system.



✓Regadless of the presense of N_2 in the fuel, the N_2 accumulates due to permeation from the cathode.

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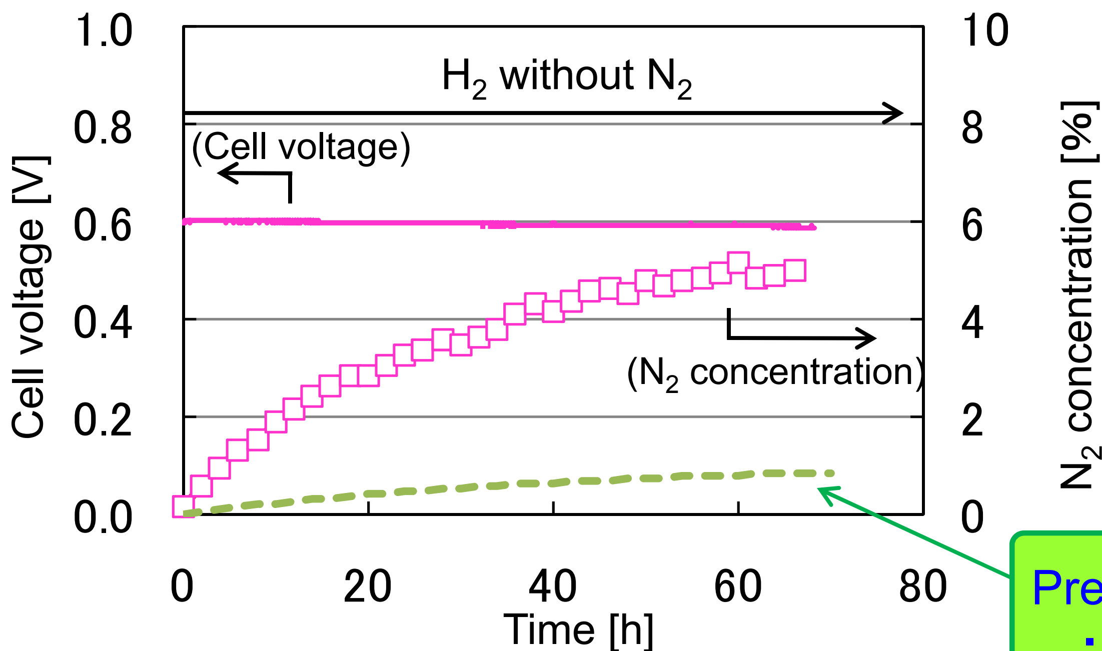
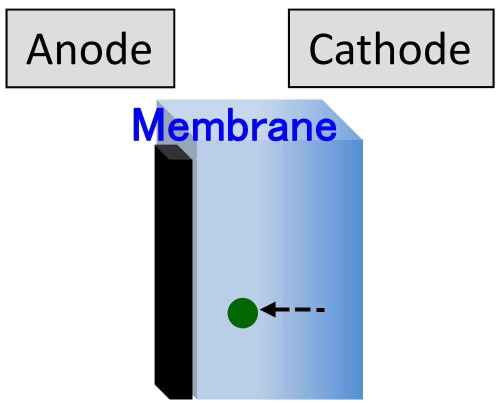


Fig. Cell voltage and N_2 concentration in the hydrogen circulation system.

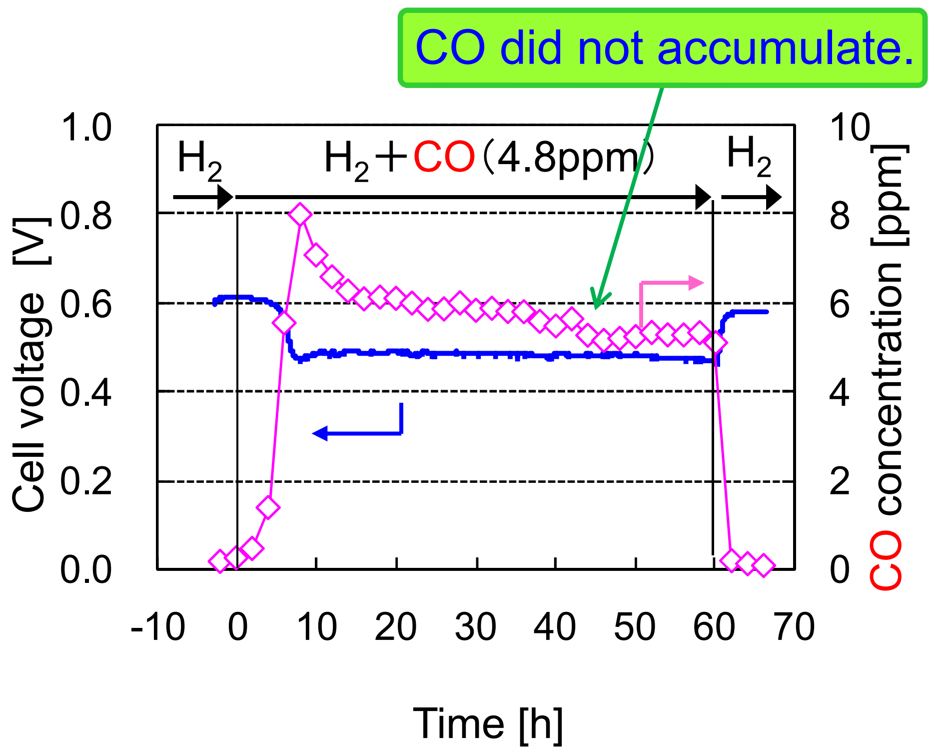


Predicted line assuming
- 100 ppm N_2 in hydrogen
- the absense of N_2 per-meation from the cathode

✓Regadless of the presense of N_2 in the fuel, the N_2 accumulates due to permeation from the cathode.

3-4. Accumulation behavior of CO

CO concentration



CO_2 concentration

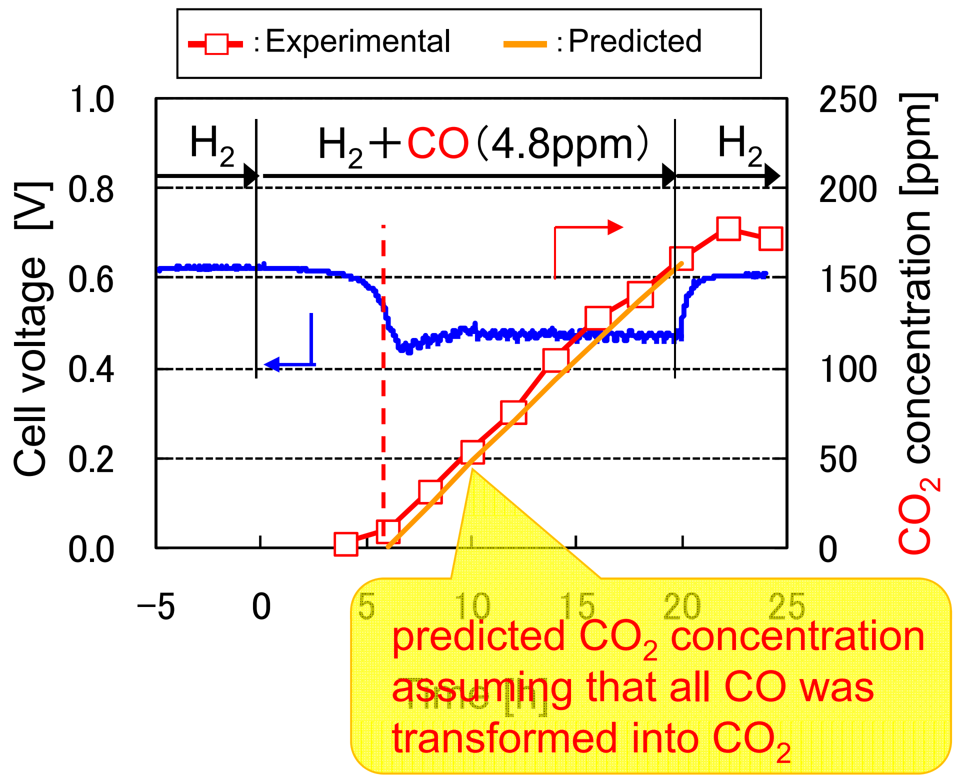


Fig. Cell voltage and CO and CO_2 concentration in the hydrogen circulation system.

- ✓CO did not accumulate.
- ✓CO was oxidized to CO_2, and then CO_2 accumulated.

3-5. Accumulation behavior of H_2S

H_2S : 1.1ppm (the concentration at the hydrogen circulation mode)

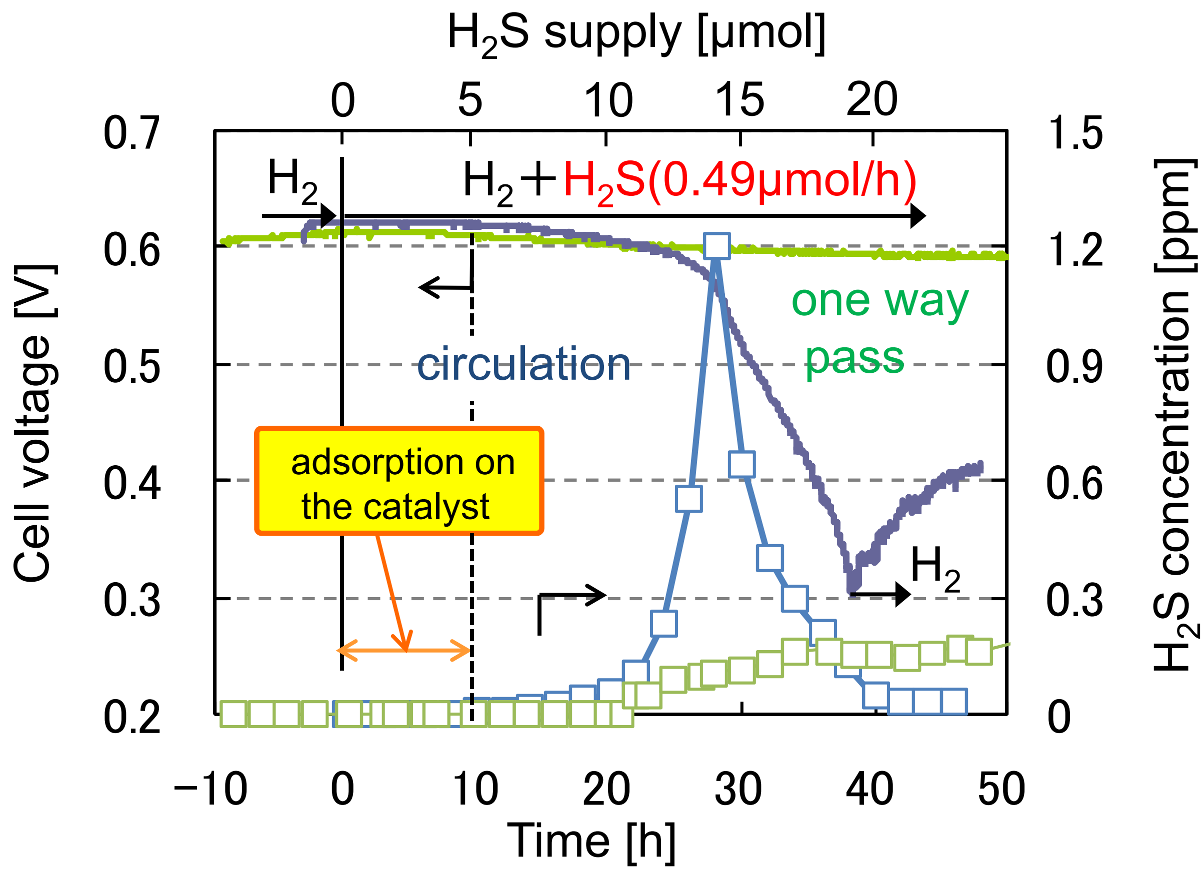


Fig. Cell voltage and H_2S concentration.

✓H_2S was not detected until 5 μmol both circulation and one way pass mode.

3-5. Accumulation behavior of H_2S

H_2S : 1.1ppm (the concentration at the hydrogen circulation mode)

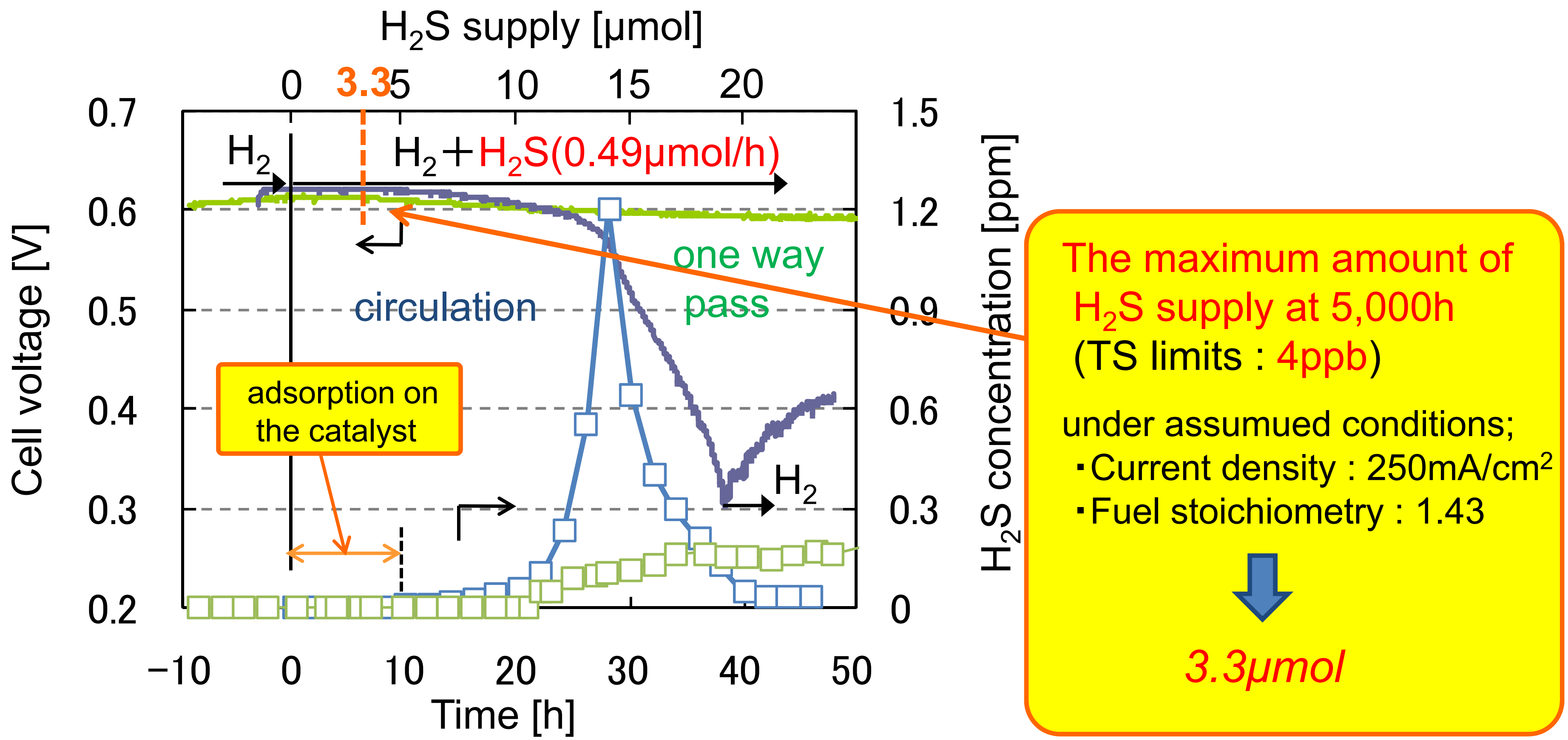


Fig. Cell voltage and H_2S concentration.

✓Under the assumed conditions, it is expected that H_2S is not accumulated in the hydrogen recirculation system.

3-6. Accumulation behavior of NH_3

Water solubility of NH_3 is large.

- Measurements of NH_3 concentration in the *circulation system*
- Measurements of the NH_4^+ in the exhaust gas and water under the condition of *one way pass test*.

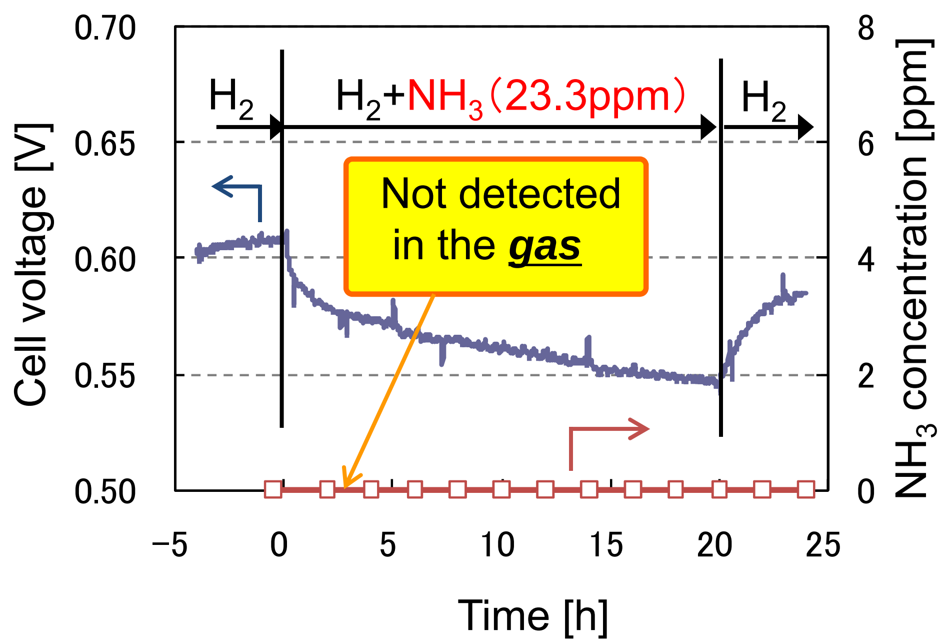


Fig. Cell voltage and NH_3 concentration *in the hydrogen circulation system*.

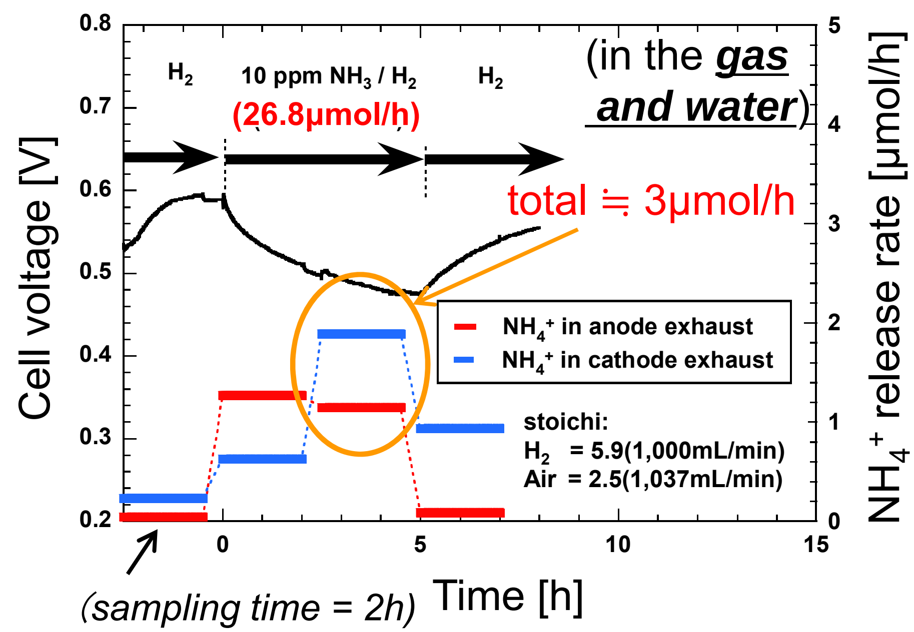


Fig. Cell voltage and NH_4^+ release rate in anode and cathode exhaust. *(one way pass mode)*

- ✓NH_3 did not accumulate in the gas phase.
- ✓Discharged NH_4^+ concentration was 1/10 of the supplied amount.

4. Conclusions

- Accumulation behavior of impurities differ according to the type of impurities.
- Current allowable concentration of some impurities may be relaxed.

Table. Accumulation of impurities in hydrogen circulation system.

Impurities	Voltage degradation	Accumu-lation	Adsorption property	Reactivity	Membrane permeability	Water solubility	Reflection to the current TS concentration
CH_4	No	Yes	No	No	-	No	
He	No	Yes	No	No	Yes (anode → cathode)	No	Possibility to be relaxed because of permeation to cathode
N_2	No	Yes	No	No	Yes (cathode → anode)	No	further discussion is needed because the permeation from cathode is large
CO	Yes	No	Yes	Yes (CO → CO_2)	-	No	They didn't accumulate, but further discussion is needed (anode platinum loading will be taken into consideration)
H_2S	Yes	No	Yes	-	-	Yes	
NH_3	Yes	No	-	-	Yes (anode → cathode)	Yes	

Acknowledgements

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Thank you for your attention!