

Short communication

Low temperature thermochemical water splitting using tungsten phosphate glass/Pd laminated membrane

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Abstract

Hydrogen is produced thermochemically from water at temperatures below 500 °C by feeding water vapour to the glass side surface of tungsten phosphate glass thick film/Pd laminated membrane and extracting selectively the hydrogen dissolved and diffused into the membrane from the opposite Pd side surface. The characteristics of the process are to be suitable for onsite production because of low temperature reactions and to be a simple membrane type reaction system with small process number but including automatic separation and purifying process of the generated hydrogen. Although a lot of relating technologies must be developed in order to find a way to practical use, the scientific basis of the hydrogen production was established.

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1. Introduction

Hydrogen based energy system is defined to be the technological solution for reducing emission of greenhouse gases. The system consists of the technologies on production of hydrogen using clean or renewable energies, efficient, safe and reliable storage and delivery of hydrogen, and conversion of the chemical energy of hydrogen to electricity and heat [1,2]. Although much effort has been concentrated to the development of relating technologies, the prospects in practical applications are in general unclear [3]. Cost competitive and safe handling-technologies of hydrogen fuel are not established yet, this suggesting importance of hydrogen production at the sites of end uses [4]. Cleanliness of hydrogen fuel depends on which material it is produced from and what kind of primary energy is used in the production. The ideal system without CO₂ evo-

lution is the production from water by using solar radiations or renewable energies. Waste heat in industries especially in nuclear power plants is practically quasi-clean energy source [5]. Thermochemical cycles produce hydrogen through a series of chemical reactions where the net result is the production of hydrogen and oxygen from water generally at 750–1000 °C. It was proposed [6] that number of chemical reactions and number of chemical separation steps involved in the cycles are important criteria for evaluating feasibility of the thermochemical splitting. The process with least numbers receives high score.

We have found [7] that water vapour is dissociated at the surface of tungsten phosphate glasses and the generated hydrogen is selectively dissolved into the glass by donating electron to W⁶⁺ ions in the temperature range of 300–550 °C. The finding stimulated an examination of constructing a new and low temperature thermochemical water splitting technologies in which the necessary energy is supplied from waste heat. Here, we show scientific basis for the thermochemical process for hydrogen production from water vapour using a laminated membrane of glass/Pd.

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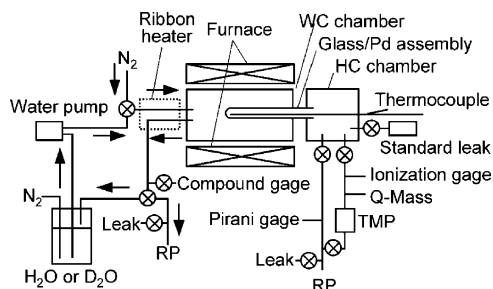


Fig. 1. Experimental setup for water vapour splitting. Water vapour is introduced to the preheated water chamber, which is silica made.

2. Experimental

Chemical composition of the glasses used in the present experiments was $30\text{PO}_{5/2} \cdot 10\text{WO}_3 \cdot 25\text{NbO}_{5/2} \cdot 10\text{BaO} \cdot 25\text{NaO}_{1/2}$ in mole. Bulk glass was produced by melting a stoichiometric mixture of appropriate raw materials in a platinum crucible at 1200°C for 2 h. The obtained glass block was coarsely crushed and re-melted in a tall alumina crucible. A glass/Pd assembly was produced by immersing the Pd tube with 30 cm long and 1 cm in outside diameter into the melt. Thickness and effective area of the glass film are about $100\ \mu\text{m}$ and $80\ \text{cm}^2$, respectively. The glass transition temperature (T_g) measured by using DTA was found to be 570°C .

Fig. 1 is a schematic diagram of the setup for water splitting experiments. The reactor consists of water vapour chamber (WC) made of a silica tube, hydrogen chamber (HC) and a water supply system. The chambers are connected by the partition assembly of one end sealed Pd tube, outside surface of which is coated with a $100\ \mu\text{m}$ thick film of the oxide glass. The glass film is exposed to atmosphere of WC and inside surface of the Pd tube is to that of HC, which is evacuated by a vacuum line to remove quickly the evolved hydrogen. A quadrupole mass spectrometer (Q-Mass, EI) and a standard leak are attached to HC in order to identify the gas species diffused into HC from WC through the partition assembly and to estimate the hydrogen flux, respectively.

It is well known that some metallic materials such as iron react with H_2O vapour and change into oxides, generating hydrogen molecule. We, therefore, designed the reactor to eliminate any possibility of directly reacting metallic materials with water vapour. Pd/glass assembly was set to the reactor so as only the glass coating was exclusively exposed to the water vapour. No surface damages such as haziness, crack and lack was observed by microscopic inspection of the glass film that was exposed to water vapour at 550°C for 3 days.

3. Results and discussion

In the water splitting experiments the output intensities of Q-Mass for the gas species in HC with m/z of 2, 3, 4, 18, 19, 20, 28 and 32 were monitored. The gas fed into WC was N_2 in the initial 2 h, water vapour (H_2O or D_2O) in the next 4 h and N_2 in the last 4 h, respectively. The reaction temperature was

varied between 300 and 550°C , which was lower than the glass transition temperature of the coating glass.

Fig. 2 shows changes in the output intensities of Q-Mass observed at 500°C . The naked Pd tube partition assembly was used as a reference. As seen in Fig. 2a, no evolution of gas species upon the introduction of H_2O vapour into WC was detected in the heating experiments. In the case of the glass/Pd partition assembly (Fig. 2b), upon switching the feed from N_2 to H_2O , H_2 generation starts to rise and reaches to a steady state level, and the hydrogen emission decays to the background level on reversing the feed from H_2O to N_2 . Simultaneously, slight increase in HD and HDO emissions are discernible. H_2O and O_2 remained in the background level during the heating experiments. Similar behaviour of the evolution of deuterium bearing species such as D_2 and HD is seen for the case of D_2O feed (Fig. 2c). We must add a remark on the detection of relatively strong intensity for HD species. The glass prepared under air is dissolving hydrogen as hydroxide in the concentration of 10^{18} to $10^{19}\ \text{cm}^{-3}$. HD might be formed by substitution of the hydrogen with the diffused deuterium. HDO and D_2O are thought to be reaction products between the generated hydrogen molecules and residual oxygen in HC.

The fact that hydrogen molecules, H_2 , D_2 and HD, are evolved in HC chamber is the direct experimental evidence for a series of the reactions, the water vapour splitting, selective dissolution of the hydrogen, distribution of the dissolved hydrogen from the glass to Pd metal, and evolution of hydrogen molecule into the atmosphere with low partial pressure of hydrogen through Pd layer. Decomposition of water to hydrogen and oxygen requires significant energy, $240\ \text{kJ mol}^{-1}$, and extreme temperature of 2500°C or more is necessary for the thermolysis. In the present process the temperature was lowered significantly by splitting the decomposition reaction into four elemental processes described above and quickly extracting the product, hydrogen, from the reaction system.

Flux of hydrogen generation was estimated by using the standard leak, of which calibrated hydrogen flux was $9.5 \times 10^{-8}\ \text{mol h}^{-1}$. The glass/Pd partition assembly in Fig. 1 was replaced with a silica glass tube of the same size with the Pd tube. Difference in the output intensities of Q-Mass for the gas species under consideration upon closing and opening of the standard leak was monitored. The results are shown in Fig. 3. The difference in the output intensities of Q-Mass for H_2 was found to be 3.5×10^{-11} . This corresponds to the calibrated flux of the standard leak. By comparing the intensity difference with those observed for the glass/Pd assembly (Fig. 2b; 6.5×10^{-10}), the hydrogen flux was estimated to be $2 \times 10^{-4}\ \text{mol h}^{-1}\ \text{m}^{-2}$.

The flux observed in the present experiments is several orders of magnitude smaller than the practically acceptable rate. It is required to examine the rate determining process of the water splitting in order to devise the technologies for increasing efficiency of the hydrogen uptake. The hydrogen flux in the present system is a function of experimental parameters such as reaction temperature, pressures of water vapour and oxygen in WC and of hydrogen in HC, thickness of the glass film. Some material

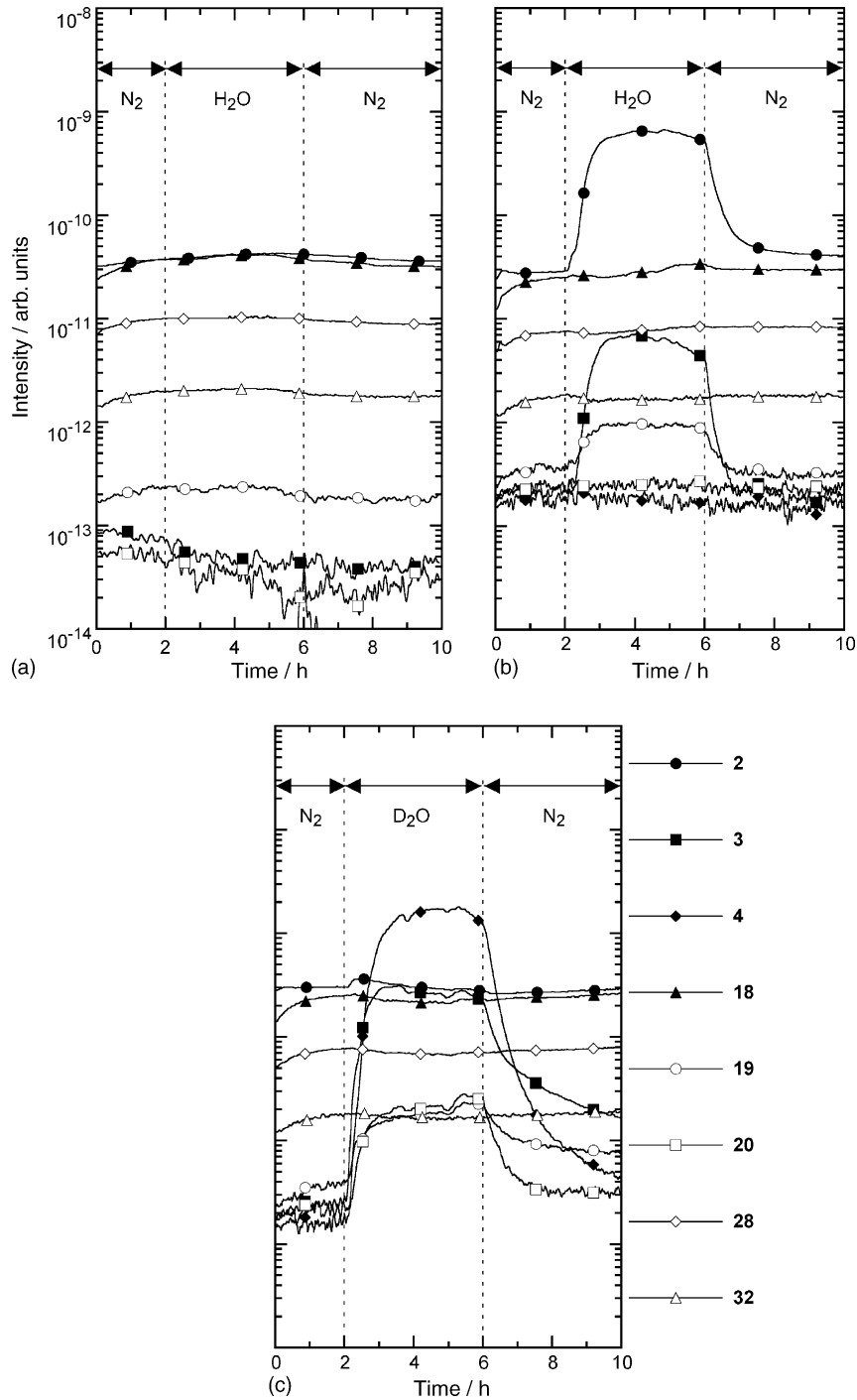


Fig. 2. Gas species diffused from the water chamber to hydrogen chamber at 500 °C through the naked Pd tube partition (a) and the glass/Pd partition assembly (b and c). Nitrogen was fed to the water chamber in the initial 2 h, and the ambient was changed to H₂O vapour (a and b) or D₂O (c). Four hours later water vapour was replaced with nitrogen. The mass numbers of the gas species monitored by Q-Mass are given in the right-hand margin.

constants concerning the glass and Pd also affect the flux. They are equilibrium concentration of the dissolved hydrogen in the glass, distribution ratio of the hydrogen between the glass and Pd film, diffusion constant of hydrogen in the glass and transfer rate of hydrogen from the glass to Pd. The diffusion constant of hydrogen in Pd is about three orders of magnitude larger than that in the glass [8], and its contribution is negligible. It is reasonably supposed that the rate determining process is the diffusion

of hydrogen in the glass film. In order to confirm the supposition the flux F of hydrogen travelled through the glass with thickness x is given by Fick's first law [9]:

$$F = -D \frac{\partial C}{\partial x} \tag{1}$$

where D and C mean the diffusion constant and concentration of hydrogen, respectively. If we put respectively

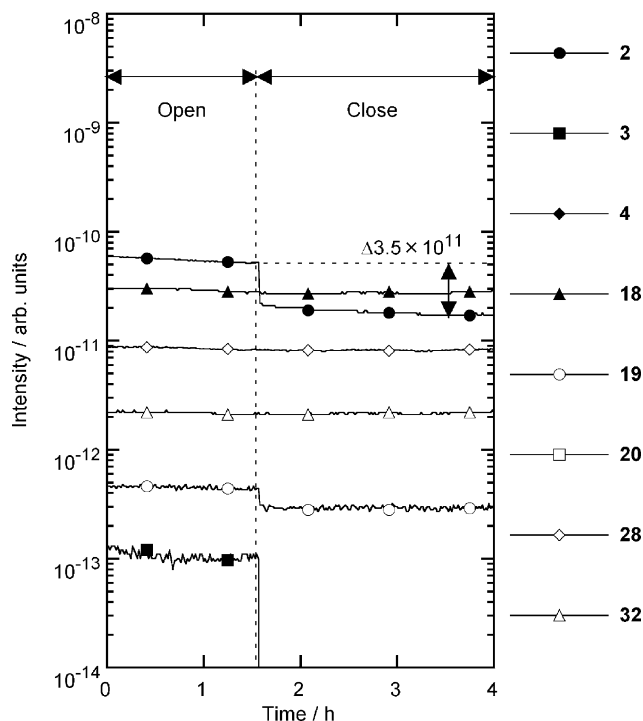


Fig. 3. Differences in the output intensities of Q-Mass for H_2 between opening and closing of the standard leak. The intensity difference of 3.5×10^{-11} is equivalent with the hydrogen flux of $9.5 \times 10^{-8} \text{ mol h}^{-1}$.

$10^{-6} \text{ cm}^2 \text{ s}^{-1}$, $10^{17} \text{ H atom cm}^{-3}$ (see Electronic supplementary material) and 0.01 cm for D , C and x , the flux is calculated to be $3 \times 10^{-4} \text{ mol h}^{-1} \text{ m}^{-2}$. The observed value is very close to the calculated, this suggesting the assumption to be valid.

Finally we add a remark on possible methods to increase the hydrogen flux. The estimated hydrogen flux under the conditions of 500°C and H_2O partial pressure of 1 atm was $2 \times 10^{-4} \text{ mol h}^{-1} \text{ m}^{-2}$, which is equivalent to $1 \text{ g day}^{-1} 100 \text{ m}^{-2}$. If we set the practically acceptable production capacity of hydrogen to be that required for a fuel cell vehicle with an ordinary size to drive 400 km day^{-1} , the production rate of 4 kg day^{-1} is requested [10]. For the reactor with reaction surface of 100 m^2 , 4×10^3 times of the flux is necessary. It is most effective to reduce thickness of the glass film because the diffusion in the layer is the flux determining process. The flux can be calculated by using the estimated diffusion constant data. We notice here that the flux at 500°C can be increased to the requested level by simply reducing the thickness from $100 \mu\text{m}$ to that in the order of 100 nm . Increase in H_2O pressure and decrease in O_2 pressure in WC chamber and operation at higher temperatures also contribute the increase in the hydrogen flux. The experiments in this line are ongoing.

4. Conclusions

It is inferred here that the unique characteristics of the glass, capabilities of water vapour decomposition and selective dissolution of hydrogen atoms, and fast diffusion of the dissolved hydrogen at temperatures lower than T_g , make the proposed system feasible for low temperature thermochemical water splitting. The characteristics of the process are to be suitable for onsite production because of low temperature reactions and to be a simple membrane type reaction system with small process number but including automatic separation and purifying process of the generated hydrogen, and to possess capability of supplying atomic hydrogen directly to the fuel cell [11] through metallic thin films without an intervening formation of molecular hydrogen which is problematic in handling. Although a lot of relating technologies must be developed in order to find a way to practical use, the scientific basis of the hydrogen production was established.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jpowsour.2006.03.051.

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