

### 3D real time monitoring of H<sub>2</sub> in FCV applications

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#### Abstract:

In order to monitor a trace amount of Hydrogen in millisecond, portable H<sub>2</sub> sensor (Sx) was made by using mass spectrometer. The method of monitoring the hydrogen pulse of millisecond in exhaust gas is the increasing needed. Determining H<sub>2</sub> concentration both inside and outside of the Fuel Cell Vehicle (FCV) for the optimized operations is becoming a critical issue. The exhaust gas of Fuel Cell Vehicle, H<sub>2</sub> consumption, flushing and disposal around Fuel cell, the real time monitoring of H<sub>2</sub> in highly humid conditions is the problematic. To solve this issue, the system volume of the sampling route was minimized with the heater and the dehumidifier to avoid condensation of water droplets. And also for an automatic calibration of H<sub>2</sub> concentration, the small cylinder of specific H<sub>2</sub> concentration was mounted into the system.

Our basic experiment started from a flow pattern analysis by monitoring H<sub>2</sub> concentration in narrow tube. The flow pattern analysis was carried out. When H<sub>2</sub> gas was introduced in the N<sub>2</sub> flow or air in the tube, the highly concentrated H<sub>2</sub> front phases were observed. This H<sub>2</sub> sensor can provide the real time information of the hydrogen molecules and the clouds. The basic characterization of this sensor showed 0-100% H<sub>2</sub> concentrations within milliseconds. Our observations showed the size of the high concentration phase of H<sub>2</sub> and the low concentration phase after mixing process. The mixed and unmixed H<sub>2</sub>, unintended concentration of H<sub>2</sub> cloud, the high speed small cluster of H<sub>2</sub> molecules in purged gas were explored by this system.

#### 1. Introduction

Towards 2020 Tokyo Olympic Game, various Hydrogen applications without CO<sub>2</sub> emission are prospectively being developed. Fuelcell in house application is expected to simultaneously generate tri-generation of electricity, heat and hot water. Fuel Cell Vehicles (FCV) in new efficient models with the dramatically optimized in mechanical, electrical, and chemical background technologies come out. From the safety point of view, the explosion limit for H<sub>2</sub>, 4% and GTR (Global technical regulation) on FCV considering the value of 4% and 8% of H<sub>2</sub> release. In production line, the H<sub>2</sub> 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<sub>2</sub> with air to find unintended concentration of H<sub>2</sub> in clouds. The real time monitoring of the process of mixing 100% H<sub>2</sub> with air in milliseconds is our study purpose. Considering real time monitoring of H<sub>2</sub> 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-Dimensional H<sub>2</sub> concentrations. The concentration profile in milliseconds by high-speed camera is taken using the Schieren technique at the same time.

GTR for H<sub>2</sub> 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 [9]. Also how to measure hydrogen pulse of millisecond in exhaust is the rising up issue. Further more, any single failure downstream of the main H<sub>2</sub> shut off valve shall not result in a H<sub>2</sub> concentration in air of 4 % or more by volume within the passenger compartment. If a single failure down stream of the main hydrogen shut off valve results in a H<sub>2</sub> concentration in air of 4 % by volume within an enclosed or semi-enclosed space in vehicle, the main H<sub>2</sub> shutoff valve shall be closed and warning to the driver shall be provided. [8] 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<sub>2</sub> concentration also Nitrogen (N<sub>2</sub>) instead of Air. In mixing experiment, H<sub>2</sub> gas was introduced in the N<sub>2</sub> & Air flow to form the various H<sub>2</sub> concentrations. H<sub>2</sub> at the point of discharge was monitored by the real time H<sub>2</sub> monitoring system Sx. The fast solenoid valve was opened within milliseconds to add H<sub>2</sub> gas in N<sub>2</sub> & Air flow, H<sub>2</sub> gas ran through the tube by mixing with N<sub>2</sub>, 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<sub>2</sub> sensor and the wave front concentration of H<sub>2</sub> during stop and release type of motions was topics. In milliseconds diffusion mechanism does not work but Reyleigh -Taylor instability might work [10].

In order to detect low concentration of H<sub>2</sub> 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<sub>2</sub>/N<sub>2</sub> mixing experiments [5,6]. In hydrogen release experiment on the mountain, high pressure H<sub>2</sub> gas was emitted from the pipe in the air to form the various H<sub>2</sub> concentrations of cloud. H<sub>2</sub> diffusion process was monitored by the real time H<sub>2</sub> monitoring system. [5, 7, 11, 12 ]

## 2. Experimental

### 2-1 Sx H<sub>2</sub> Sensor



Fig.1 H<sub>2</sub> Sensor(Sx)

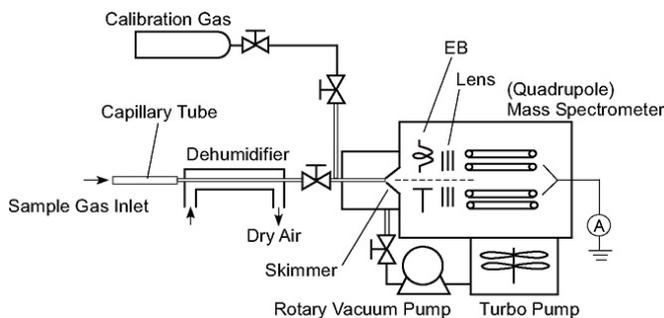


Fig.2 Schematic diagram of Sx

Schematic diagram of Sx is shown in Fig.2. The weight of Sx is 25kg and portable for the outdoor mountain experiment [5]. 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. For the real time monitoring system inside volume of Sx is minimized. Sampling inlet of this system is 150-250  $\mu m$  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  $m/Z=300$ . [7] Schlieren Photograph (SP) is applied to monitor the movement of hydrogen cloud and mixed gases density profile. So from gas exit we can monitor the concentration profile by Sx and density profile by SP at the same time. SP is monitored by high-speed camera in 1 msec.

### 2-2 Mixing Hydrogen with Nitrogen or Air by Vertical mixing (right-angle mixing head)

Nitrogen and air is controlled by Mass flow controller (Kofloc Kyoto Model 38100SII-V-1,  $N_2$ , In 0.15/out 0Mpa, 100SLM, 20°C, 1 atm) with solenoid valve (CKD AB41-02-7 0.25Mpa) to maintain constant flow rate of 5L/min. Hydrogen is added vertically to nitrogen or air. At the constant flow rate through Mass flow controller (Kofloc Kyoto Model 3810DS-V,  $H_2$ , In 0.20/out 0.1Mpa, 100SLM, 20°C, 1 atm) and solenoid valve (CKD AB41-02-7 0.25Mpa) to maintain and check flow rate.  $H_2$  flow start by quick solenoid valve (KOGANEI K2-100SA-09, 0.2-0.5Mpa) controlled by pulse generator shown in Fig.3. 1 to 100ms intervals pulse start flow by valves into constant airflow and mixing process to be observed. Expecting concentration of mixed gas in equilibrium state is 4% (LEL of  $H_2$ ).

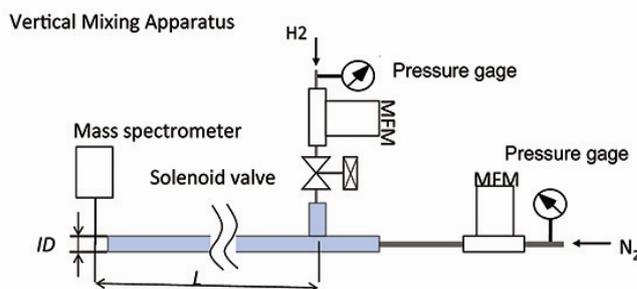


Figure 3. Vertical mixing (right-angle mixing head) equipment with Sx

### 2-3 $H_2$ /Air Mixing and Combustion/Explosion process by Sx

Experiments are conducted using air instead of nitrogen with ignition equipment. Two tungsten wires are set the head to tail distance of 1cm for the spark where the high voltage of AC12KV is applied. So if  $H_2$  concentration is more than 4%, the ignition process is activated, monitored by SP (Schlieren Photograph) with high-speed camera at the same time 6 Sxs measure the 3D  $H_2$  concentration changes. Explosion data are measured and analyzed.

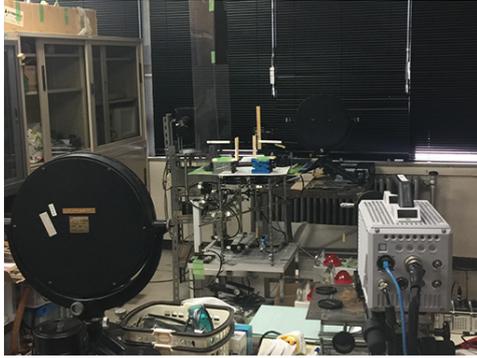


Figure 4. Experimental setup for the mixing and combustion experiment with high speed camera for Schleiren Photograph



Figure 5. Experimental setup of Sxs

#### 2-4 Schleiren Photograph and Sxs

Schleiren Photograph and Sx set up is schematically described below in Fig.6. 3 capillary positions of Sxs have the different height on the exit of the pipe, and each height different by 1cm. The distant between the top of the pipe to the sampling point start from 0.0cm up to 20cm. The photos of Schleiren images were taken by high speed camera at the same time.

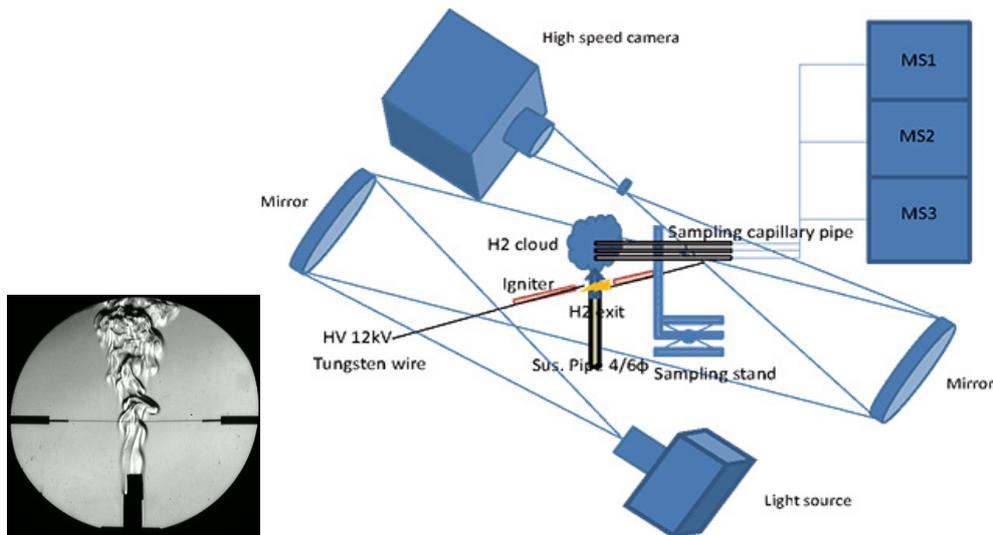


Figure 6. Schematic Diagram of Shleiren Photograph setup

### 3 Results and Discussions

#### 3-1 Real Time Monitoring of Purged H<sub>2</sub> into Nitrogen flow

Under constant flow of N<sub>2</sub> 5L/min controlled by massflow controller, pure hydrogen were introduced by quick valve by the interval of 1ms by using vertical mixing with right-angle mixing head shown in Fig.3. The preset concentration of H<sub>2</sub> in N<sub>2</sub> of flow controller is 4% of 0.2L/min under contantaneous flow condition. The result of H<sub>2</sub> concentration by time was shown in Fig.7. Single channel was used to monitor H<sub>2</sub> concentration by 2ms intervals. Concentration profile of front hydrogen wave came with the spike head where the highest concentration of hydrogen (C<sub>max</sub>) reached by open up quick valve. Hydrogen was introduced into N<sub>2</sub> flow without diffusion and kept higher concentration as expected. The concentration of spike was more than the expected concentration and also above the pre-set value of H<sub>2</sub> 4%. Three Sxs (I,O,U) monitored H<sub>2</sub> concentration profile at the different positions of 1,2,3cm from the exit of the pipe, and the maximum concentration H<sub>2</sub> at the centre position exceed 13%. This is more than pre-set value of 4%.

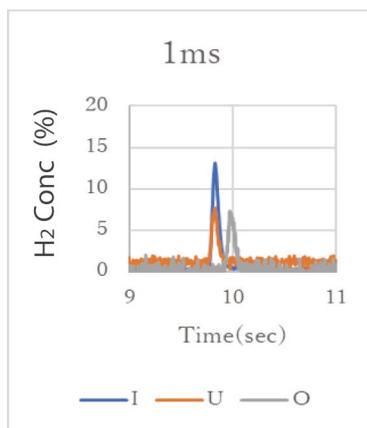


Fig.7 H<sub>2</sub> Response by Quick Valve

#### 3-2 Real Time Monitoring of Purged H<sub>2</sub> into N<sub>2</sub> by changing Pulse width 1-100ms

By changing the duration time of quick valve open from 1 to 100ms, the H<sub>2</sub> profile change the shapes and the result are shown in Fig.8. The comparison of H<sub>2</sub> profiles were taken at the same height and showed in Fig.9. At duration time of 1ms, the quick valve motion did not complete open and less volume of hydrogen moved into N<sub>2</sub> flow. The height of spike head reached the maximum concentration of H<sub>2</sub> at the duration time of 10 and keep

constant concentrations up to 100ms. When the duration time reach 100ms, the height of spike head became a bit lower but the width of spike became wider shown in Fig. 8&9. This means that the open to close time of 100ms, hydrogen volume increased compared to lower duration time data shown in Fig. 8&9. At the start point to the maximum concentration of H<sub>2</sub>, the slope of the increasing curve was steep compared to the decreasing concentration profile. This means that the head front of H<sub>2</sub> cloud keep the higher concentration compared to the tail portion. Also this means that more mixing process took place including diffusion in all condition.

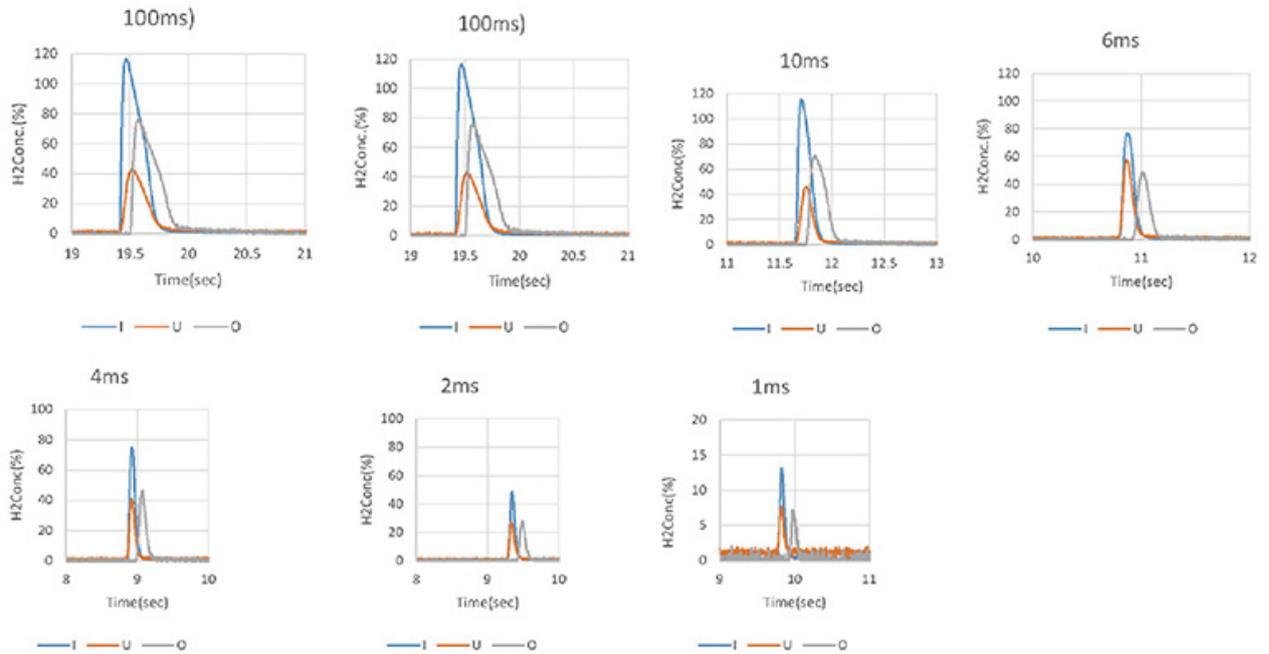


Fig.8 Spike heads changes by response time 1-100m

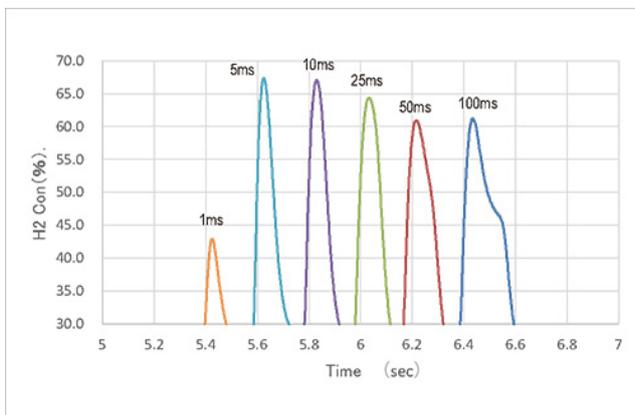


Fig.9 Shape of Spike heads in pulse width 1-100ms.

By changing the sampling position in 0cm to 20cm in x-axis and 1cm to 3cm in y-axis, hydrogen concentration profile were examined through the vertical mixing equipment. All data were plotted and shown in Fig.10. The slope of line shown in this figure explained that the maximum concentration of ejected H<sub>2</sub> clouds decreased with the distance from the exit of pipe and decreased inverse proportionally to the distance between the exit and sampling point. The maximum concentration and the distance L showed the upper slope line in Fig.10.

### 3-3 Real Time Monitoring of the spike head of H<sub>2</sub> purged by changing position X-Y

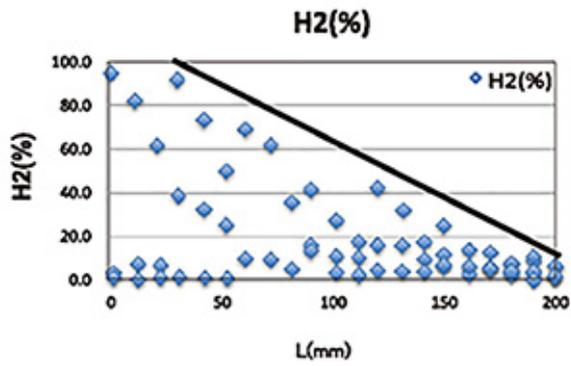


Fig.10 H<sub>2</sub> concentration at Spike head by changing X-Y MS gas sampling positions

; preset H<sub>2</sub> of 4% , H<sub>2</sub> 100%100ms release in Air

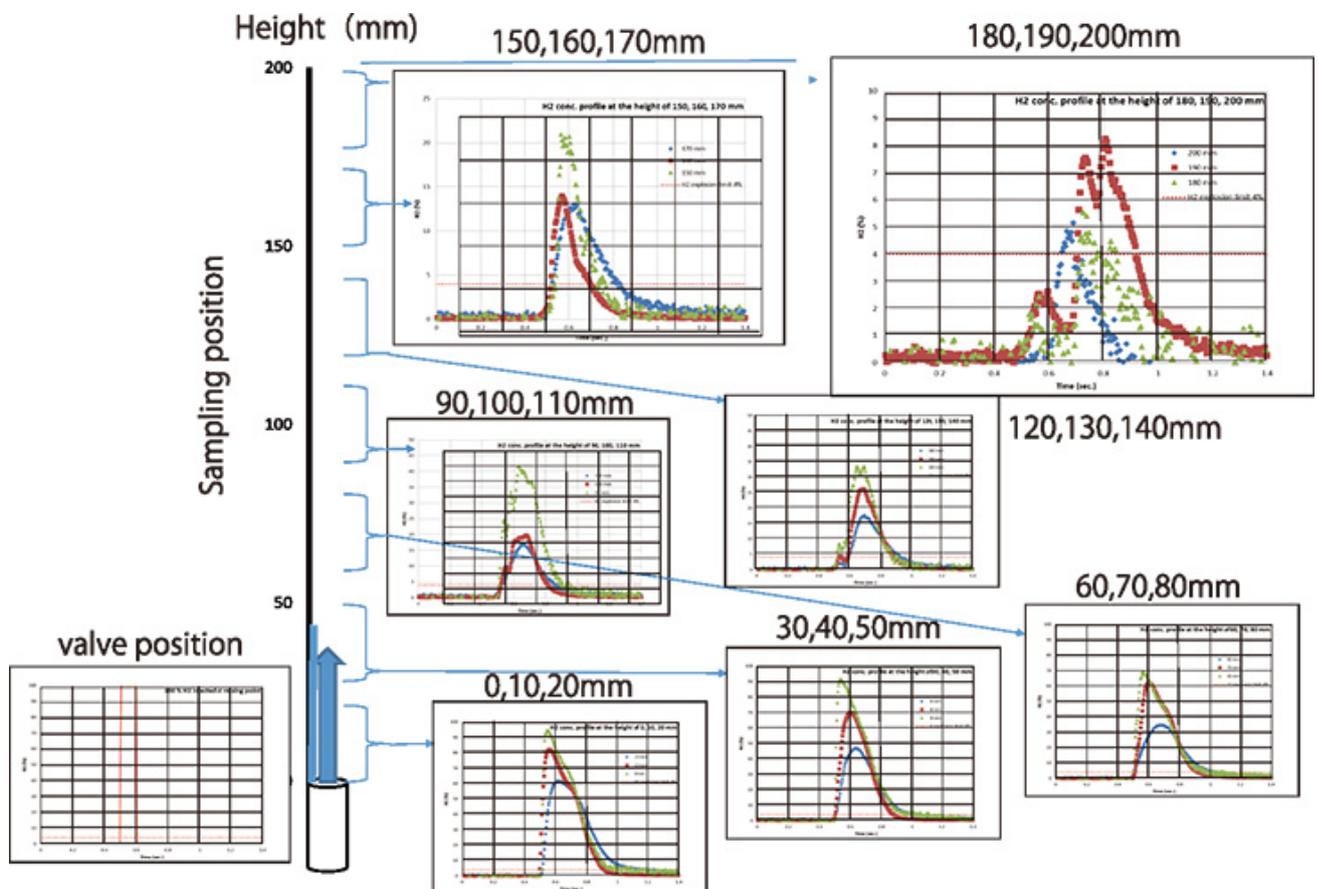


Fig.11 H<sub>2</sub> Concentration profiles at the Spike head by changing X-Y MS gas sampling positions

; Preset H<sub>2</sub> concentration of 4%

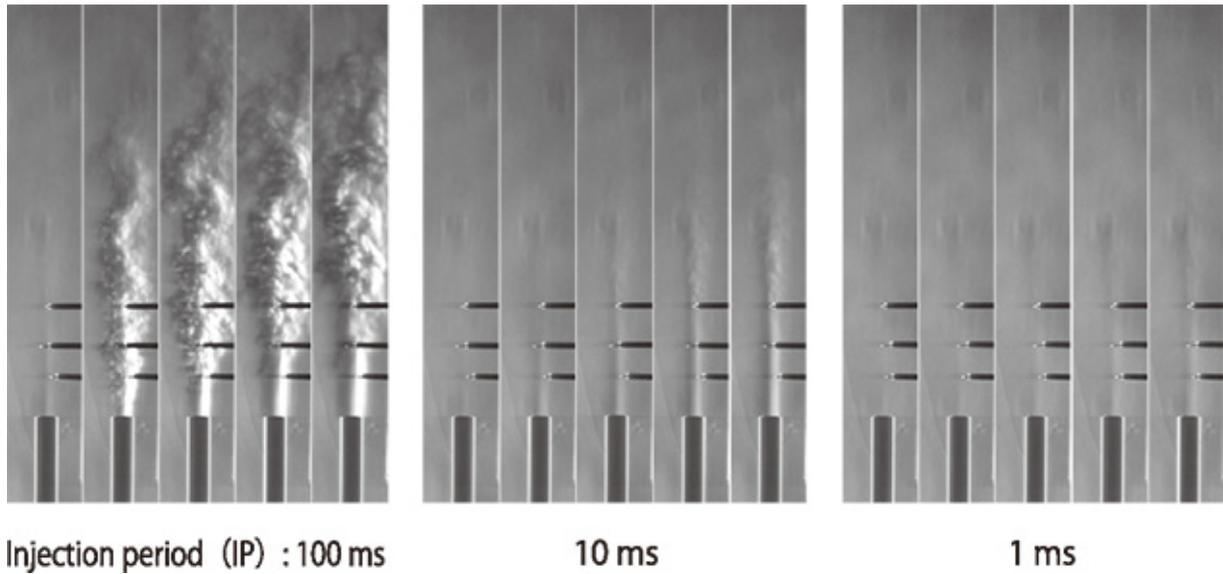


Fig.12 H<sub>2</sub> Injection Period 1,10,100ms into Air Flow (H<sub>2</sub> was introduced at the ratio of 4% in Air flow by the system shown in Fig. 3, Each Flame taken by 5ms intervals)

By comparison of Fig.11& Fig.12, we easily realized the 3D Hydrogen concentration profiles. The outside shape of clouds in Fig.12 and inside concentration of H<sub>2</sub> in Fig.11. MS monitored inside concentration of clouds and the Schlieren Photograph showed the outside appearance of upstream turbulence. The result showed that MS has more and linear sensitivity toward low to high concentration of H<sub>2</sub> than the Schlieren Photograph. In Fig.12, we recognized the out-coming cloud images of 100ms but for 10 and 1ms. In Fig 8&9, MS data showed the out-coming cloud precisely. The Schlieren Photograph showed the outside appearance of cloud and large volume of H<sub>2</sub> which created more density changes in space. The Schlieren Photograph had no sensitivity towards air movement. Typical flow pattern was shown in Fig.12 in 100ms H<sub>2</sub> purge experiment. The cloud front goes upward by waving a bit but forming main updraft axis. MS data showed in all position inside updraft, all shapes of the spike heads are similar and the head concentration has higher than tail.

#### 3-4 Real Time Monitoring of combustion (4%, 100 ms )

Combustion tests were carried out and photos by high speed camera showed explosion of H<sub>2</sub> in pre-set of 4% and purge of 100ms. When the head of cloud approached to the tungsten wires with high voltages, the severe explosion took place by the head at 37ms. The explosion spread up first at 71ms and propagated upward and downstream with turbulence at 81-89ms. The combustion continued with constant updraft. The most turbulent premixed explosion took place above and the premixed flame propagation continued with cone inside at 89-275 ms .

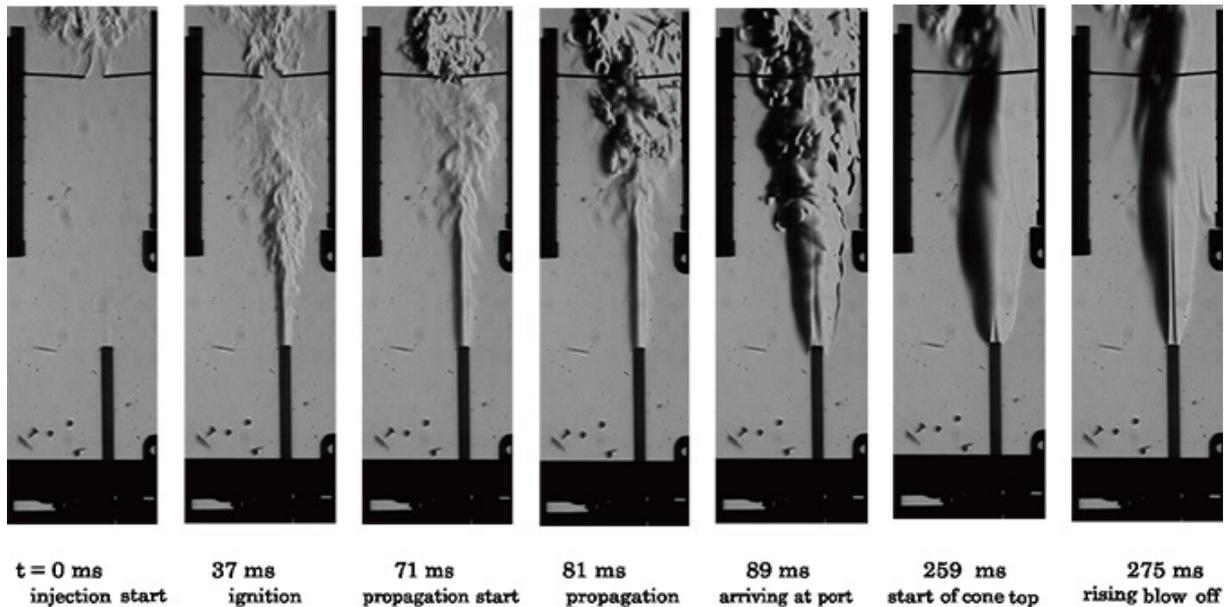


Fig.13 The Schlieren Photograph of Combustion 4% H<sub>2</sub>,100ms in Air (H<sub>2</sub> was introduced at the ratio of 4% ,100ms,in Air flow by the system shown in Fig. 3 interval of 5ms )

### 3-5 Real Time Monitoring of combustion (4%,1ms)

The same experiment but pre-set H<sub>2</sub> concentration of 4% and purge 1ms took place. This Schlieren Photograph of explosion and combustion showed the existence of the higher concentration of H<sub>2</sub>. The head of spike kept the higher concentration of H<sub>2</sub> to lead the explosion. In these phenomena the cone showed up in the persistent updraft to demonstrate the existence of the premixed flame.

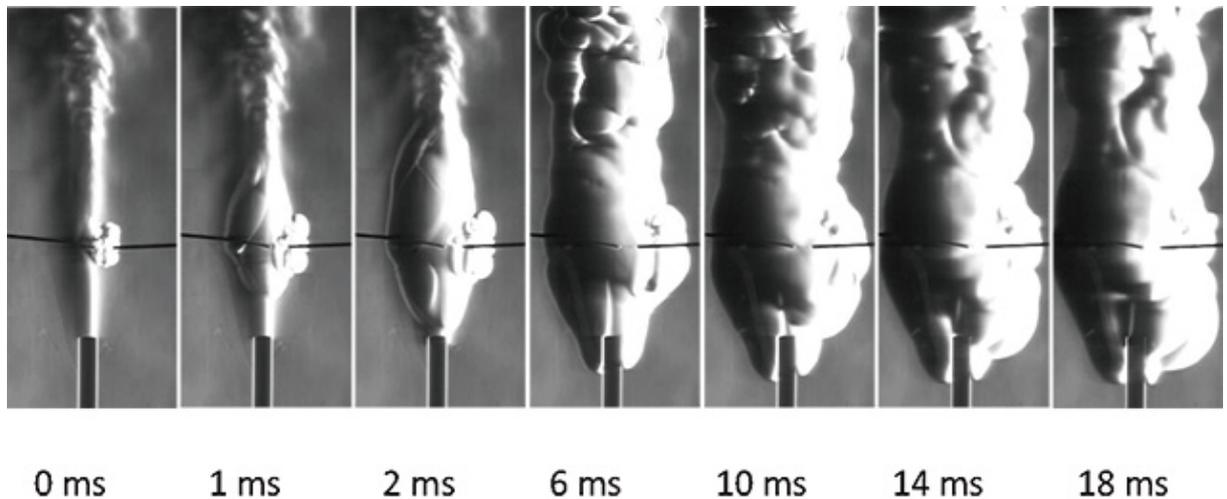


Fig. 14 The Schlieren Photograph of Combustion 4% H<sub>2</sub> in Air (H<sub>2</sub> was introduced at the ratio of 4% in Air flow by the system shown in Fig. 3 )

### 3-6 Hydrogen Spike Head by FCV Exhaust Gas

The Schematic diagram of fuel cell is shown in Fig17. In Typical FCV, H<sub>2</sub> is introduced from the pressure tank to fuel cell by decreasing pressure. H<sub>2</sub> purge into fuel cell through ejector. H<sub>2</sub> flow through hundreds of membrane with anode electrodes and come out from fuel cell to recirculate pass. The exhaust gas from typical FCV contains various gases including H<sub>2</sub>. Hydrogen gas concentration of Typical FCV Exhaust Gas was monitored by Sx by fitting sampling cappillary at the discharging point of the center of exhaust pipe exit with small protector plate

toward water droplet to come in Fig.15,16,17. The hydrogen measurement was conducted by 2-10ms interval when FCV was parked and while idling position. So every 2ms the hydrogen concentration was taken by time. Six data were shown in Fig. 18 and 19. In Fig.19. About every 60 second, H<sub>2</sub> spike came out from exhaust gas as spike. The width of spike was about 1-2 second of time. By spike analysis shown in Fig. 19, one spike peak was composed of 2 or 6 spikes within 1 second and shape of spike reflecting structure of Fuel Cell stack structures. These data was taken in very short millisecond measurement and under the existence of water. These spike heads spectra analysis is pretty important to maintain the optimized operation of fuel cell and cut H<sub>2</sub> consumption.



Fig15 Typical FCV



Fig16 Point of Exit of FCV Exhaust System

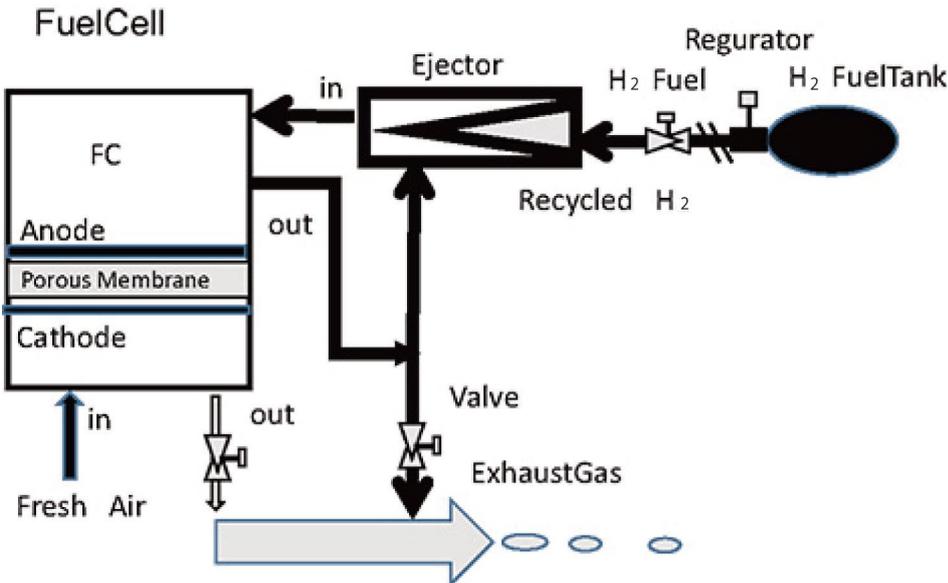


Fig.17 Schematic Diagram of Fuel Cell System in FCV

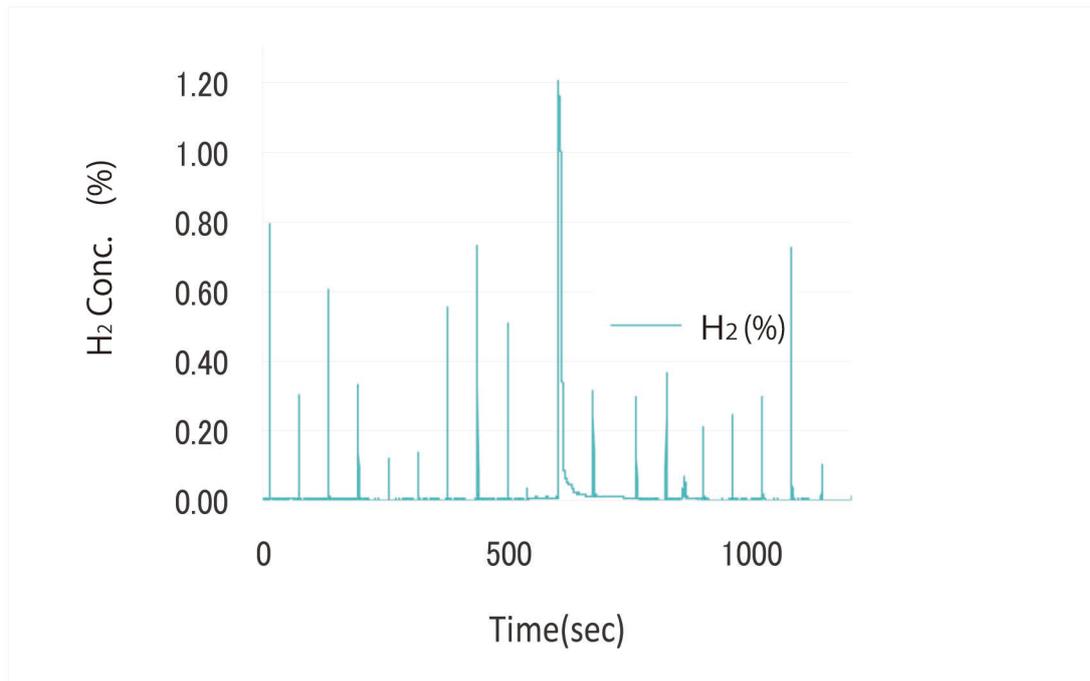


Fig. 18 H<sub>2</sub> Concentration Spectra at the point of Exit of FCV Exhaust System in seconds

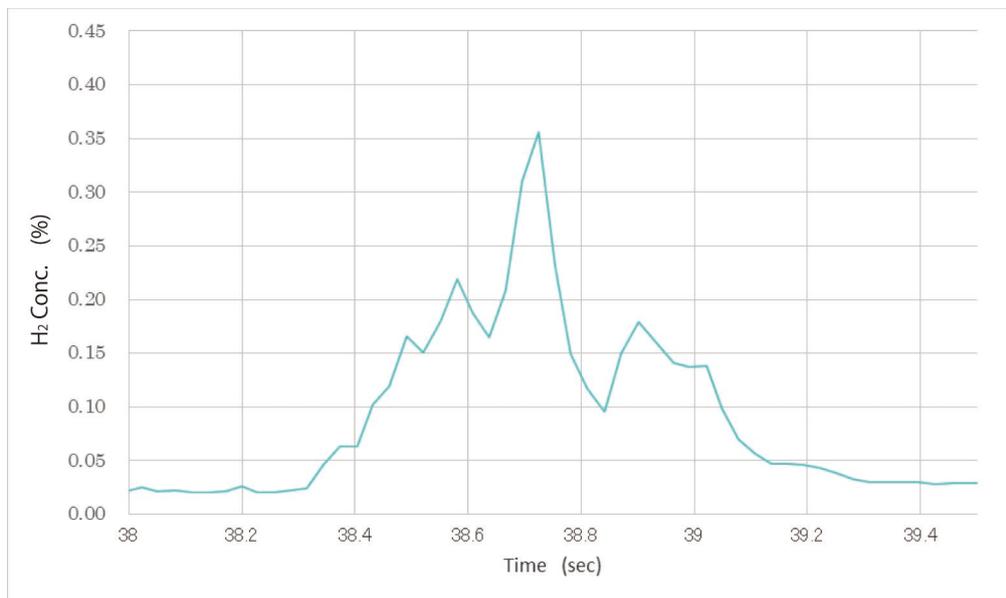


Fig.19 Spectrum of Hydrogen Concentration in FCV Exhaust Gas

#### 4 Conclusion

Real time monitoring of Hydrogen by Sx showed the existence of the hydrogen clouds before diffusion in the mixing process. In the mixing process, pure H<sub>2</sub> purged into air and nitrogen did not flow by forming homogeneous phase but formed heterogeneous phaslike comet structure of cloud. Head and tail of cloud called the spike head and tail. The spike head

analysis was carried out and demonstrated that the head portion contained high concentration of hydrogen rather than tail. Near the exit of the tube, the head of cloud, in other words, spike head contained pure hydrogen and this high concentration volume changed by injected volume. The concentration of hydrogen decreased gradually at the tail portion of this cloud.

In vertical mixing equipment, the high concentration phase of hydrogen clouds survives and moves upward by buoyancy. Once ignition equipment with high voltages applied, the explosion with premixed flame was observed by The Schlieren Photograph of Combustion 4% H<sub>2</sub>, 100ms. When mixing proceeds, the head of hydrogen cloud moves straight to form the spike head like bullet head as observed in millisecond monitored by Sx. As in the previous cylinder experiment and also the transparent plastic tube experiment, H<sub>2</sub> cloud moves upward rather than diffusing in all directions. In spike head H<sub>2</sub> stays with high concentration forming cloud and the similar spike was appeared in FCV exhaust gas in every purging actions. In basic theory of Rayleigh-Taylor instability, if the two gas phases instead of the two fluids with different densities was considered, the spike head might be came out as a cloud which we observed by Sx. The instability of the plane interface between the two fluids, when it occurs, is called the Rayleigh-Taylor instability”

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