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# Hydrogen production tests by hydrogen iodide decomposition membrane reactor equipped with silica-based ceramics membrane

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## ABSTRACT

The decomposition of hydrogen iodide in the thermochemical water splitting iodine–sulfur process at an intermediate temperature (400 °C) using a catalytic membrane reactor was reported here, for the first time. The performance of a catalytic membrane reactor based on a hexyltrimethoxysilane-derived silica membranes ( $H_2$  permeance of  $9.4 \times 10^{-7} \text{ mol Pa}^{-1} \text{ m}^{-2} \text{ s}^{-1}$  and  $H_2/N_2$  selectivity of over 80.0.) was evaluated at 400 °C by varying the HI flow rates of 2.6, 4.7, 6.9, 8.4, and 9.7 mL min<sup>-1</sup>. The silica membranes were prepared by counter-diffusion chemical vapor deposition method on  $\gamma$ -alumina-coated  $\alpha$ -alumina tubes. Hydrogen was successfully extracted from the membrane reactor using the silica membrane at 400 °C. A significant increase in HI conversion was achieved. The conversion achieved at an HI flow rate of 2.6 mL min<sup>-1</sup> was approximately 0.60, which was greater than the equilibrium conversion in HI decomposition (0.22).

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## Introduction

Hydrogen is one of the most widely used new energy sources, because it is a non-polluting and renewable gaseous energy carrier. The thermochemical water-splitting iodine–sulfur cycle (IS process) is one of the most promising approaches due to its potential for large-scale and CO<sub>2</sub> free hydrogen production [1]. This cycle consists of three coupled chemical reactions. The first reaction is known as the Bunsen reaction ( $SO_2(g) + I_2(l) + 2H_2O(l) \rightarrow H_2SO_4(aq) + 2HI(aq)$ , ca. 100 °C). The second reaction is the hydrogen iodide (HI)

decomposition reaction ( $2HI(g) \rightarrow H_2(g) + I_2(g)$ , ca. 500 °C). The third reaction is the sulfuric acid decomposition reaction ( $H_2SO_4(g) \rightarrow H_2O(g) + SO_2(g) + 0.5O_2(g)$ , ca. 900 °C). The entire process requires only water and high-temperature heat and releases only hydrogen, oxygen, and low-temperature heat. All reagents are recycled; there are literally no effluents. The IS process has been studied since the process was first proposed in 1976 [2]. Japan Atomic Energy Agency (JAEA) has been carrying out R&D since around the end of 1980s. Extensive screening tests and corrosion performance evaluation tests for candidate materials under simulated IS process conditions and evaluation of the IS

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process featuring membrane techniques by total thermal efficiency were undertaken as preparation of following hydrogen production demonstrations [3–8]. Integrity test facility (corresponding standard hydrogen production rate of  $100 \text{ L h}^{-1}$ ) is under operation to verify integrity of process components and stability of hydrogen production.

An extreme high temperatures ( $900 \text{ }^\circ\text{C}$ ) that are required for the decomposition of  $\text{SO}_3$  to  $\text{SO}_2$  and  $\text{O}_2$  limits the practical application of the IS process [9]. A catalytic membrane reactor, containing a permeable membrane and catalysts, enables the selective extraction of products in parallel with a reversible reaction that breaks the equilibrium limitations and results in a higher reaction conversion even at lower temperatures [10,11]. Meng et al. [12] theoretically evaluated possibility of using a catalytic membrane reactor to accomplish an intermediate-temperature  $\text{SO}_3$  decomposition ( $600 \text{ }^\circ\text{C}$ ) in the thermochemical water-splitting IS process, and later this group also experimentally demonstrated the intermediate-temperature  $\text{SO}_3$  decomposition in a catalytic membrane reactor that combined packed  $\text{Pt}/\text{Al}_2\text{O}_3$  catalysts with a tubular microporous silica membrane prepared by sol-gel processing.

As for the HI decomposition, silica ceramic membrane reactor to improve the efficiency of HI decomposition in the IS process has been explored by researchers of JAEA [13–15]. HI decomposition produces hydrogen, which is a principal product of the IS process. The homogeneous decomposition of HI could be used directly in a water-splitting scheme; however, to do so would involve going to relatively high temperature in order to achieve workable reaction rates. Even so, the conversion at these kinds of temperatures would be rather low. The low value of decomposition reaction ratio causes to an increase in the cost and effort involved in the production of  $\text{H}_2$  via this cycle and also a reduction in the thermal efficiency of the cycle [16]. One study using silica-based membrane for HI decomposition has been reported in the early 2000s [13]. In that study, the HI decomposition conversion was improved to 76.4% from equilibrium value (25%) at  $600 \text{ }^\circ\text{C}$  with a utilization of the membrane reactor based on a silica membrane that was prepared by a counter diffusion chemical vapor deposition (CVD) of tetraethoxysilane supported on  $\gamma$ -alumina-coated  $\alpha$ -alumina tubes. Silica membranes supported on alumina are strong and re-generable, and could be act as a stable at high temperature and harsh experimental conditions [17–22].

For realization of industrial hydrogen production by the IS process, it is desirable to construct a large-scale reactor using metallic materials. When the working temperature is decreased to approximately  $400 \text{ }^\circ\text{C}$ , metallic materials could be used to replace high-cost structural materials (Ni-based alloys and Hastelloy used for HI decomposer). Hwang et al. [14] investigated theoretically the catalytic decomposition of HI in a membrane reactor, thermochemical water-splitting IS process. This simulation study showed that an HI conversion of over 0.90 would be attainable at operation temperature of  $423 \text{ }^\circ\text{C}$  using the membrane reactor based on a silica membrane prepared by CVD of tetraethoxysilane ( $\text{H}_2/\text{HI}$  selectivity of 650). However, no experimental work dealing with the investigation of an intermediate-temperature ( $400 \text{ }^\circ\text{C}$ ) HI decomposition in a catalytic membrane reactor of the IS process has so far been reported.

We previously developed a high-performance  $\text{H}_2$ -permselective silica membrane derived from hexyltrimethoxysilane (HTMOS:  $\text{Si}(\text{OCH}_3)_3\text{C}_6\text{H}_{13}$ ) at the application for HI decomposition in the thermochemical IS process at an intermediate-temperature ( $400 \text{ }^\circ\text{C}$ ) [15]. An operation temperature of  $400 \text{ }^\circ\text{C}$  was selected owing to the corrosion rate of the structural material and the material cost of the membrane reactor used for HI decomposition. HTMOS-derived silica membranes were prepared via counter-diffusion CVD on  $\gamma$ -alumina-coated  $\alpha$ -alumina support tubes with an outer diameter (o.d.) of 0.01 m and an inner diameter (i.d.) of 0.007 m. A silica membrane prepared in deposition conditions of  $450 \text{ }^\circ\text{C}$  for 300 s was successfully demonstrated to be stable upon exposure to HI at a temperature of  $400 \text{ }^\circ\text{C}$  for 11 h with a corresponding high  $\text{H}_2/\text{HI}$  selectivity ( $>175$ ) and high  $\text{H}_2$  permeance of  $5.9 \times 10^{-7} \text{ mol Pa}^{-1} \text{ m}^{-2} \text{ s}^{-1}$ . Hence, the HTMOS-derived silica membranes supported on  $\gamma$ -alumina-coated  $\alpha$ -alumina support tubes represent promising candidates for achieving further increases in the HI decomposition conversion by the effective separation of  $\text{H}_2$  at a working temperature of  $400 \text{ }^\circ\text{C}$ .

The present study is the first to report an intermediate ( $400 \text{ }^\circ\text{C}$ ) HI decomposition in a catalytic membrane reactor based on based on a silica membrane prepared by a counter diffusion CVD of HTMOS supported on  $\gamma$ -alumina-coated  $\alpha$ -alumina tubes. With the goal of obtaining high-performance silica membranes for use in the membrane reactor, the work of previous studies was extended by investigating the effects of the thickness of the  $\gamma$ -alumina layer on membrane performance, as well as the effects of deposition conditions such as the deposition period and velocity of the  $\text{N}_2$  carrier gas. The performance of the membrane reactor based on the silica membranes was investigated in an attempt to increase the conversion of HI decomposition, extract  $\text{H}_2$  from the membrane reactor, and demonstrate the production of  $\text{H}_2$  from the decomposition of HI.

## Experimental

### Preparation of HTMOS-derived silica membranes

Three types of porous alumina tubes (o.d. 0.01 m, i.d. 0.007 m, and length 0.095 m), supplied by Noritake Co., Ltd., were used as supports. The effective length of membrane was 0.03 m at the center of the each support. Lengths of 0.0325 m at both ends of tube were glazed (GA-13, Nippon Electric Glass Co., Ltd.) and calcinated at  $1150 \text{ }^\circ\text{C}$  for 1 h except for the permeating portions of 0.03 m. One (named Tube I) was made of  $\alpha$ -alumina and had a two-layer structure: an  $\alpha$ -alumina support layer and a second  $\alpha$ -alumina layer, whose porosities were approximately 47% and 34%, and average pore sizes were  $0.82 \text{ } \mu\text{m}$  and  $0.16 \text{ } \mu\text{m}$ , respectively. The other two support tubes (Tube II and Tube III), in contrast to Tube I, had a three-layer structure: an  $\alpha$ -alumina support layer (pore size of  $0.82 \text{ } \mu\text{m}$  and porosity of 47%), a second  $\alpha$ -alumina layer (pore size of  $0.16 \text{ } \mu\text{m}$  and porosity of approximately 34%), and a  $\gamma$ -alumina layer.

Many groups have incorporated a  $\gamma$ -alumina layer in their membranes [17,19,21–24]. Because of the large pore sizes of the alumina supports, it was thought that the presence of a

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