**Type of this paper:**

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**Title:**

Direct production of hydrogen-rich gas and/or pure-hydrogen with high-pressure from alcohol/water/metal-powder mixture at low processing temperature

**Authors:**

Seiichi Deguchi[*], Noriyuki Kobayashi[*], Norifumi Isu[**] and Mitsunori Ito[***]

**Affiliations:**

*)      Department of Chemical Systems Engineering, Nagoya University, Nagoya 464-8603 JAPAN

**)      Material and Property Analysis Laboratory, Technology Research Division, LIXIL Corporation, 2-1-1 Ojima, Koutou, Tokyo 136-8535 JAPAN

***)      Department of Energy Engineering and Science, Nagoya University, Nagoya 464-8603 JAPAN

Correspondence should be addressed to Seiichi Deguchi;

E-Mail: deguchi.seiichi@material.nagoya-u.ac.jp, Tel: +81-52-789-3383, Fax: +81-52-789-3841

Present address: Department of Chemical Systems Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603 JAPAN

**Abstract:**

　　　　High-pressure hydrogen-rich gas producing experiments from various alcohol/water/metal-powder mixtures at low processing temperatures from 473 to 723 K are carried out in a prototype airtight apparatus possessing a withstand pressure of 15 MPa in the aim of technologizing an incidentally emerged high-pressure hydrogen-rich gas production from a methanol/water/aluminum-powder mixture at 723 K. Methanol/water due to a proven track record and ethanol/water in order to make an allowance for replacing the reagent to commercially-available potable alcohols are

selected as main hydrogen sources. As tested metal-powders, aluminum, cobalt, iron, magnesium and nickel are chosen, taking their ready-availabilities and costs into consideration.

Among tested metal-powders, aluminum and cobalt are found optimal adding metals for the high-pressure hydrogen-rich gas productions from 60.0 wt% methanol/water and ethanol/water solutions, respectively. From 60.0 wt% methanol/water and Al-powder mixture at 723 K, pure-hydrogen with 10.0 MPa is produced at a great hydrogen producing rate of 24.9 $L_N$/(dm$^2$min). All carbons discharged from methanol are fixed as a wide variety of solid higher hydrocarbons and organic liquid residues of benzyl alcohol and toluene. Almost all oxygens from methanol/water solution are fixed as aluminum-compounds of aluminum oxide hydroxide and aluminum hydroxide. From 60.0 wt% ethanol/water and Co-powder mixture, pure-hydrogen with pretty high pressure over 15 MPa can be produced at 723 K with simultaneous fixations of all the carbons and oxygens from the main hydrogen source as solid/liquid residues of wide variety of solid higher hydrocarbons, benzyl alcohol, toluene, cobalt oxide, cobalt hydroxide, tricobalt tetroxide and cobalt carbonate. Responding to the outcome from 60.0 wt% ethanol/water and Co-powder mixture, a certain rice-wine having an alcohol degree 60 with Co-powder at 723 K is experimented, and provides high-pressure hydrogen-rich gas with hydrogen concentration of 80 % and hydrogen partial pressure of around 8 MPa.

All the produced hydrogen-rich gases are confirmed to keep a full declared potential in polymer electrolyte fuel cell for over 24 hours without any exceptions. These findings speak by themselves that this developing high-pressure hydrogen-rich gas (pure-hydrogen) direct producing method is surely approaching a self-operating dispersed hydrogen producing appliance (i.e. a part of a dispersion type power source) anywhere whole the world. And, this method still leaves unlimited room for far higher pure-hydrogen pressures and hydrogen producing rates by slight changing the operating conditions, and its applicable fields are broadening for eternity. Finally, some recommended future strategies to improve this method so as to supply complete solutions to any global-scale issues are also proposed in every part through this paper.

**Highlights:**

Pure-hydrogen with 10.0 MPa is produced from methanol/water/Al-powder at 723 K.

Maximum pure-hydrogen producing rate is 24.9 $L_N$/(dm$^2$min).

Pure-hydrogen with above 15 MPa is produced from ethanol/water/Co-powder at 723 K.

Hydrogen-rich gas with around 8 MPa is produced from rice-wine/Co-powder at 723 K.

All produced hydrogen-rich gases keep a full potential in PEFC for over 24 hours.


**Introduction**

The world has been facing many critical problems such as global warming and exhaustion of fossil fuels. Thus, one of the essential achievements for the current generation is to find exhaustless renewable energies alternative to fossil fuels emitting an appreciable amounts of carbon dioxide ($CO_2$). Hydrogen is one of the most promising energies since it does not emit any $CO_2$ when it is used, and can be used as fuel for FC (Fuel Cells), keeping anthropic activities stable and realizing energy sustainable for eternity.

During our developing investigations for new annealing processes of inorganic powders in critical water together with metal-salt [1,2], high-pressure hydrogen-rich gas could be incidentally produced from a methanol/water/aluminum-powder mixture at 723 K [3,4]. Some existing hydrogen producing methods are compared with this incidental high-pressure hydrogen-rich gas production in **Table 1** [5-11].


**Table 1 Comparisons among existing hydrogen producing methods and our incidental hydrogen-rich gas production**

| comparing terms | existing hydrogen producing methods | | | incidental hydrogen-rich gas production |
| --- | --- | --- | --- | --- |
| | catalytic methane steam reforming [5-10] | industrial by-product | water electrolysis (WE-NET) [11] | |
| hydrogen source | methane/water | - | water | methanol/water |

| | catalysts | | | aluminum-powder |
|---|---|---|---|---|
| operation | 823 K (1023 K) | - | electrolysis | 723 K |
| hydrogen concentration | 70 ~ 80 % | around 60 % | 100 % | 59 % |
| hydrogen partial pressure | < 0.08 MPa | < 0.06 MPa | 0.1 MPa | > 2.1 MPa |
| drawbacks and/or requirements | purification compression lifeline dependency | purification compression land transportation | compression sea/land transportations | further experimental investigations |
| product | high-pressure pure-hydrogen | | | |

Of course, all the existing hydrogen producing methods are well-investigated, reliable and have firm public acceptances. Catalytic methane steam reforming (MSR) is widely adopted since methane can be obtained for a little longer from the ground, under the sea, fermentation and so on [5-10], and be easily widespread by existing gas line. Catalytic MSR is normally operated at 1023 K, or the temperature can be reduced down to about 823 K, which is still comparatively high, when a hydrogen separating membrane is applied. Hydrogen discharged as industrial by-product holds a great deal of promises because it is obtained at no charge, but huge energy consuming operations such as purification, compression and land transportation are indispensable. The international Energy Network (WE-NET) project provided significant credits on the basic policy of pure-hydrogen production by water electrolysis using electric-power generated from renewable energy sources such as hydro-power and wind-power [11], but this scenario also requires compression and sea/land transportations, consuming vast amounts of energy. There are still plenty of hydrogen producing methods such as biological conversion [12-15], catalytic steam reforming of hydrocarbons [5-10,16-29], thermal dissociation of water and photocatalytic water splitting [30-37], being far-out technologies and/or requiring technical breakthroughs for practical applications.

It is seen from **Table 1** that our incidental hydrogen-rich gas production outclasses other hydrogen producing methods in terms of a single and simple operation, a high hydrogen partial pressure, a relative low processing temperature and independency on any lifelines. However, its drawback lies on further experimental investigations for much higher

hydrogen concentration aiming for pure-hydrogen and much higher hydrogen partial pressure heading off for over 80 MPa by changing hydrogen source compositions of alcohol/water/metal-powder mixtures and processing temperatures.

In the present study, high-pressure hydrogen-rich gas producing experiments were carried out with various alcohol/water/metal-powder mixtures at different processing temperatures in the aim of technologizing our incidental high-pressure hydrogen-rich gas production. As main hydrogen sources, methanol/water and ethanol/water were selected from the actual achievement of our incidental high-pressure hydrogen-rich gas production and for antedating to pass in a direction toward commercial alcoholic beverages (i.e. ethanol) so as to improve this method up to a complete carbon-neutral process, respectively. Concerning these alcohols, catalytic steam reformings have been preceded [19-29]. However, most of the preceding works have been focused on improving each catalyst in terms of chemical stability, cost reduction and elevated selectivity at lower-temperatures. In contrast, our incidental high-pressure hydrogen-rich gas production occurs through chemical reactions, getting away from conventional catalyzed reactions [5-10,16-29], so as to accomplish hydrogen purity 100 %, pressure close to 15 MPa (over 80 MPa in future) and producing rate greater than $20\,L_N/(dm^2min)$ simultaneously at lower processing temperatures below 723 K for practical applications. Though there are some similar hydrogen productions from various aqueous solutions together with metals [38-46], almost all the precedent works have been performed at normal pressures. Therefore, it can be said that one of the most outstanding features for the present study locates on quite high-pressure experiments close to 15 MPa, exceeding ever achieved 6.9 MPa [38]. Furthermore, ubiquitous materials (e.g. commercially-available rice-wine) were utilized as far as possible in order to make our incidental high-pressure hydrogen-rich gas producing method self-operating process (i.e. a dispersed hydrogen producing appliance or a part of a dispersion type power source) anywhere throughout the world.

Concretely, a prototype hydrogen producing apparatus possessing a withstand pressure of 15 MPa was firstly manufactured [3,4]. As tested metal-powders, aluminum (Al), cobalt (Co), iron (Fe), magnesium (Mg) and nickel (Ni) were chosen, taking their ready-availability and costs into consideration. And, alumina ($Al_2O_3$) was also experimented as blank tests. **Table 2** shows approximate current costs of tested metal-powders in Japan (FUJIFILM Wako Pure Chemical Corporation, Japan).


**Table 2 Costs of metal-powders tested**

| metal | aluminum | cobalt | iron | magnesium | nickel | alumina |
|-------|----------|--------|------|-----------|--------|---------|
| cost [$/kg] | 65 | 495 | 35 | 85 | 230 | 35 |

60.0 vol% of methanol/water solution, various vol% of ethanol/water solution and/or a certain commercially-available rice-wine (alcohol degree: 60 = 60 vol%) were utilized as the main hydrogen sources. High-pressure hydrogen-rich gas producing experiments were carried out at lower processing temperatures between 473 and 723 K. Chemical compositions of produced gases were quantitatively measured by TCD and FID gas-chromatography. Solid and liquid residues were analyzed by means of TEM with EDX, XRD and pyrolysis-GC/MS [47].

## 2. Experimental

### 2.1. Experimental apparatus

**Fig. 1** illustrates a schematic drawing of the prototype high-pressure hydrogen-rich gas producing apparatus possessing the withstand pressure of 15 MPa manufactured [3,4]. A main reactor was made of a SUS304 pipe with ¼ inch of outer diameter and 200 mm in height. A pressure indicator (W232-111, Migishita Seiki MFG. CO., LTD. Japan) was installed to monitor the ever-changing pressure inside the apparatus, and its value could be recorded by a remote system consisted of a web-camera and a PC image logger. A safety valve was also attached, which automatically opened if the pressure inside the apparatus surpassed 15 MPa, assuring safe experiments. Then, an inside volume of the whole laboratory-scale airtight apparatus came to 31.4 mL, including all attached SUS304 joints, valves (Swagelok Company, Japan) and other instruments.
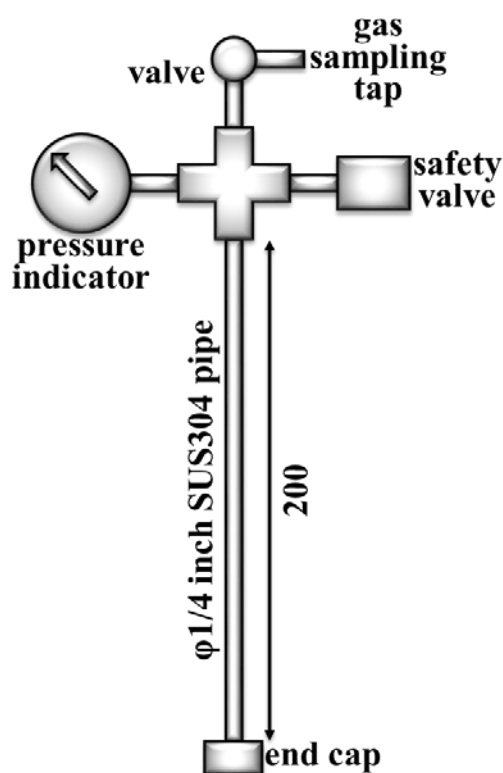
**Fig. 1 Schematic drawing of prototype high-pressure hydrogen producing apparatus**

## 2.2. Experimental procedure

Firstly, predetermined amounts of alcohol/water and metal-powder of 0.50 g were fed into the main reactor of SUS304 pipe with an end cap at its bottom. Initial alcohol concentration of the main hydrogen sources of methanol/water solution, ethanol/water solution and the commercially-available rice-wine were constant 60.0 vol%, various vol% and alcohol degree of 60 (60 vol%), respectively. The tested spherical metal-powders, which were all reagent grade (FUJIFILM Wako Pure Chemical Corporation, Japan), were Al, Co, Fe, Mg and Ni, having over 99.98 % purity and about 0.5 μm of mean diameter. And, $Al_2O_3$ spherical powder was also experimented as blank tests. Then, the upper manifold composed of some SUS304 joints, valves (Swagelok Company, Japan), gas sampling tap, safety valve and pressure indicator was mounted, making the apparatus airtight. The gas initially existed inside the prototype airtight apparatus was evacuated by a vacuum pump, resulting to the inside pressure less than 30 torr. Lastly, the main reactor was submerged in a large water bath with 20 L, and then ultrasonic waves (US-5, SND Japan, ultrasonic frequency: 38.0 kHz, output power: 300 W) were irradiated for 30 min to homogenize all materials inside the apparatus.

High-pressure hydrogen-rich gas producing experiment was started by inserting the main reactor into a cylindrical electric furnace (ARF-60EC, Asahikawa Corporation, Japan) preheated at a preset lower processing temperature between 473 and 723 K. When the inside pressure kept a certain constant value for over 5 min, any chemical reactions were determined to achieve equilibrium, deciding an equilibrium time accordingly. Then, the main reactor was soaked into a large water bath at room-temperature for quenching so as to cease any reactions for subsequent quantitative and qualitative analyses described in next segment. Providing the inside pressure surpassed 15 MPa, the main reactor was immediately soaked into the large water bath to cease any reactions, and then the following analyses were implemented.

Concentrations of hydrogen and other gaseous by-products in the produced hydrogen-rich gas were measured by TCD and FID gas-chromatography (GC-8A and GC-2014, Shimadzu Corp., Japan). Forms and chemical compositions of solid and liquid residues were analyzed by means of TEM with attaching EDX (H-7650, Hitachi, Ltd., Japan), XRD (RINT2550H, Rigaku Corporation, Japan) and pyrolysis-GC/MS (TGA-50H, Shimadzu Corp., Japan, GC/MS:6890N, Agilent Technologies Japan, Ltd., Japan) [47] in order to discuss the obtained properties of high-pressure hydrogen-rich gas logically.
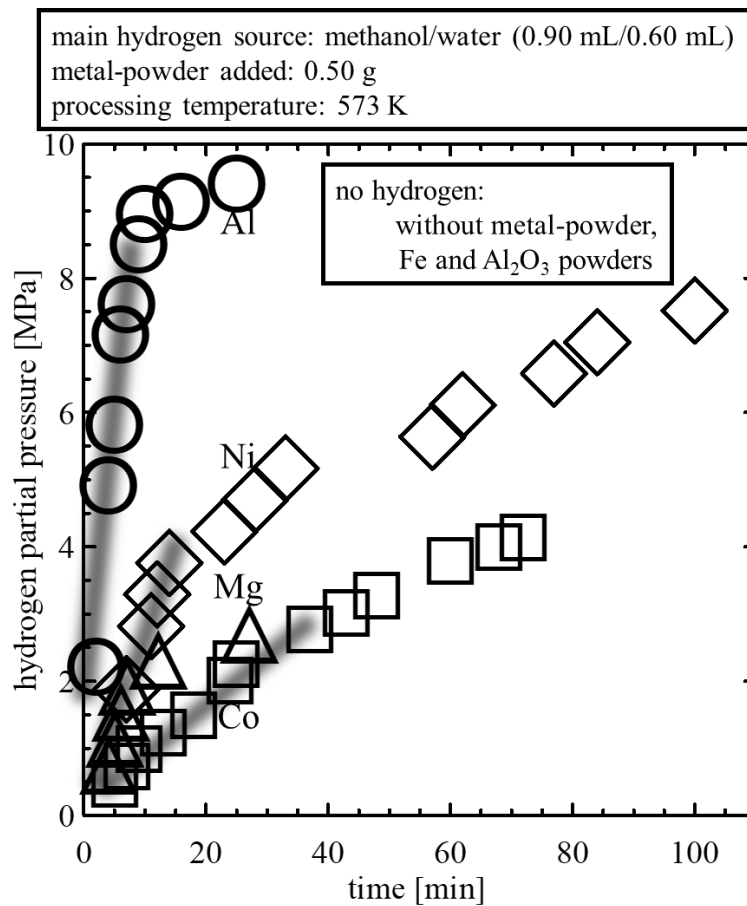
## 3. Results and discussion

### 3.1. High-pressure hydrogen-rich gas production from methanol/water/metal-powder mixture

### 3.1.1. Optimal metal-powder for methanol/water solution

**Fig. 2** presents time trends of hydrogen partial pressures from 1.50 mL of methanol/water (0.90 mL/0.60 mL) solution together with various metal-powders at a constant processing temperature of 573 K. Since no hydrogen was produced without metal-powder, any metals composing the prototype high-pressure hydrogen producing apparatus could be confirmed to have no capabilities to react with methanol/water solution to hydrogen. And, no hydrogen was also produced from methanol/water solution with Fe and $Al_2O_3$. While, it is seen from **Fig. 2** that the hydrogen partial pressures rose steeply at the start of respective experiments with each metal-powder of Al, Co, Mg and Ni, and then increased continuously with time. Hydrogen producing rates were calculated from proportional increasing hydrogen partial pressures to time as denoted by semi-transparent gray belts shown in **Fig. 2**.

main hydrogen source: methanol/water (0.90 mL/0.60 mL)
metal-powder added: 0.50 g
processing temperature: 573 K

no hydrogen:
without metal-powder,
Fe and $Al_2O_3$ powders

**Fig. 2 Hydrogen productions from methanol/water solution with various metal-powders**

**Table 3** summarizes properties of the produced high-pressure hydrogen-rich gases under the same conditions shown in **Fig. 2**. Quite high hydrogen concentrations of 90 and 94 % could be obtained from methanol/water/Al-powder and methanol/water/Ni-powder mixtures, respectively. Comparing other properties of the hydrogen-rich gases between these two cases, both hydrogen partial pressure and hydrogen producing rate from the methanol/water/Al-powder mixture were superior to those from the methanol/water/Ni-powder mixture. Moreover, taking ready-availability and costs of these two metal-powders (concretely, 65 $/kg-Al and 230 $/kg- Ni, see **Table 2**) into consideration, the optimum metal-powder for methanol/water solution to high-pressure hydrogen-rich gas among tested was then decided to Al-powder in a comprehensive manner. In order to accomplish hydrogen purity 100 % and high-pressure close to 15 MPa simultaneously, the methanol/water/Al-powder mixture has been further investigated in the following four subsections in this section **3.1.**.

**Table 3 Hydrogen-rich gases from methanol/water solution with various metal-powders**

main hydrogen source: methanol/water (0.90 mL/0.60 mL)

amount of metal-powder added: 0.50 g, processing temperature: 573 K

| metal | equilibrium time [min] | total pressure [MPa] | properties of hydrogen-rich gas | | |
|---|---|---|---|---|---|
| | | | concentration [%] | pressure [MPa] | producing rate [$L_N/(dm^2 min)$] |
| Al | 25 | **10.5** | **90** | **9.5** | **40.3** |
| Ni | 109 | 8.0 | **94** | 7.5 | 16.8 |
| Co | 72 | 8.2 | 51 | 4.2 | 2.7 |
| Mg | 12 | 4.0 | 78 | 3.1 | 17.2 |

Here, since the present study was aimed at technologizing our incidental high-pressure hydrogen-rich gas production [3,4], initial conditions of high-pressure hydrogen-rich gas producing experiments from methanol/water solution were well-selected such as constant amount of methanol/water solution of 1.50 mL, concentration of methanol/water solution of 60.0 vol%, amount of metal-powder of 0.50 g and limited processing temperatures ranging between 473 and 723 K. As will be clear in the later subsections **3.1.3.** and **3.2.2.**, all the variable initial conditions and processing temperature affect the properties of high-pressure hydrogen-rich gas produced. For example, a rate of the hydrogen partial pressure rise must be directly affected by the initial volume of methanol/water solution and metal-powder (i.e. a void volume inside the prototype airtight apparatus). In short, it is undeniable that Co, Mg, Ni-powders and other easily-available metal-powders as well have a great deal of potentials to outstrip Al-powder for much higher hydrogen concentration, hydrogen partial pressure and hydrogen producing rate from the methanol/water solution by regulating initial conditions and processing temperatures adequately. Such gigantic numbers of experiments described in this segment are near future works in conjunction with further optimizations, scale-up, seeking alternative hydrogen sources and public acceptance formation in order to bring our incidental high-pressure hydrogen-rich gas direct production into practical applications.

As a final concluding remark in this subsection, all the produced high-pressure hydrogen-rich gases from methanol/water solution were by no means inferior to commercial pure-hydrogen as a fuel for the polymer electrolyte

fuel cell (PEFC, 10205301, Heliocentris Academia International GmbH, Germany). Furthermore, all the hydrogen-rich

gases throughout this paper also kept a full declared potential in the PEFC for over 24 hours. These facts indicate that our

high-pressure hydrogen-rich gas direct producing method has strong possibility to be the self-operating process for the

part of the dispersion type power sources (i.e. the dispersed hydrogen producing appliances) anywhere whole entire the

world, and contributes to realize the hydrogen society.

### 3.1.2. Adding effectivity confirmation of methanol to water as main hydrogen source

Al and its alloys are well-known as one of the most suitable metals applicable for hydrogen production from

only water [31-36]. Taking device dependency into account, high-pressure hydrogen-rich gas producing experiment from

water/Al-powder mixture was performed with the proto-type airtight apparatus (**Fig. 1**) manufactured for the present study.

In **Table 4**, properties of the produced high-pressure hydrogen-rich gases from methanol/water/Al-powder and

water/Al-powder mixtures at 573 K were compared. Though hydrogen concentration was slightly decreased with adding

methanol to water, it was obvious from **Table 4** that methanol/water solution was superior to only water as the main

hydrogen source because of its apparent higher hydrogen partial pressure and hydrogen producing rate, indicating

effectivity of methanol addition to water as hydrogen source.

**Table 4 Properties of produced hydrogen-rich gases from methanol/water/aluminum-powder and**

**water/aluminum-powder mixtures**

amount of main hydrogen source: 1.50 mL

metal-powder added: Al (0.50 g), processing temperature: 573 K

| main source | | equilibrium | total | properties of hydrogen-rich gas | | |
|---|---|---|---|---|---|---|
| methanol | water | time | pressure | concentration | pressure | producing rate |
| [mL] | [mL] | [min] | [MPa] | [%] | [MPa] | [$L_N/(dm^2 min)$] |
| 0.90 | 0.60 | **25** | **10.5** | 90 | **9.5** | **40.3** |
| 0.0 | 1.50 | 47 | 6.3 | 96 | 6.0 | 6.4 |

### 3.1.3. Effect of processing temperature on hydrogen-rich gas production from methanol/water/aluminum-powder mixture

Table 5 shows properties of the produced high-pressure hydrogen-rich gases from 1.50 mL of methanol/water (0.90 mL/0.60 mL) solution together with Al-powder at various processing temperatures ranging from 473 to 723 K. It can be seen that all the hydrogen properties were greatened with an increase in the processing temperature. All the properties of the produced hydrogen-rich gas at 723 K (i.e. 90 %$_{hydrogen}$, 10.8 MPa$_{hydrogen}$ and 56.0 L$_{N,hydrogen}$/(dm$^2$min)) were fairly high as compared to outcomes reported in literatures [5-10,12-25,29-38].

**Table 5 Hydrogen-rich gases from methanol/water/aluminum-powder with various processing temperatures**

main hydrogen source: methanol/water (0.90 mL/0.60 mL), metal-powder added: Al (0.50 g)

| processing temperature [K] | equilibrium time [min] | total pressure [MPa] | properties of hydrogen-rich gas | | |
|---|---|---|---|---|---|
| | | | concentration [%] | pressure [MPa] | producing rate [L$_N$/(dm$^2$min)] |
| 473 | 31 | 5.0 | 73 | 3.7 | 3.0 |
| 573 | 25 | 10.5 | 90 | 9.5 | 40.3 |
| 673 | 23 | 10.8 | 90 | 9.7 | 44.2 |
| **723** | 26 | **12.0** | **90** | **10.8** | **56.0** |

However, hydrogen purity 100 % must be presumably one of the essential qualifications for realizing the hydrogen society (e.g. energies costs reductions, high-density hydrogen transportations, application to FCV (Fuel Cell Vehicles) hydrogen stations and pollution-free clean combustions). In the following two subsections, fortuitously emerged direct production of pure-hydrogen from the methanol/water/Al-powder mixture will be shown and discussed logically.

### 3.1.4. Pure-hydrogen direct production from methanol/water/aluminum-powder mixture

In the present study, an equilibrium time in our high-pressure hydrogen-rich gas producing experiment was

determined when the pressure inside the prototype airtight apparatus kept a certain constant value for over 5 min as already described in section **2.2.**. Accidental longer thermal treatment over the above-mentioned equilibrium time, which is named "a primary equilibrium" and used hereafter, for each experiment prescribed in **Table 5**, the pressure inside the airtight apparatus was gradually decreased in the case only at 723 K and attained a subsequent "secondary equilibrium". Additionally, pure-hydrogen was acquired as shown in **Table 6**. Concretely, pure-hydrogen with high-pressure of 10.0 MPa could be directly produced at a relative great producing rate of 24.9 $L_N/(dm^2min)$ from the methanol/water/Al-powder mixture at the processing temperature of 723 K.

**Table 6 Pure-hydrogen direct production from methanol/water/aluminum-powder**

main hydrogen source: methanol/water (0.90 mL/0.60 mL)

metal-powder added: Al (0.50 g), processing temperature: 723 K

| equilibrium times [min] | | total | properties of hydrogen-rich gas | | |
|---|---|---|---|---|---|
| primary | **secondary** | pressure [MPa] | concentration [%] | pressure [MPa] | producing rate [$L_N/(dm^2min)$] |
| 26 | | 12.0 | 90 | 10.8 | 56.0 |
| 26 | 41 | 10.0 | **100** | **10.0** | **24.9** |

Here, total volumes of hydrogen produced could be simply calculated on the basis of numeric data listed in **Table 6** as following two formulas.

$$56.0 \times \underline{\mathbf{26}} \times \pi \times \frac{0.0653^2}{4} \cong \underline{\mathbf{4.9}} \ L_N \qquad \text{(up to primary equilibrium)} \qquad (1)$$

$$24.9 \times (26 + 41) \times \pi \times \frac{0.0653^2}{4}$$

$$= 24.9 \times \underline{\mathbf{67}} \times \pi \times \frac{0.0653^2}{4} \cong \underline{\mathbf{5.6}} \ L_N \qquad \text{(up to secondary equilibrium)} \qquad (2)$$

Naturally, the thermal processing time up to the secondary equilibrium was lengthened about twice-and-a-half in

comparison with that up to the primary equilibrium (concretely, $67 \div 26 \cong 2.58$ times, from 26 to 67 min), and hydrogen producing rate was concomitantly reduced from 56.0 to 24.9 $L_N/(dm^2min)$. However, a lapse rate of the hydrogen producing rate at the secondary equilibrium stayed by nearly half (accurately, $24.9 \div 56.0 \cong 0.44$) towards that at the primary equilibrium, nevertheless the thermal processing time was lengthened about twice-and-a-half. Pursuantly, newly-hydrogen must be produced even in a period between the primary and the secondary equilibriums. Accordingly, total volume of hydrogen produced was increased from 4.9 $L_N$ up to the primary equilibrium to 5.6 $L_N$ up to the secondary equilibrium at about 14 % percent (concretely, $5.6 \div 4.9 \cong 1.14$, from 4.9 to 5.6 $L_N$).

Of course, pure-hydrogen with much higher pressure and producing rate can be immensely expectable even from the methanol/water solution due to increasing the processing temperature, optimizing initial compositions, increasing amount of the initial main hydrogen source of the methanol/water, added metal alternation, increasing the amount of metal-powder (i.e. Al-powder under the present case) and apparatus alternations. As for the former one parameter, 723 K or its little less are considered optimal processing temperature for methanol/water/Al-powder mixture since higher temperatures above 723 K can be efficiently converted into electricity in diverse other ways such as gas turbine and steam turbine. Concerning the latter five parameters/modifications, future modeling and simulating works [16,48-54] and their subsequent experiments will yield beneficial outcomes, hence let us forgo any final decision for the time being.

## 3.1.5. Detailed analyses and possible phenomena for pure-hydrogen direct production from methanol/water/aluminum-powder mixture

In order to suppose possible phenomena to explain pure-hydrogen direct production from methanol/water/Al-powder mixture denoted in the foregoing subsection **3.1.4.** (**Table 6**), TEM observations were performed before and after the pure-hydrogen acquired experiment.

**Figs. 3** present some quintessential TEM photos of Al-powders before and after the pure-hydrogen acquired experiment, shot with checking Al inclusions by EDX attached to TEM. All the initial Al-powders were confirmed to be involved in chemical reactions with methanol/water solution to pure-hydrogen since no Al-powder kept intact after the pure-hydrogen acquired experiment.
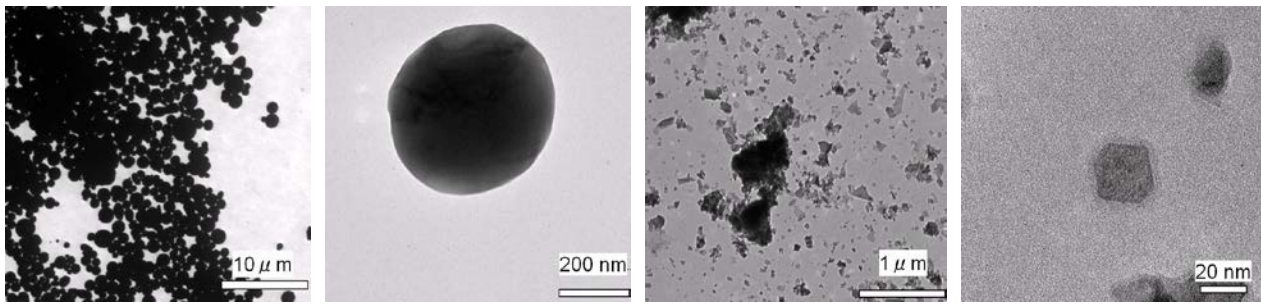
initial Al-powders            Al-compounds after experiment

**Figs. 3 TEM images of initial aluminum-powders and aluminum-compounds after pure-hydrogen acquired experiment**

**Figs. 4** show representative TEM photos of organic solid residues after the pure-hydrogen acquired experiment, shot with checking Al-free by EDX. Wide-ranging shapes of the organic solid residues as ribbon, string, floc, granular cloud, film agglomerate and pillar were observed, being distinctly different from the Al-compounds after the pure-hydrogen acquired experiment. This may point out that a generous quantity of carbons composing the main hydrogen source of methanol was fixed as the solid residues, endowing to pure-hydrogen direct production from methanol/water/Al-powder mixture denoted in the foregoing subsection **3.1.4.** (**Table 6**). Regardless of fruitful database [47] consulted, it was too hard to identify exact compositions of these organic solid residues (**Figs. 4**). However, all the organic solid residues were speculated various higher hydrocarbons [47].
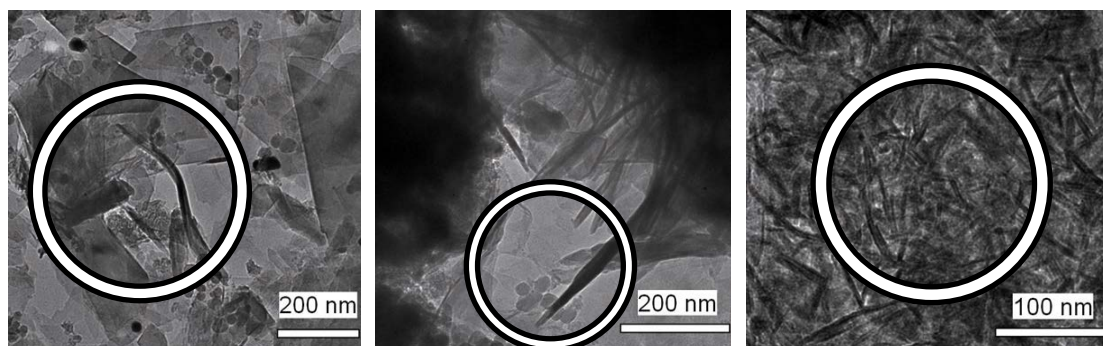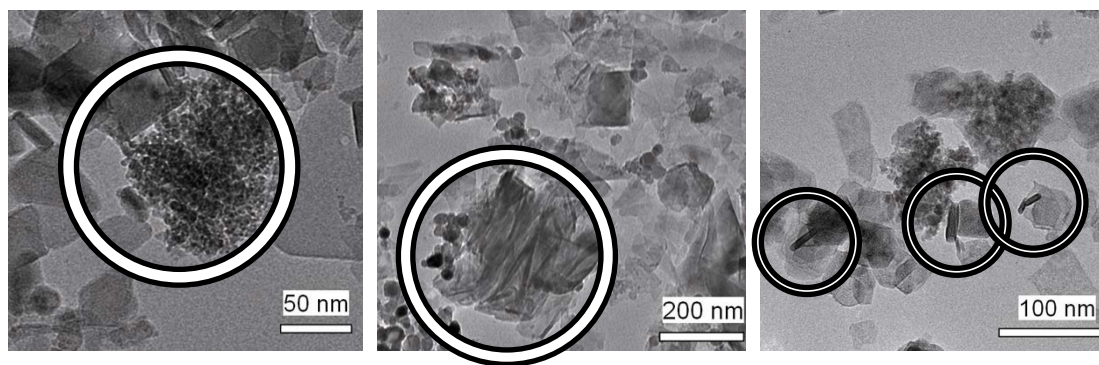
**Figs. 4 TEM images of organic solid residues in liquid residue after pure-hydrogen acquired experiment**

**Table 7** summarizes qualitative and/or qualitative analyzed data (e.g. hydrogen-rich gas by TCD and FID gas-chromatography, Al-compounds by XRD and other residues by pyrolysis-GC/MS [47]) so as to explain supposed possible phenomena for pure-hydrogen direct production from methanol/water/Al-powder mixture as hereinafter described in this subsection.

In a period up to the primary equilibrium, most of carbons discharged from methanol were unreleased to the gas phase due to their fixations as organic liquid residues of benzyl alcohol ($C_6H_5CH_2OH$) and toluene ($C_6H_5CH_3$) and wide variety of solid higher hydrocarbons of uncertain compositions. However, some carbons were emitted to the gas phase as gaseous lower hydrocarbons (i.e. contaminations for hydrogen-rich gas) such as methane ($CH_4$: 700 ppm), ethane ($C_2H_6$: 0.5 %) and ethylene ($C_2H_4$: 5 %) in the period up to the primary equilibrium, lowering the hydrogen concentration of the produced high-pressure hydrogen-rich gas. Almost all oxygens from methanol/water solution reacted with the Al-powders, and were fixed as solid Al-compounds of aluminum oxide hydroxide (AlOOH) and aluminum hydroxide ($Al(OH)_3$) as be also stated in literatures [41-46], although some of the initial Al-powders remained intact, indicating their remaining hydrogen producing potentials. And, other small amount of oxygens were fixed as $C_6H_5CH_2OH$ and various solid higher hydrocarbons. These phenomena might occur along with hydrogen production simultaneously, leading to hydrogen-rich gas from methanol/water/Al-powder mixture at the primary equilibrium.

In a period between the primary and the subsequent secondary equilibriums, all the gaseous hydrocarbons such as $CH_4$, $C_2H_6$ and $C_2H_4$ must be slowly converted to hydrogen with simultaneous fixing reactions of carbons to organic liquid residues of $C_6H_5CH_2OH$ and $C_6H_5CH_3$ and various solid higher hydrocarbons in view of the facts that pure-

hydrogen production denoted in **Table 6**. The remaining Al-powder itself was not detected by XRD at the so-called secondary equilibrium, meaning exhaustion of whole Al-powders potentials for hydrogen production, resulting to increment of total volume of hydrogen from 4.9 $L_N$ (up to the primary equilibrium) to 5.6 $L_N$ (up to the secondary equilibrium) as stated in the subsection **3.1.4.**. Thus, this secondary equilibrium must be considered a "complete equilibrium" for high-pressure pure-hydrogen production from 1.50 mL of methanol/water (0.90 mL/0.60 mL) solution together with Al-powder at 723 K.

**Table 7 Summary of produced gases, solid and liquid residues from methanol/water/aluminum-powder at 723 K**

main hydrogen source: methanol/water (0.90 mL/0.60 mL)

metal-powder added: Al (0.50 g), processing temperature: 723 K

| | original materials | qualitative and/or qualitative analyzed data |
|---|---|---|
| primary equilibrium | methanol/water | hydrogen concentration: **90 %** |
| | | gaseous hydrocarbons (methane, ethane, ethylene etc.) |
| | | water, benzyl alcohol and toluene |
| | | solid higher hydrocarbons |
| | aluminum-powder | **aluminum** |
| | | aluminum oxide hydroxide and aluminum hydroxide |
| secondary equilibrium | methanol/water | hydrogen concentration: <u>**100 %**</u> **(pure-hydrogen)** |
| | | water, benzyl alcohol and toluene |
| | | solid higher hydrocarbons |
| | aluminum-powder | <u>**no aluminum**</u> |
| | | aluminum oxide hydroxide and aluminum hydroxide |

Nevertheless methanol contains carbons, neither $CO_2$ nor carbon monoxide (CO) was comprised in all the produced high-pressure hydrogen-rich gases from methanol/water/Al-powder mixture. Then, keeping the full declared

potential in the PEFC for over 24 hours mentioned in the subsection **3.1.1.** could come to natural consequence since all the produced high-pressure hydrogen-rich gases were CO-free. Hence, our high-pressure hydrogen-rich gas production must be justly termed by environment-conscious and sustainable-energy system.

## 3.2. High-pressure hydrogen-rich gas production from ethanol/water/metal-powder mixture

### 3.2.1. Optimal metal-powder for ethanol/water solution

**Table 8** summarizes properties of the produced high-pressure hydrogen-rich gases from 1.50 mL of ethanol/water (0.90 mL/0.60 mL) solution together with various metal-powders at 723 K. In contrast to high-pressure pure-hydrogen direct production from methanol/water/Al-powder mixture at 723 K shown in **Table 6**, no secondary equilibrium had been emerged in any high-pressure hydrogen-rich gas producing experiments from ethanol/water solution.

As be already denoted the passable high hydrogen producing rate of 17.2 $L_N/(dm^2min)$ from methanol/water/Mg-powder mixture listed in **Table 3**, the highest hydrogen producing rate of 14.3 $L_N/(dm^2min)$ was also obtained from ethanol/water/Mg-powder mixture. This high-pressure hydrogen-rich gas from ethanol/water/Mg-powder mixture of-course kept the full declared potential in the PEFC for over 24 hours as well as all other produced high-pressure hydrogen-rich gases from any mixtures. Plainly, the optimal metal-powder differs, according to what hydrogen properties are focused on. Because the present study was aimed at technologizing our incidental high-pressure hydrogen-rich gas production to be applicable for the FCV hydrogen stations, the pollution-free clean combustions, dispersed hydrogen producing appliances (i.e. part of the dispersion type power sources) and so on, hydrogen concentration must be the most significant property, contributing to realize the hydrogen society and energies costs reductions. Then, the optimum metal-powder for ethanol/water solution to high-pressure hydrogen-rich gas among tested was decided to Co-powder under the present circumstances. Al, Mg and Ni-powders have again significant potentials to be the optimal for ethanol/water solution to high-pressure hydrogen-rich gas, and then further experiments to seek respective appropriate initial conditions to fit the trends of the times remain as continuous future works.

**Table 8 Hydrogen-rich gases from ethanol/water solution with various metal-powders**

| metal | equilibrium time [min] | total pressure [MPa] | properties of hydrogen-rich gas | | |
|---|---|---|---|---|---|
| | | | concentration [%] | pressure [MPa] | producing rate [$L_N/(dm^2min)$] |
| Co | 78 | 7.5 | **91** | **6.8** | 4.4 |
| Al | 24 | 2.5 | 77 | 1.9 | 6.2 |
| Mg | 34 | 5.0 | 87 | 4.4 | **14.3** |
| Ni | 120 | > 15 | 28 | 4.2 | 9.4 |
| Fe | 41 | 3.5 | 0 | 0 | 0 |
| $Al_2O_3$ | 15 | 2.3 | 0 | 0 | 0 |
| - | 55 | 5.0 | 0 | 0 | 0 |

Here, Co-powder, which was determined the optimum metal-powder for ethanol/water solution to high-pressure hydrogen-rich gas, is slightly expensive ($495/kg-Co, see **Table 2**), comparing with other metal-powders of Al, Mg and Ni. However, there are quite a lot of personal belongings and substances in the environment containing Co-compounds such as cyanic dyes, pigments, lacquer compositions, clays, medical goods, desiccating agent and accumulator batteries. Provided effectivities of these belongings and substances as enough alternative for the commercial Co-powder used in the present study were confirmed for high-pressure hydrogen-rich gas production from ethanol/water solution, this hydrogen source of ethanol/water/alternative-Co mixture should be driven by only ubiquitous materials and the self-operating process, leading to the part of dispersion type power sources (i.e. dispersed hydrogen producing appliances anywhere through the world). Hence, such confirming experiments stated in this segment are near future works.

### 3.2.2. Effects of operating parameters on properties of produced hydrogen-rich gas from ethanol/water/cobalt-powder mixture

In the subsection **3.1.1.**, it has been already described that all the variable initial conditions such as initial volume and composition of the main hydrogen source and processing temperature influence the properties of high-pressure

hydrogen-rich gas produced. On the basis of the champion outcome obtained from 1.50 mL of ethanol/water (60.0 vol%) with Co-powder mixture at 723 K in the previous subsection, high-pressure hydrogen-rich gas producing experiments from different initial volumes of the main hydrogen source (i.e. 2.0 mL of ethanol/water (60.0 vol%)) with Co-powder mixture at the same processing temperature of 723 K was carried out. The properties of the high-pressure hydrogen-rich gas are compared in **Table 9**.

**Table 9 Hydrogen-rich gases from ethanol/water/cobalt-powder with different initial ethanol/water solution volumes**

main hydrogen source: ethanol/water (60.0 vol%)

metal-powder added: Co (0.50 g), processing temperature: 723 K

| main source | | | equilibrium | total | properties of hydrogen-rich gas | | |
|---|---|---|---|---|---|---|---|
| ethanol | water | total volume | time | pressure | concentration | pressure | producing rate |
| [mL] | [mL] | [mL] | [min] | [MPa] | [%] | [MPa] | [$L_N/(dm^2min)$] |
| 1.20 | 0.80 | 2.0 | 167 | **> 15** | **100** | **> 15** | 3.4 |
| 0.90 | 0.60 | 1.50 | 78 | 7.5 | 91 | 6.8 | 4.4 |

As be already explained in the subsection **3.1.1.**, the pressure inside the airtight apparatus (i.e. hydrogen partial pressure) was consequently increased by just increasing the initial volume of ethanol/water solution since increment of the initial hydrogen source volume reduced the void volume in the prototype airtight apparatus. The pressure inside the airtight apparatus might exercise a critical impact on this high-pressure hydrogen-rich gas producing method, resulting to production of pure-hydrogen over 15 MPa from ethanol/water (0.20 mL/0.80 mL) solution with Co-powder mixture. Briefly, one of the targeted values of this high-pressure hydrogen-rich gas producing method, which is the hydrogen pressure close to 15 MPa described in **Introduction**, was accomplished. However, the thermal processing time was lengthened (accurately, 167 min), and total hydrogen volumes calculated on the basis of numeric data in **Table 9** as the following formula (3) was reduced in comparison with the cases of high-pressure hydrogen-rich gas productions from

methanol/water/Al-powder (see formulas (1) and (2)).

$$3.4 \times 167 \times \pi \times \frac{0.0653^2}{4} \cong 1.9 \ \text{L}_\text{N} \qquad \text{(from 2.0 mL of 60.0 vol\% ethanol/water)} \qquad (3)$$

Here, $C_6H_5CH_2OH$ and $C_6H_5CH_3$ and wide variety of solid higher hydrocarbons of uncertain compositions were also detected from the organic liquid and solid residues by the same token as the cases from the methanol/water/Al-powder mixtures. And, added Co-powders were reacted to cobalt oxide (CoO), cobalt hydroxide ($Co(OH)_2$), tricobalt tetroxide ($Co_3O_4$) and cobalt carbonate ($CoCO_3$) as be also stated in literatures [55,56]. Such chemical conversions played important role of fixations of carbons discharged from the ethanol and oxygens discharged from the ethanol/water solution, leading to pure-hydrogen production from the ethanol/water/Co-powder mixture.

Furthermore, the safety valve was activated in the cases of the high-pressure pure-hydrogen direct production from 2.0 mL of ethanol/water (60.0 vol%) and Co-powder mixture as shown in **Table 9**. This fact speaks accomplishment of pure-hydrogen with much higher pressure above 15 MPa for itself, however, experimental evidences surpassing 15 MPa and pure-hydrogen as well must be needed, remaining our near future works so as to be applied to the FCV hydrogen stations, high-density hydrogen energy transportations, the pollution-free clean combustions and so on.

**Table 10** presents properties of the produced high-pressure hydrogen-rich gases from 2.0 mL of ethanol/water (1.20 mL/0.80 mL) solution together with Co-powder at various processing temperatures. It is found that the main hydrogen source of the ethanol/water solution was extremely sensitive to the processing temperature in comparison to methanol/water solution shown in **Table 5**, resulting to almost no hydrogen productions at lower-temperatures less than 723 K. This may be considered due to differences of intricate synergistic and chemical interacting effects between methanol and ethanol such as their different carbon-hydrogen ratios, critical pressures and above-described reaction paths attributed to different metal-powders of Al and Co. All the same, modeling and simulating works [16,48-54] in order to compare these high-pressure pure-hydrogen direct productions from methanol/water/Al-powder and ethanol/water/Co-powder mixtures are again quite effective for broadening applicable fields of this high-pressure pure-hydrogen direct producing method.

**Table 10 Hydrogen productions from ethanol/water/cobalt-powder with various processing temperatures**

main hydrogen source: ethanol/water (1.20 mL/0.80 mL), metal-powder added: Co (0.50 g)

| processing temperature [K] | equilibrium time [min] | total pressure [MPa] | properties of hydrogen-rich gas | | |
|---|---|---|---|---|---|
| | | | concentration [%] | pressure [MPa] | producing rate [$L_N$/(dm$^2$min)] |
| 723 | 167 | > 15 | 100 | > 15 | 3.4 |
| 703 | 32 | 2.5 | 32 | 0.8 | 0.6 |
| 673 | 30 | 1.8 | 0 | 0 | 0 |
| 653 | 10 | 1.5 | 0 | 0 | 0 |
| 633 | 30 | 1.8 | 0 | 0 | 0 |
| 573 | 24 | 1.5 | 0 | 0 | 0 |

**Table 11** shows properties of the produced high-pressure hydrogen-rich gases from 2.0 mL of various initial vol% ethanol/water solution together with Co-powder at 723 K. It is seen that similar properties of high-pressure hydrogen-rich gases (partly, > 15 MPa pure-hydrogen from 60.0 vol% ethanol/water solution as be also listed in **Table 10**) were produced under the wide-ranging initial ethanol concentrations from 50.0 to 80.0 vol%. Specifically, high-pressure hydrogen-rich gases with its concentration above 80 %, which is the maximum hydrogen concentration by traditional pure MSR as stated in **Table 1** [5-10], could be obtained with the initial ethanol concentrations from 50.0 to 80.0 vol%, and the safety valve was always activated. Therefore, hydrogen-rich gas and/or pure-hydrogen with much higher hydrogen pressure above 15 MPa is again considered promising, taking into consideration the contiguous critical point of water (concretely, 22.12 MPa at 647.3 K) close to ever attained hydrogen pressure of 15 MPa.

**Table 11 Hydrogen productions from ethanol/water/cobalt-powder with various initial ethanol concentrations**

amount of main hydrogen source: 2.0 mL

metal-powder added: Co (0.50 g), processing temperature: 723 K

| main source | | ethanol concentration | equilibrium time | total pressure | properties of hydrogen-rich gas | | | |
|---|---|---|---|---|---|---|---|---|
| ethanol | water | | | | concentration | pressure | producing rate | total volume |
| [mL] | [mL] | [vol%] | [min] | [MPa] | [%] | [MPa] | [$L_N$/(dm$^2$min)] | [$L_N$] |
| 0.80 | 1.20 | 40.0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **1.0** | **1.0** | **50.0** | 90 | **>15** | 93 | 14.0 | 5.1 | 459 |
| **1.20** | **0.80** | **60.0** | 167 | **>15** | **100** | **>15** | 3.4 | 568 |
| **1.40** | **0.60** | **70.0** | 30 | **>15** | 91 | 13.7 | 8.6 | 258 |
| **1.60** | **0.40** | **80.0** | 22 | **>15** | 86 | 12.9 | **45.1** | 992 |
| 1.80 | 0.20 | 90.0 | 0 | 0 | 0 | 0 | 0 | 0 |

Here, the most beneficial and obvious outcome must be effective vol% range of ethanol/water solution, which was pretty broad from 50.0 to 80.0 vol%, as the main hydrogen source. This fact indicates strong possibilities of any commercially-available potable alcohols as alternative hydrogen sources for this developing high-pressure hydrogen-rich gas (pure-hydrogen) direct producing method. Then, details of high-pressure hydrogen-rich gas from a certain commercially-available rice-wine at 723 K will be shown as a closing result of this section **3.2.** in the next subsection.

### 3.2.3. Commercial rice-wine trial

**Fig. 5** shows time trends of hydrogen partial pressures from 2.0 mL of the rice-wine (MAIFUNA, IRINAMIHIRASHUZO CO., LTD. Japan, alcohol degree of $60 = 60$ vol%) and from 2.0 mL of 60.0 vol% ethanol/water solution together with Co-powder at 723 K. It can be seen that almost the same transitions of hydrogen partial pressures over time revealed. However, slightly lower hydrogen concentration of 80 %, earlier equilibrium time of 60 min and comparatively low hydrogen pressure of around 8 MPa were emerged from the rice-wine/Co-power mixture. These might be attributed to minor components contained in the rice-wine such as 3-deoxyglucosone, esters, amino-acids, organic acids, saccharides and minerals probably. Anyway, this rice-wine trial to high-pressure hydrogen-rich gas, which was confirmed to keep the full potential in the PEFC for over 24 hours, must be a first step straight towards one of the goals of structuring the self-operating dispersed hydrogen producing appliances (i.e. the part of the dispersed power sources)

anywhere in the world as mentioned in **Introduction** because of its carbon-neutral feature, semi-exhaustlessness, commercial availability, local productivity of the main hydrogen source of alcohols (i.e. distilled spirits, vodkas, tequilas, wines and rums) and so on.

Here, regional potable alcohols obviously possess different alcohol degrees and minor components. And, ready-available metal-species vary regionally. Moreover, chemistry compatibilities of respective regional potable alcohols and ready-available metal-species on that district for this developing high-pressure hydrogen-rich gas direct producing method are obscure in the present circumstances. Conversely, the authors believe firmly that this method keeps retaining exhaustless possibilities of further developments and broadening applicable fields for eternity, and supplies complete solutions to any global-scale issues.
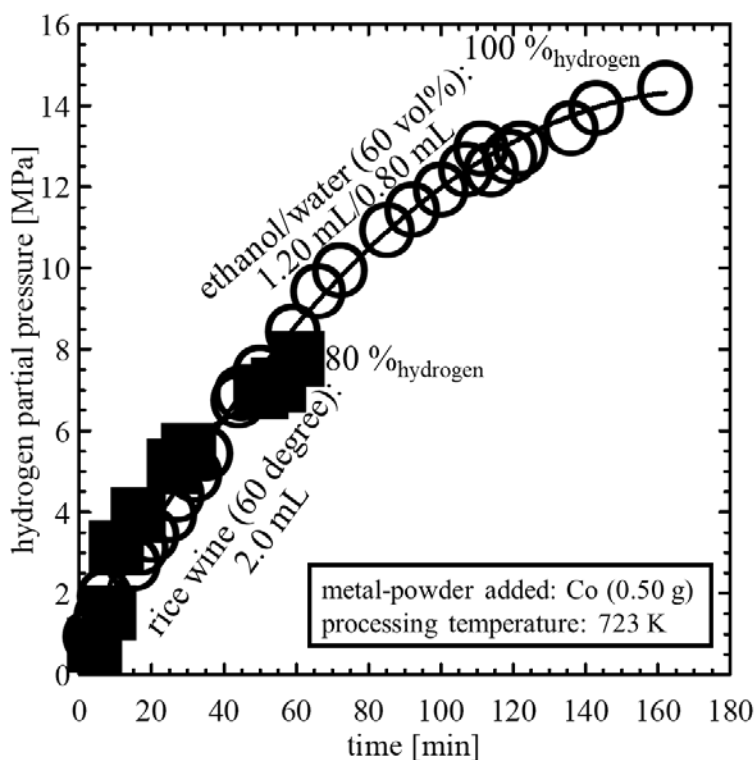


**Fig. 5 Comparison between rice-wine and ethanol/water solution**

## 3.3. Comparisons among this work, our previous works and outcomes by others

**Table 12** summarizes high-pressure pure-hydrogen productions through this work, our previous works and accomplished outcomes by other well-talented researchers.

Optimal hydrogen producing method differs according to TPO (time, place, occasion), varying given situations with passing time, circumstances, occasionally differing requirements for hydrogen qualities, its intended purposes and so forth. Nevertheless, it can be seen from **Table 12** that this developed high-pressure pure-hydrogen producing method through this work are superior to our previous works and outcomes by promising others in terms of hydrogen purity of 100%, pretty high hydrogen pressures of 10 MPa or over 15 MPa, relatively low processing temperature of 723 K, high hydrogen producing rate of 3.4 or 24.9 $L_N/(dm^2min)$, repeatability, stability, safeness and so on. Especially, the quite high-pressures of pure-hydrogen obtained with only "the single and simple operation" from methanol/water/Al-powder and ethanol/water/Co-powder outclass others, and are the world first achievements. Furthermore, this developed high-pressure pure-hydrogen producing method from alcohol/water/metal-powders mixtures still leaves unlimited room for far higher pure-hydrogen pressures and hydrogen producing rates by slight changing the operating conditions (i.e. much further optimization works). Methanol/water/Al-powder and ethanol/water/Co-powder mixtures indicated respective outstanding features, therefore, it is too difficult to determine which the better system for high-pressure pure-hydrogen production is at the present stage.

Recently, FC systems are increasing their diversification such as the FCV hydrogen stations, FC combined cycles and dispersion type power sources, and importance of hydrogen is growing year by year as one of the foremost key chemicals for ensuring the prosperity and stability of the world. Since experimental conditions through the present study were consequently well-selected in a positive good sense, the authors keep developing this high-pressure pure-hydrogen producing method in order to realize energy sustainability and to supply the complete solutions to any global-scale issues.

**Table 12 Comparisons of hydrogen-rich gas and/or pure-hydrogen productions**

| main source | | additive [g] | processing temp. [K] | produced hydrogen | | | ref. |
| | | | | conc. [%] | pressure [MPa] | producing rate $[L_N/(dm^2min)]$ | |
| --- | --- | --- | --- | --- | --- | --- | --- |
| methanol | water | Al | 723 | 100 | 10.0 | 24.9 | this |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 0.90 mL | 0.60 mL | 0.50 | | | | | work |
| ethanol 1.20 mL | water 0.80 mL | Co 0.50 | 723 | 100 | > 15 | 3.4 | this work |
| 50 mol% glycerol/water 1.50 mL | | Al Mg Co 0.50 | 723 | 64~91 | 2.3~4.0 | 5~43 | previous work 3 |
| 50 vol% methanol aqueous solution | | $TiO_2/Pt$ | 353 | 100 | 0.1 | $3.7\times10^{-8}$ | previous work 32 |
| water organic sacrifice agents | | $TiO_2/Pt$ | room temp. | 100 | 0.1 | $2.9\times10^{-5}$ | previous work 33 |
| water | | Al | 503 | 100 | 6.9 | - | 38 |
| 2.5 mol/L methanol 0.5 mol/L NaOH 0.26 mol/L $H_2SO_4$ | | carbon cloth (60% Pt-Ru) Pt foil | room temp. | - | - | $4.4\times10^{-5}$ | 57 |
| ethanol/water (1/10.5) | | Pd alloy/Ag | 473~773 | 29~37 | 0.07 | about 1.1 | 58 |
| methane/water (350/1) | | Ni-form /Pd-Ag | 803~853 | 45~55 | 0.8~1.2 | about 1.3 | 59 |
| 5 mol/L NaOH 75mL | | Al | 348 | - | - | about 124 | 44 |
| 1 mol/L KOH 75mL | | Al/Si(88/12) alloy | 298 | - | - | about 8.4 | 44 |
| $H_2$(75.76%), CO(21.80%) and $CO_2$(2.44%) | | 95% $Fe_2O_3$ 5% $Al_2O_3$ | 1073 | > 99.9 | 9.3 | about 1.44 | 60 |

## 4. Conclusions

High-pressure hydrogen-rich gas producing experiments from various alcohol/water/metal-powder mixtures at

low processing temperatures from 473 to 723 K were carried out in the prototype airtight apparatus possessing the withstand pressure of 15 MPa in the aim of technologizing our incidental high-pressure hydrogen-rich gas production. Methanol and ethanol were selected as main hydrogen sources, and metal-powders of aluminum, cobalt, iron, magnesium and nickel were chosen as tested metal-powders, taking their ready-availability and costs into consideration.

Aluminum and cobalt were found optimal metal-powders for high-pressure pure-hydrogen productions from 60.0 wt% methanol/water and 60.0 wt% ethanol/water solutions, respectively. Pure-hydrogen with 10.0 MPa was produced at a relative great rate of 24.9 $L_N/(dm^2min)$ from 60.0 wt% methanol/water solution together with aluminum-powder mixture at 723 K. Pure-hydrogen with pretty high pressure of over 15 MPa was produced from 60.0 wt% ethanol/water solution together with cobalt-powder at 723 K. Then, the rice-wine having 60 alcohol degree together with cobalt-powder provided high-pressure hydrogen-rich gas with hydrogen concentration of 80 % and hydrogen pressure of around 8 MPa at 723 K.

Here, the organic liquid residues were benzyl alcohol and toluene for all the experiments, regardless of main hydrogen source, added metal-powder and processing temperature. As the organic solid residues, all the residues were identified wide variety of higher hydrocarbons, and quite similar spectrums could be emerged by pyrolysis-GC/MS analyses, irrespective of the experimental conditions. As the inorganic solid residues, aluminum oxide hydroxide and aluminum hydroxide, and cobalt oxide, cobalt hydroxide, tricobalt tetroxide and cobalt carbonate were detected from the methanol/water/aluminum-powder and ethanol/water/cobalt-powder mixtures, respectively. Such fixations of all the carbons and oxygens as solid/liquid residues were considered to bring about the above-mentioned pure-hydrogen productions.

This developed high-pressure hydrogen-rich gas direct producing method can supply wide variety of high-pressure hydrogen-rich gases, and all the produced hydrogen-rich gases were confirmed to keep the full declared potential in the polymer electrolyte fuel cell for over 24 hours without any exceptions. These remarkable findings speak by themselves that this developing high-pressure hydrogen-rich gas (pure-hydrogen) direct producing method is surely approaching the self-operating dispersed hydrogen producing appliances (i.e. the part of the dispersion type power sources) anywhere whole entire world.

Some recommended future strategies such as experiments over 15 MPa, replacement of reagent alcohols by

commercially-available regional potable alcohols together with ready-available metal-species on that district and further optimizing ideas were also proposed in every part through this paper. This paper will be enough trigger for supplying the complete solutions to any global-scale issues.

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