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Visualization technique for time-variant hydrogen concentration distribution in porous materials using hydrogen storage alloy thin film

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ABSTRACT

An understanding of the mechanism whereby hydrogen is transported in porous materials is a key factor when developing hydrogen-utilizing equipment. For instance, studying the start-up and degradation characteristics of Polymer Electrolyte Fuel Cell (PEFC) requires the distribution of the time-variant hydrogen concentration to be measured at times of the order of 10^{-1} s. However, few studies on time-variant hydrogen transport in porous materials have been reported, and conventional measuring methods are insufficient in terms of their time resolution. This study led to the development of a visualization technique using the characteristics of a MgNi thin film, the reflection rate of which changes along with the hydrogen concentration. The new visualization technique makes it possible to investigate and understand the distribution of the time-variant hydrogen concentration.

Introduction

In recent years, energy problems associated with global warming and the depletion of fossil fuels have become a serious concern. Consequently, the utilization of new forms of energy such as hydrogen has attracted significant attention. This, in turn, has led to an increase in research and development relating to hydrogen-utilizing equipment with porous materials, such as fuel cells, water electrolyzers [1], reformers, filters, heat exchangers, and other reactors.

It has therefore become important to understand the hydrogen transport characteristics of porous materials [2]. For instance, in PEM-type fuel cells, the coexistence of hydrogen and oxygen transported through porous materials at the start-up of operation was reported to cause corrosion of the catalyst, resulting in remarkable deterioration in the power generation performance of these cells [3–9]. The transport occurs in a very short period, reported to be as short as 0.6 s [10]. Hence, understanding the mechanism by which hydrogen is transported requires the time-variant hydrogen concentration distribution to be measured quantitatively in a duration of the order of 10^{-1} s.

Various methods have been established for detecting hydrogen leakage and measuring hydrogen concentration. These include metal oxide semiconductors [11–13],

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electrochemical techniques [14], contact combustion [15,16], and heat conduction [17,18]. Optical measurement methods have also been developed: the fiber Bragg grating-based hydrogen sensor, which monitors the central wavelength shift of the reflected Bragg spectrum [19–21], and the evanescent field hydrogen sensor, which measures the hydrogen concentration by monitoring the intensity of the transmitted optical signal [22–24]. In addition, a technique capable of mechanically measuring hydrogen concentration has been reported [25]. This method utilizes the expansion of the Pd thin film caused by the adsorption of hydrogen, and the current is measured when a very small nano-crack in the Pd thin film comes into contact with the hydrogen. Although the measurement methods cited above can quantitatively evaluate low hydrogen concentrations, they can only be used for spot measurements. Ichikawa [9] tried to capture the mass transfer in a flow field using a mass spectrometer. He set several gas sampling points to measure hydrogen concentration, but the concentration distribution could not be measured.

The fact that many hydrogen sensors are limited to spot measurements has prompted researchers to turn their attention to techniques capable of distribution measurement. For example, Okazaki et al. [26,27], Song et al. [28], and Geng et al. [29] used a catalyst-supported tungsten oxide (Pt/WO_3 and PdO/WO_3) thin film. Pt/WO_3 and PdO/WO_3 react with hydrogen to form tungsten bronze with a deep blue color, which enables two-dimensional hydrogen distribution measurements. Sakaue et al. [30] established a luminescence-based hydrogen sensing method that used palladium and temperature-sensitive luminophores, which translate heat into a luminescent signal. However, their response speed was in the order of 10^0 s, insufficient for time-variant hydrogen concentration measurements.

Kyushu Keisokki Co. developed a hydrogen visualization system using hydrogen storage alloy thin films and multiple probes [31]. This system enables two-dimensional monitoring of hydrogen leakage in the order of 10^{-1} s; however, the authors could not find any literature that dealing with quantitative evaluation of hydrogen concentration.

Therefore, we propose a simple measurement method that utilizes the variation of reflectance of a hydrogen storage alloy thin film with hydrogen concentration, which enables two-dimensional measurements of hydrogen concentration quantitatively in durations of the order of 10^{-1} s.

Experimental equipment and methods

Principal of color change of hydrogen storage alloy thin film

A sheet with hydrogen storage alloy thin film (HSAF), produced by ATSUMITEC CO., LTD., was used to measure the distribution of the hydrogen concentration. Fig. 1 shows a schematic drawing of an HSAF with a poly(ethylene terephthalate) (PET) film substrate, onto which Mg_xNi_y (for reaction with hydrogen) and Pd (as the catalyst) layers were evaporated. Because Mg_xNi_y has low tolerance to moisture and oxidation, the Pd catalyst layer was coated with a hydrophobic protective film to protect against oxidation. The reflectance of the HSAF changes when it comes into contact with hydrogen, causing its color to change from metallic to transparent [32].

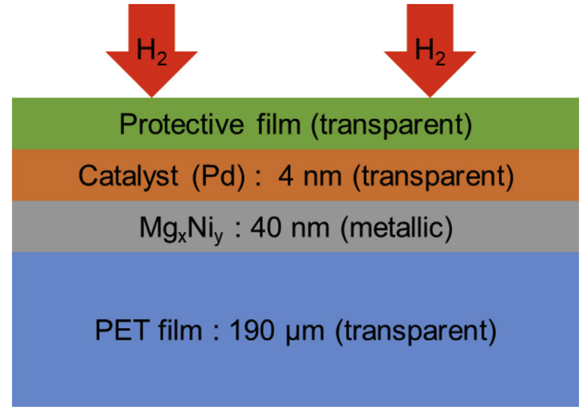

Fig. 1 – Schematic of a HSAF [33].

The following examples are the relevant reactions of the Mg_xNi_y. The Mg_xNi_y consists of Mg_2Ni and Mg. When they encounter hydrogen, the reaction given in Eq. (1) occurs. Next, hydrogen is transferred rapidly from Mg_2NiH_4 to Mg, according to the reaction in Eq. (2), and the metallic Mg becomes transparent as it is converted to MgH_2 [34–36].

$$Mg_2Ni + 2H_2 \rightarrow Mg_2NiH_4 \quad (1)$$

$$Mg + H_2 \rightarrow MgH_2 \quad (2)$$

Visualization apparatus

Fig. 2 shows the visualization apparatus. An aluminum frame was fixed to the workbench. A visualization device as described in Sections 2.3 and 2.4 was fixed to the test section. A high-speed camera (Redlake, Motionpro HS-1) was set above the test section to record changes of the HSAF with 60 fps, 8-bit grayscale video. The video was transferred to a PC, and image processing was performed in 32-bit grayscale using the ImageJ (ver. 1.50i) image processing software. The camera and two LED lights were attached to the aluminum frame to

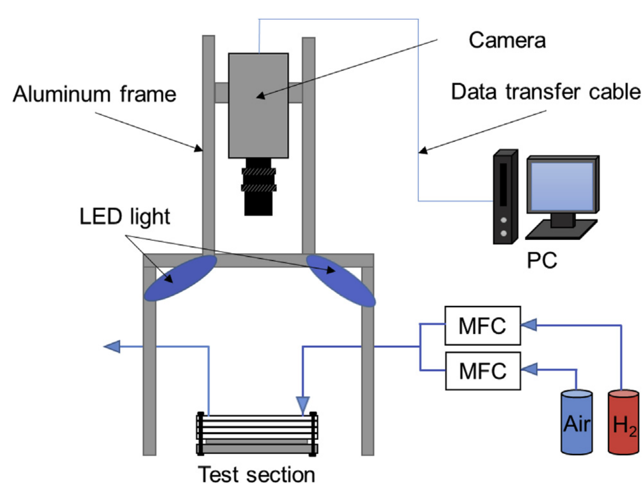

Fig. 2 – Overall view of the visualization apparatus.