Exhaust gas characteristics of Mirai I and II (FCV) on and off the Highway

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ABSTRACT

In order to achieve carbon neutrality by 2050, the use of H_2 is being promoted among various energy sources that do not emit CO_2. Regarding fuel cell vehicles (FCVs), a new model, Second Generation the Mirai by Toyota called the Mirai II that is dramatically more efficient and compact has been released. And compared with the Mirai I. When using H_2, the safety considerations are also important due to its wide explosive range and impact. According to the Global Technical Regulation (GTR) on FCV exhaust gas standards, the H_2 concentration level of a fuel cell exhaust system must not exceed 4% by volume average during any 3-second time interval during normal operation, including start-up and shutdown, at the exhaust point [1]. Therefore, the challenge is how to quickly measure the hydrogen concentration in the exhaust gas in msec.
In this study, we monitored the characteristic features of exhaust gases of H_2 and other gases of a new and old model on and off the highway and comparing the results with those obtained when the vehicle is idling. [7]
In the Mirai I, the hydrogen concentration in the exhaust gas was less than 1%, and less than 0.5% when idling, while in the Mirai II, it was recorded as 6% when idling, and less than 3% when driving. When real-time hydrogen measurements were carried out, the Mirai I had a high-resolution spectrum that formed a stepped peak, but the Mirai II had a single peak. From this, it can be inferred that the Mirai I had a diffuser that did not emit hydrogen all at once, while the Mirai II had direct injection. If the hydrogen content in the exhaust gas exceeds 4%, there is a risk of explosion, so care must be taken[8].

1.Introduction

Towards 2025 Osaka World Expo, various Hydrogen applications without CO_2 emission are prospectively being developed. Fuel cell in house applications is expected to simultaneously generate tri-generation of electricity, heat and hot water. Fuel Cell Vehicles in new efficient models (2nd Gen. Mirai by Toyota called Mirai II) with the dramatically optimized in mechanical, electrical, and chemical background technologies come out. From the safety point of view, the explosion limit for H_2, 4% and GTR (Global technical regulation) on FCV considering the value of 4% of H_2 release[1]. In production line, the H_2 concentration limit of 0.1% and 1% are the comprehensible upper limit. By GTR, Fuel cell discharge system at the vehicle exhaust system`s point of discharge, the hydrogen concentration level shall not exceed 4 % average. Our focus is to analyze the mixing process of 100% H_2 with air to find unintended concentration of H_2 in clouds. The real time monitoring of the process of mixing 100% H_2 with air in milliseconds is our study purpose. Considering real time monitoring of H_2 concentration, the portable hydrogen sensor (Sx) is built using mass spectrometer to measure gas mixtures in millisecond intervals. Several Sxs are located to measure the real time images of 3-Demensional H_2 concentrations. The concentration profile in milliseconds by high-speed camera is taken using the Schieren Photography at the same time.

GTR for H_2 disposal; Agreement concerning the establishing of GTR for wheeled vehicles, equipment and parts which can be fitted and/or be used on wheeled vehicles is mostly solidified. According to GTR on FCV, fuel cell discharge system at the vehicle exhaust system`s point of discharge, the hydrogen concentration level shall not exceed 4 % average by volume during any moving three- second time interval during normal operation including start-up and shut down.[1]

FC stack needs to be washed out by the concentrated hydrogen as the purge gas and how to exhaust gas without exceeding 4 % is the most concerns.

How to measure hydrogen pulse of millisecond in exhaust is the rising up issue. Further,any single failure downstream of the main H_2 shut off valve shall not result in a H_2 concentration in air of 4 % or more by volume within the passenger compartment. If a single failure get down stream of the main hydrogen shut off valve results in a H_2 concentration in air of 4 % by volume within an enclosed or semi-enclosed space in vehicle, the main H_2 shutoff valve shall be closed and warning to the driver shall be provided. In this paper, model of FCV hydrogen discharge system was composed of plastic tube with pressure gage, Mass Flow controllers and Highspeed Solenoid valves. Variety of simple experiments, injection, mixing, change flow rate and change tube inside diameter were carried out to control the H_2 concentration also Nitrogen (N_2) instead of Air. In mixing experiment, H_2 gas was introduced in the N_2 & Air flow to form the various H_2 concentrations. H_2 at the point of discharge was monitored by the real time H_2 monitoring system Sx. The fast solenoid valve was opened within milliseconds to add H_2 gas in N_2 & Air flow, H_2 gas ran through the tube by mixing with N_2, and the wave front at the point of discharge was observed. In the milliseconds following the mixing process the separated phases were shown by the real time H_2sensor and the wave front concentration of H_2 during stop and release type of motions was topics. In milliseconds diffusion mechanism does not work but Reyleigh -Taylor instability might work.

In order to detect low concentration of H_2 in real time at the same time other gases, various kinds of hydrogen detectors exist but each sensor presents difficulty to measure 0-100 % concentration of hydrogen. Semiconductor gas sensor, for example, cannot measure 100 % hydrogen. Catalytic gas sensor with filter needs time for hydrogen to penetrate filter. Laser detector does not work in millisecond and humid condition.In order to detect hydrogen in real time, mass spectrometer system with differential pumping stage was selected to develop real time monitoring system and applied to H_2/N_2 mixing experiments. In hydrogen release experiment on the mountain, high pressure H_2 gas was emitted from the pipe in the air to form the various H_2 concentrations of cloud. H_2 diffusion process was monitored by the real time H_2 monitoring system.[5,6,7,8]

2. Experimental

2-1 H_2 sensor (Sxi)

H_2 sensor (Sxi) and it`s Schematic diagram o is shown in Fig.1 and 2. The weight of Sx is 25kg and portable for the outdoor mountain experiment [2]. When Sx measure H_2, alarm red light is on. Liquid crystal touch panel is used to control Sx to start by open valves. Sx has self-calibration system having certain concentration of single to mixed calibration gases. And having these calibration lines for each gas, Sx can monitor and show the concentration of each gas immediately. Real time monitoring is carried out from 2ms and longer intervals. For the real time monitoring system inside volume of Sx is minimized. Sampling inlet of this system is 150-250 μm SUS capillary tube by 1m. Gas sample is introduced from capillary through dehumidifier and skimmer to ionization chamber. This system has the differential pumping stages and ionization system by electron bombardment method (EB). To minimize water product and humidity influence, Sx has dehumidifier with heater. Mass Spectrometer system works up to m/Z=300. Schlieren Photograph (SP) is applied to monitor the movement of hydrogen cloud, mixed gases density profile and the explosions. So from gas exit we can monitor the concentration profile by Sxi and density profile by SP at the same time. SP is monitored by high-speed camera in 1 msec[2,3,4,6,7].

Fig.1 H_2 Sensor (Sxi)

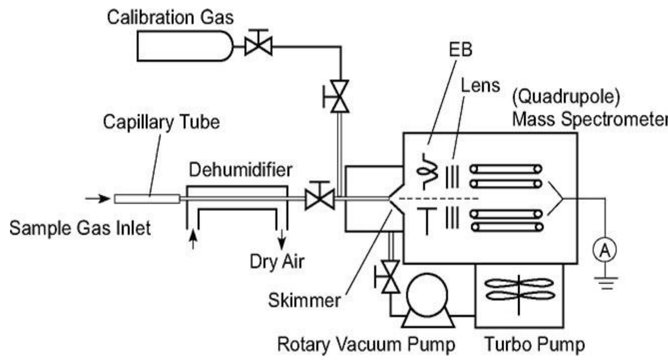

Fig.2 Schematic diagram of Sxi

2-2 Exhaust gas monitoring

A sampling capillary (inner diameter/outer diameter = 250/500 μm, length 2.5 m) for exhaust gas monitoring was attached to the center of the tip of the opening of the exhaust pipe outlet of a Mirai FCV, and mounted on the rear seat of the Mirai and battery located in the car trunk room and connected to a mass spectrometer Sxi (HysafeNohmi), to sample exhaust gas and monitor the gas concentrations of H_2, N_2, O_2, Ar, and CO_2. Since the Sxi requires a certain amount of startup power when starting up, an inverter (Lvyuan/F-4000P) was connected to a battery (GS/YUASA 115D31Lx2) to provide power for the Sxi during idling test to Highway driving test.
When measuring exhaust gas, water may be discharged from the exhaust pipe during test, so a filter was placed on the tip of the capillary. Measurements were taken at 200 millisecond intervals while the FCV was idling and running (60 and 110 km/h).

3.Result and Discussion
3-1 During idling

The concentration of components in the exhaust gas during idling is shown in Fig. 3. Fig. 3-1 shows the time-dependent changes in the concentration of five types of gases: H2, N2, O2, Ar, and CO2.
The timing of the fluctuations in nitrogen and oxygen was consistent, with a cycle of about 100 seconds.
Although hydrogen fluctuated periodically, it did not match the cycle of nitrogen and oxygen,and a wider range of fluctuations was confirmed, with a cycle of 100–150 seconds. Fig. 3-2 shows the time-dependent changes in the concentrations of N_2 and O_2. From an atmospheric composition of about 78% nitrogen and about 21% oxygen, oxygen dropped to 8% for about 30 seconds, rose to 92%, and then returned to atmospheric composition for about 60 seconds. This cycle was repeated. It is thought that oxygen in the air was consumed at the anode, causing the nitrogen concentration to rise.
Next, the time-dependent changes in the hydrogen peaks were shown, the peak immediately after engine start (Fig.3-3) and the periodic peaks (Fig.3-4). The H_2 peak immediately after engine start

was released at a concentration of 1-3% for about 5 seconds, followed by a large hydrogen emission peak of 6% for about 1 second. Meanwhile, the periodic peaks showed three successive peaks of up to 4%, as shown in Fig.3-4.

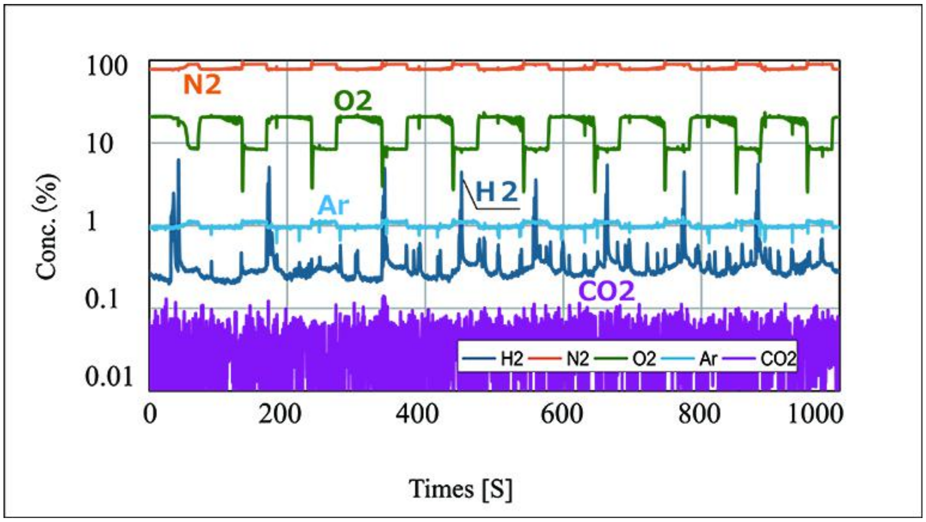

Fig 3-1 In Idling Mode ,Exhaust Gas analysis of Mirai II

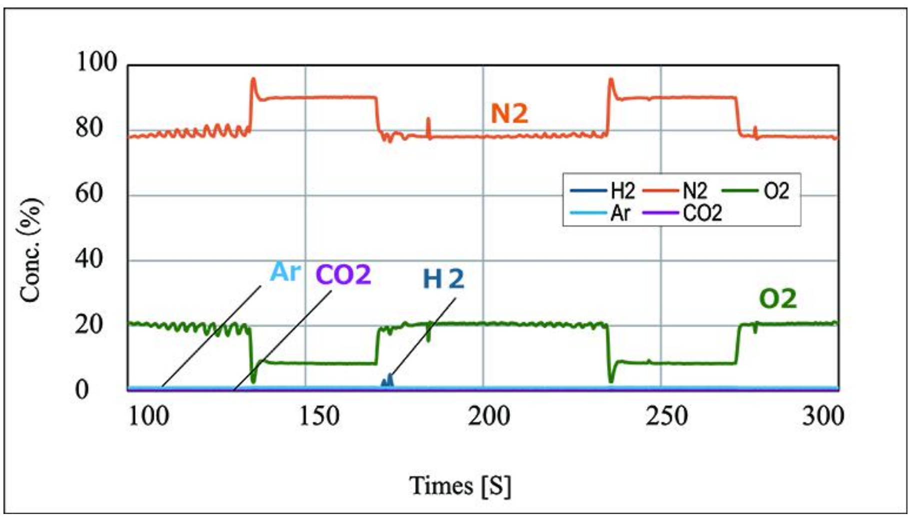

Fig 3-2 In Idling Mode, N2 and O2 gases by time in Exhaust Gas of Mirai II

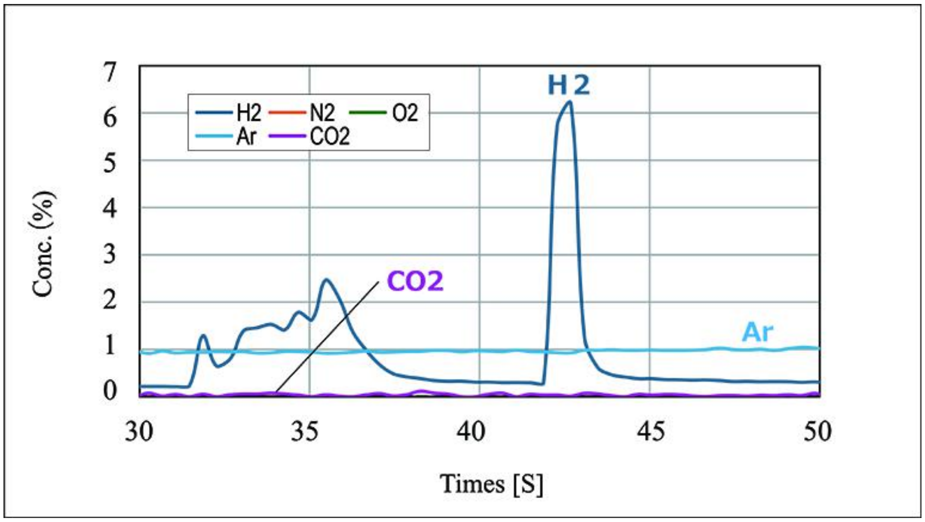

Fig 3-3 H_2 concentrations vs time in the exhaust gas in idling Mode

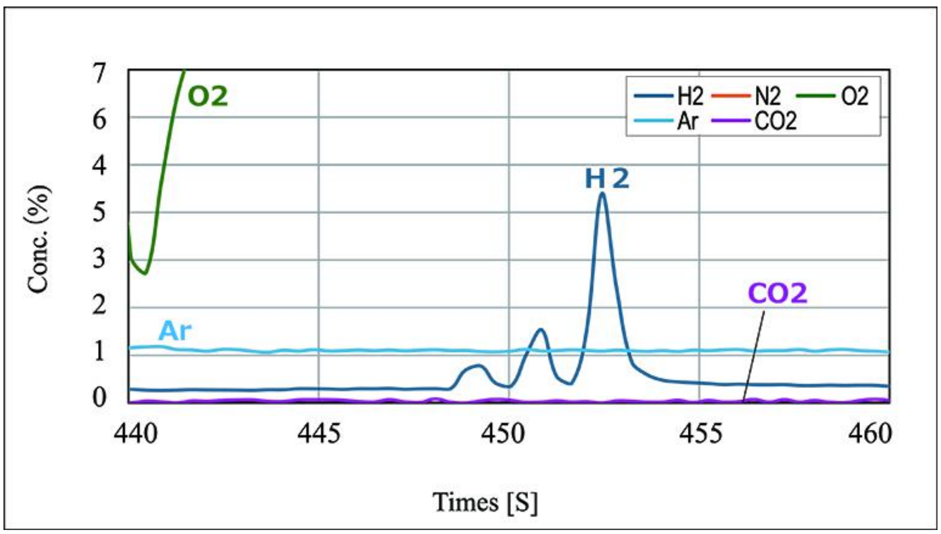

Fig 3-4 H_2 concentrations vs time in the exhaust gas in idling Mode

3-2 Driving at 60km/h

The hydrogen concentration in the exhaust gas when driving at 60km/h is shown in Fig. 4.
In the 1000-second H2 gas concentration measurement results shown in Fig. 4-1, hydrogen peaks were observed almost every 100 seconds, just like when idling, but the maximum concentration was 3%, and the rest were less than 0.5%, which was lower than when idling. In addition, when the peak where the maximum concentration was observed was enlarged with increased resolution (Fig. 4-2), it was confirmed to be a single peak. Although three peaks were observed when idling, there were no peaks that increased or decreased in stages.

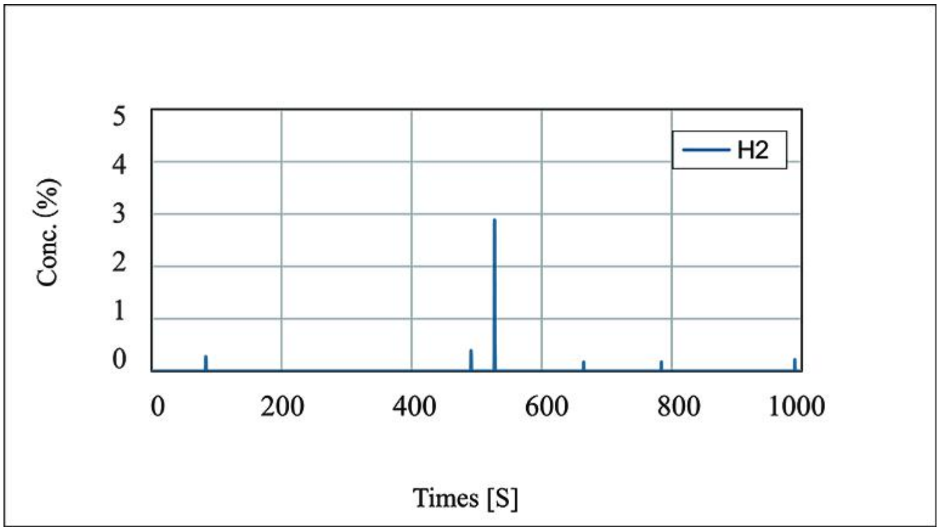

Fig.4-1 Constant 60Km/hr Mode H_2 concentration in Exhaust Gas

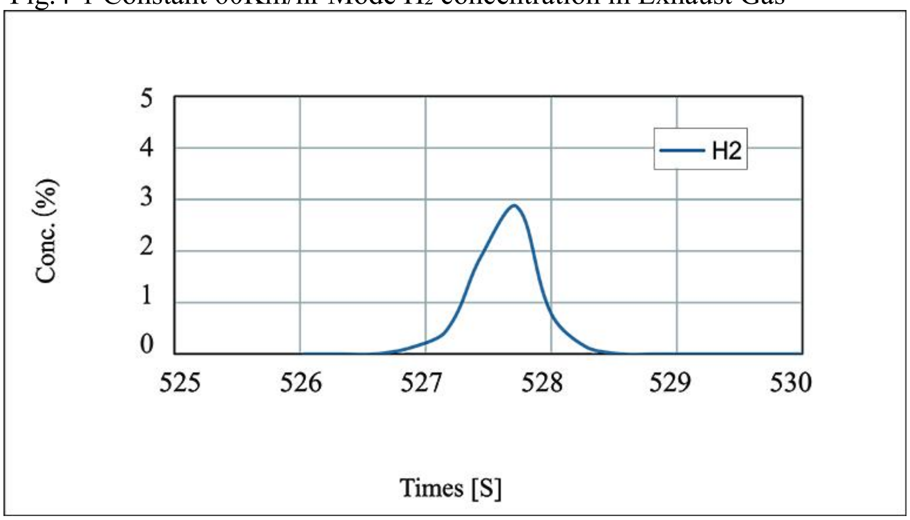

Fig.4-2 H_2 concentration in magnified scale

3-3 At 110km/hr high speed

Fig. 5 shows the component concentrations in the exhaust gas when driving at 110km/h. Fig. 5-1 shows the time-dependent changes in the measured gas concentrations of all components on a logarithmic scale. As with idling, for nitrogen and oxygen, atmospheric composition and a decrease in oxygen concentration and an increase in nitrogen concentration are repeated at intervals of about 100 seconds. It can be seen that the time ratios of these two states are different. It was also confirmed that the intervals at which peaks are detected for hydrogen are shorter than when the vehicle is stopped. Fig. 5-2 shows the changes in nitrogen and oxygen concentrations. When driving, the oxygen consumption state continues for about 90 seconds, and the cycle of returning to atmospheric composition for about 10 seconds is repeated. Considering that the oxygen consumption state when the vehicle is stopped is 60 seconds, it is thought that oxygen is consumed for a long time. Fig. 5-3 shows the hydrogen concentration, and Fig. 5-4 shows the hydrogen concentration at an even higher resolution and shorter time interval. Looking at Fig. 5-3, it can be seen that the hydrogen detection interval was 10–50 seconds, which is a very short interval compared to when idling or driving at 60km/h. Meanwhile, the detected hydrogen concentration was low, at a maximum of less than 4%, the same as when driving at 60km/h, and a relatively low concentration compared to when idling. This is thought to be because the measurement point was at the tip of the exhaust port, and outside air mixes in when driving. Looking at the peaks in Fig. 5-4, they were detected as one peak, just like when driving at 60km/h. It is thought that this was also detected as one large peak when driving due to outside air mixing in.

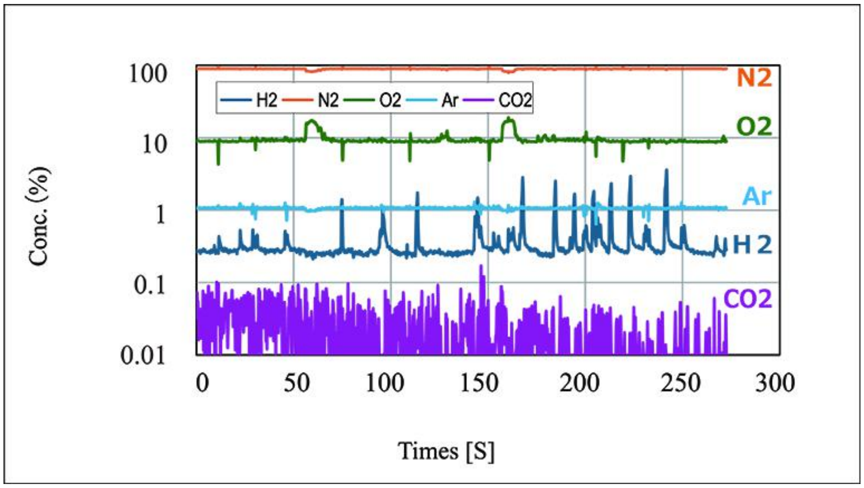

Fig.5-1 110Km/hr highway drive Mode H_2, monitoring Exhaust Gases vs time
Gas concentrations profiles of exhaust gas on 110km/h highway driving

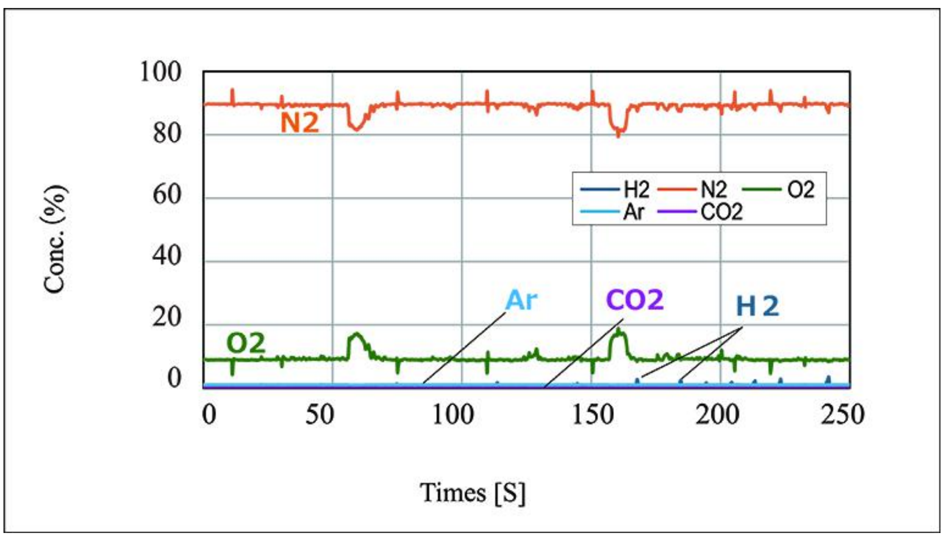

Fig.5-2 O2 and N_2 concentration vs time

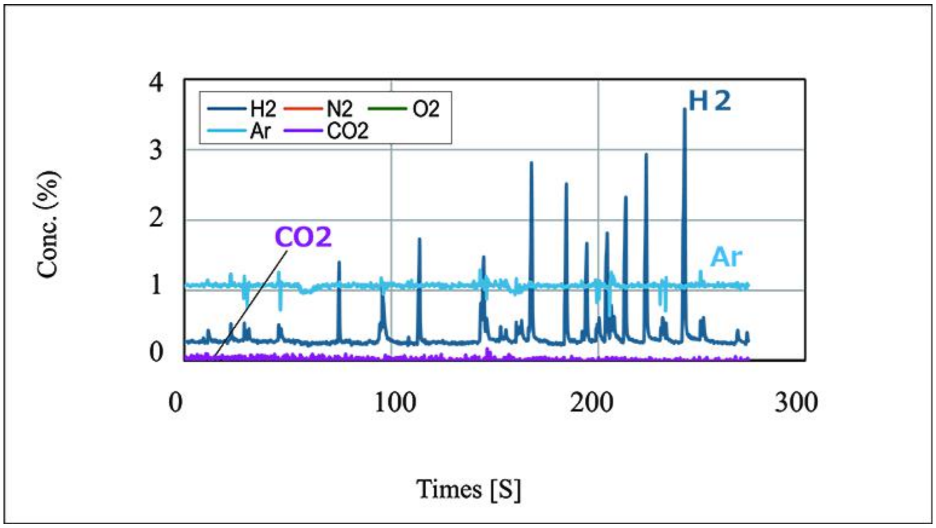

Fig.5-3 H_2 concentration profile vs time

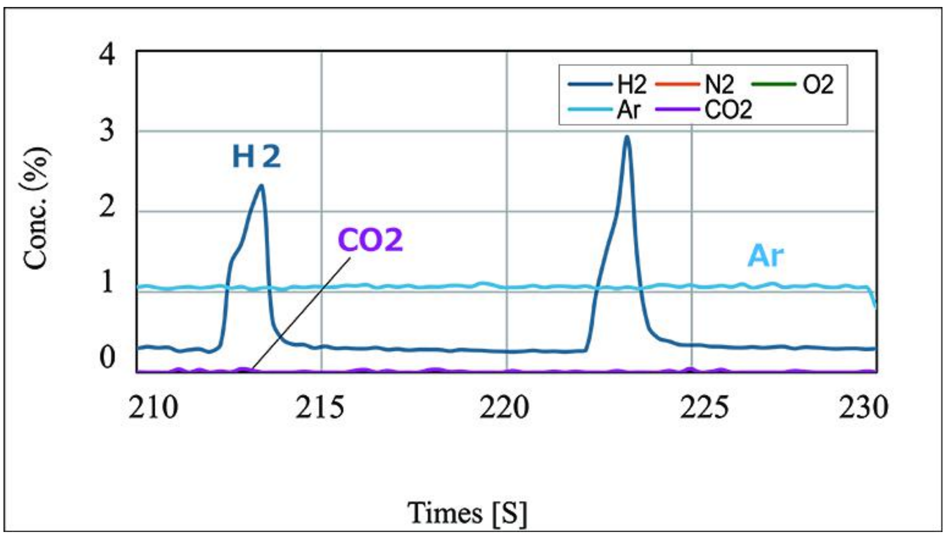

Fig.5-4 Magnified H_2 peak vs time

3-4 Comparison between Mirai I and Mirai II

The results of the Mirai II driving experiment reveal the following. Focusing on the changes in oxygen and nitrogen consumed at the anode, it was found that the atmospheric composition and the atmospheric composition show a periodic cycle of oxygen decrease and nitrogen increase, both when idling and when driving. It was confirmed that one cycle lasts about 100 seconds. However, the time during which oxygen is consumed is about 30 seconds when idling, but increases to about 90 seconds when driving at 110 km/h, confirming that the oxygen consumption situation affects the power generation of the fuel cell.
Next, the periodic hydrogen peaks at the cathode were observed every 100–200 seconds when idling and driving at 60 km/h, but at very short intervals of 10–50 seconds when driving at 110 km/h. Unlike the periodic changes in oxygen and nitrogen, it is thought that the intervals between emissions are variable and change depending on the accelerator speed and power consumption.
Finally, looking at each of these hydrogen peaks, three peaks were observed during periodic detection while idling (Fig. 3-4), whereas a single peak was observed regardless of speed while

driving (Fig. 4-2, 5-4). In addition, the maximum concentration observed was 6% while idling, whereas a relatively low concentration of up to 3% was observed while driving. When idling, hydrogen is less likely to mix with outside air, and small changes were observed, whereas when driving, the hydrogen concentration decreases due to mixing with the outside air caused by the air flow around the exhaust port as the vehicle moves, and as a result, the low hydrogen concentration peak was not detected[8].

Comparison between the first and second generations

In the first generation future experiment, monitoring was only performed during idling. The timing of hydrogen emission was constant at about 60 seconds, and the hydrogen concentration was 0.2-1.2% at the time of measurement, and the hydrogen concentration was not constant during measurement. When the fine structure of this single pulse is analyzed by high-speed measurement, it is found that the single peak is a collection of several small peaks, which suggested that the hydrogen in the exhaust gas is traveling on different routes with different flight distances, and suggest the presence of a diffusion layer that prevents the hydrogen concentration from becoming too high. Since the fine structure could not be confirmed in the second generation from the above experimental results, it is believed that the hydrogen is directly injected sometimes the concentration of H_2 is increased, and it is confirmed that there is a difference in the way the hydrogen gas is discharged between the first and second generations[5,6,7,8]

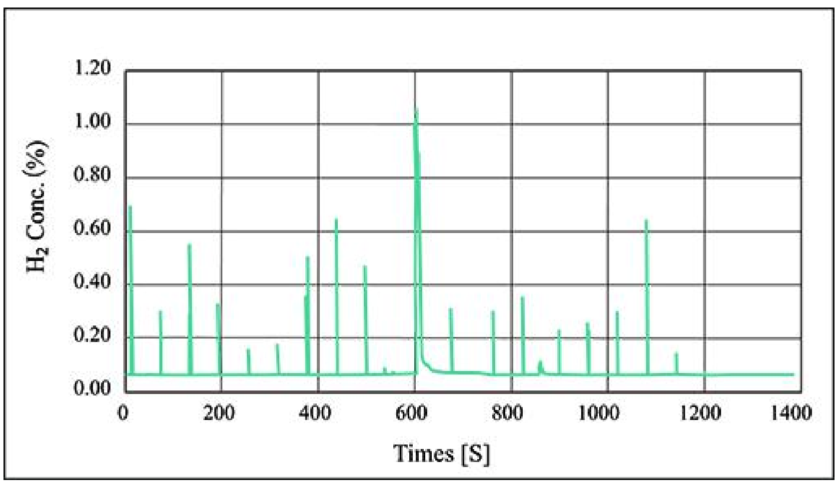

Fig.6-1 H_2Concentration Idling Mode, H_2 monitoring in Exhaust Gas First Gen. Mirai I

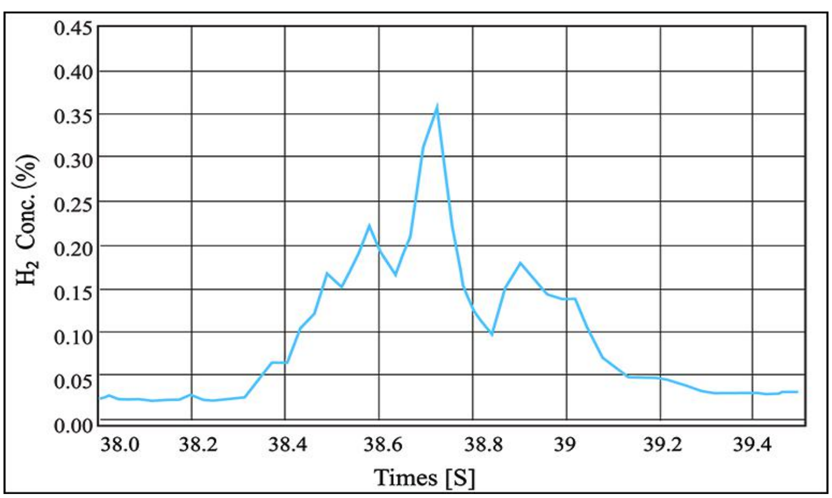

Fig.6-2 Spectrum of Hydrogen Concentration
Idling Mode, Spectral fine structure of H_2 monitoring in Exhaust Gas of Mirai I

Fig.6-3 Image of First Generation Mirai I

Fig.6-4 Exhaust pipe and the exit of gas of Mirai I

Fig7-1 Image of Second Generation

Fig7-2 Refuelig at the H_2 gas station of Mirai II

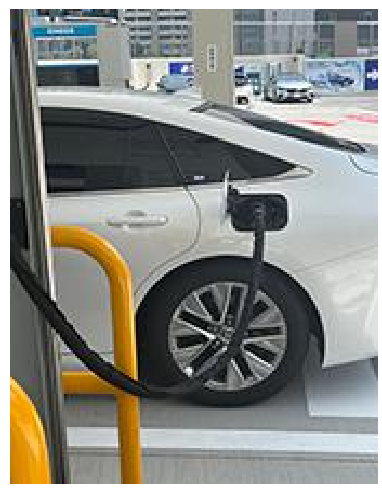

Fig.7-3 H_2 gas station Hydrogen refueling

Fig.7-4 H_2 gas monitoring from the exhaust exit of Mirai II

Fig7-5 Converts DC power supply to Ac100 V by connecting to the inverter Starting of Sx Hydrogen sensor by battery

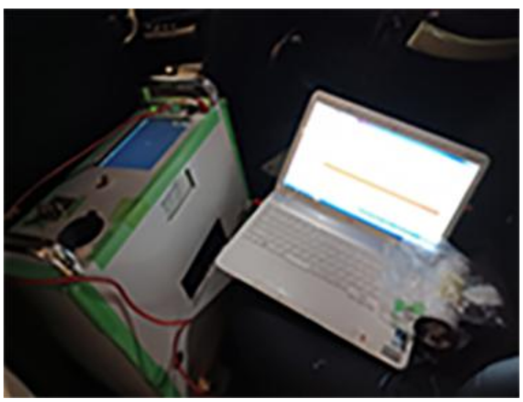

Fig7-6 Real Time monitoring of from the exhaust pipe using hydrogen sensor installed in vehicle

Fig7-7 Adaptor to the exhaust gas sampling from the center of the exhaust pipe of Mirai I

3-5 Hydrogen concentration and explosion

Compared to the Mirai I, the Mirai II is more compact and more comfortable to live in. However, because the diffusion layer used previously was eliminated, high concentrations of hydrogen were observed during idling. There are no problems when driving, but in experiments where a 4% pre-mixed hydrogen-nitrogen gas mixture is injected and ignited from the nozzle, an explosion will occur if there is an ignition source, so caution is required. It is believed that this was caused by direct injection due to the elimination of the diffusion layer.

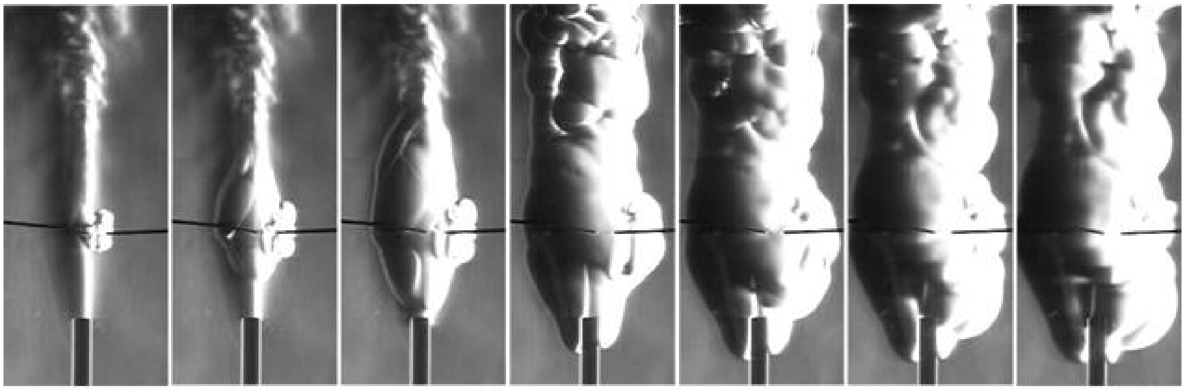

Fig. 8 The Schlieren Photograph ;Combustion of 4% premixed gas H_2 in Air where H_2 was introduced at the ratio of 4% in Air flow by the system

4.Conclusion

Measurements were taken at intervals of several hundred milliseconds for five components including hydrogen (H_2, N_2, O_2 Ar, CO_2) during idling and driving. The measurement results showed that when idling, one peak of about one second intervals was observed with a maximum of 6%. When driving on the highway at 60km/h and 110km/h, a maximum of 3% peaks of hydrogen gas were emitted, which were a lower concentration than when idling, and the interval increased with speed the concentration of H_2 became weaker by dilution. In this measurement, sampling was performed at the tip center of the exhaust pipe, so the concentration was measured just before it was released into the atmosphere. However, when driving, phenomena such as the peak becoming unclear and the concentration decreasing due to mixing with outside air, which was different from when idling, were observed. In order to further analyze the exhaust gas before mixing with outside air and the relationship with fuel efficiency, we would like to sample from the neck of the exhaust pipe in the future and analyze the state without the influence of outside air.

5.References

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