

HYDROGEN PRODUCTION BY HIGH-TEMPERATURE WATER SPLITTING USING MIXED OXYGEN ION-ELECTRON CONDUCTING MEMBRANES

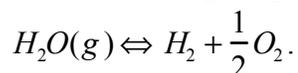
T. H. Lee, S. Wang, S. E. Dorris, and U. Balachandran
Energy Technology Division
Argonne National Laboratory
Argonne, IL 60439, USA

ABSTRACT

Hydrogen production from water splitting at high temperatures has been studied with novel mixed oxygen ion-electron conducting cermet membranes. Hydrogen production rates were investigated as a function of temperature, water partial pressure, membrane thickness, and oxygen chemical potential gradient across the membranes. The hydrogen production rate increased with both increasing moisture concentration and oxygen chemical potential gradient across the membranes. A maximum hydrogen production rate of 4.4 cm³/min-cm² (STP) was obtained with a 0.10-mm-thick membrane at 900°C in a gas containing 50 vol.% water vapor in the sweep side. Hydrogen production rate also increased with decreasing membrane thickness, but surface kinetics play an important role as membrane thickness decreases.

INTRODUCTION

Water dissociates into oxygen and hydrogen at high temperatures, and the dissociation increases with increasing temperature:



Because of the small equilibrium constant of this reaction, the concentrations of generated hydrogen and oxygen are very low even at relatively high temperatures, i.e., 0.1 and 0.042% for hydrogen and oxygen, respectively, at 1600°C (1). However, significant amounts of hydrogen or oxygen could be generated at moderate temperatures if the equilibrium were shifted toward dissociation by removing either oxygen or hydrogen using a mixed-conducting membrane. While hydrogen can also be produced by high-temperature steam electrolysis, the use of mixed-conducting membranes offers the advantage of requiring no electric power or electrical circuitry. A schematic description of hydrogen production with a mixed oxygen ion-electron conducting membrane is shown in Fig. 1. The rate at which oxygen is removed from the sweep gas depends on the oxygen permeability of membrane, which is a function of the ambipolar conductivity and surface oxygen exchange kinetics of the membrane, and on the oxygen partial pressure (pO₂) gradient across the membrane (2-5). Therefore, membranes should have high ambipolar conductivity as well as good surface exchange properties and high

oxygen partial pressure gradient in order to obtain a high hydrogen production rate in the sweep side. Previous studies on hydrogen production from water splitting with mixed-conducting membranes showed only a modest hydrogen production rate above 1500°C (6,7), i.e., 0.6 cm³/min-cm² (STP) at 1683°C (6), mainly because of the low electronic conductivity of those membranes.

We made composites of metal and oxygen conductor to develop mixed oxygen ion-electron conducting membranes. In order to study hydrogen production from water splitting with these membranes, hydrogen was used as a model feed gas to obtain a high pO₂ gradient across the membrane. In this arrangement, the hydrogen is consumed at the feed side by reacting with the permeated oxygen; therefore the overall reaction is similar to the hydrogen permeation from the high partial pressure of hydrogen (pH₂) side (the feed side) to the low-pH₂ (sweep) side. Alternatively, another reducing feed gas such as methane could be used to maintain a high pO₂ gradient across the membrane, in which case hydrogen and syngas could be produced in the sweep and feed gas, respectively. This paper presents the results of hydrogen production from water splitting with cermet membranes.

EXPERIMENTAL

Acceptor-doped CeO₂ with a high BET surface area (20~40 m²/g) was obtained from Praxair Surface Technologies Specialty Ceramics. ANL-1b type composite membranes (8-9) were prepared by mixing the ceramic and metal (40 vol.%) powders in isopropyl alcohol with a mortar and pestle. After evaporating the isopropyl alcohol, the dried powder was pressed into disks at 200 MPa and then sintered in 200 ppm H₂/balance N₂ for 10 h at 1430°C.

For measurement of hydrogen production rate, the sintered disks were polished to desired thickness with 600-grit SiC polishing paper. A polished disk was then affixed to an Al₂O₃ tube by using the assembly described elsewhere (8-9). A gas-tight seal formed when the assembly was heated to 900°C and spring-loaded rods squeezed a gold ring between the membrane and the Al₂O₃ tube. During sealing, 4% H₂ /balance He flowed over one side of the sample, while 100 ppm H₂/balance N₂ flowed over the other side.

A small concentration of H₂ (≈100 ppm) was added to the sweep gas (N₂) to prevent oxidation of the metal phase in the membrane and was subtracted in calculating the hydrogen production rate. Gas concentrations in the sweep gas were analyzed with a Hewlett-Packard 6890 GC using a thermal conductivity detector. Leakage of hydrogen, which happened through pinholes in the membrane and the seal, was corrected by monitoring the concentration of helium on the sweep side. The flow rates of both the sweep and feed gases were controlled with MKS mass flow controllers. Water partial pressure in the sweep gas was controlled by bubbling the sweep gas through water at various temperatures.

RESULTS AND DISCUSSION

Dependence on Water Partial Pressure

The hydrogen production rate for the ANL-1b membrane was measured as a function of water partial pressure ($p_{\text{H}_2\text{O}}$) in the sweep gas. Measurements were made for a 0.97-mm-thick membrane at 900°C in the $p_{\text{H}_2\text{O}}$ range from 0.03 atm (25°C water bath) to 0.49 atm (81°C water bath) with dry 80% H_2 /balance He feed gas and 100 ppm H_2 /balance N_2 sweep gas. Results of these measurements are shown in Fig. 2. The hydrogen production rate increased from 1.1 to 2.0 $\text{cm}^3/\text{min}\cdot\text{cm}^2$ (STP) as the sweep $p_{\text{H}_2\text{O}}$ increased from 0.03 to 0.49 atm; the hydrogen production rate showed a logarithmic dependence on $p_{\text{H}_2\text{O}}$ in the sweep gas. As the $p_{\text{H}_2\text{O}}$ in the sweep gas increases, the p_{O_2} increases. This increases the driving force for oxygen permeation from the sweep side (where the oxygen is produced through water splitting) to the feed side (where the oxygen is consumed through reaction with hydrogen). As a result, the hydrogen production rate increases as the $p_{\text{H}_2\text{O}}$ in the sweep gas increases. The reason for the logarithmic dependence of the hydrogen production rate on the $p_{\text{H}_2\text{O}}$ in the sweep gas is explained in the following subsection.

Dependence on Hydrogen Partial Pressure

The influence of feed side p_{H_2} on the hydrogen production rate is shown in Fig. 3. The $p_{\text{H}_2\text{O}}$ in the sweep gas was 0.49 atm for these measurements. Hydrogen concentration in the feed gas was controlled by mixing ultrahigh-purity (UHP) H_2 and UHP He with mass flow controllers. The hydrogen production rate increased with increasing p_{H_2} in the feed gas, showing a logarithmic dependence on p_{H_2} in the feed gas. As the hydrogen concentration in the feed gas increases, the p_{O_2} on the feed side decreases, thus increasing the driving force for oxygen permeation from the sweep to the feed side. As a result, the hydrogen production rate on the sweep side increases as the p_{H_2} in the feed gas increases.

The hydrogen production rate is replotted in Fig. 4 as a function of p_{O_2} gradient. The p_{O_2} levels on the feed and sweep side are those estimated in the down streams of the feed and sweep side, respectively. The p_{O_2} on the sweep side was estimated from the measured hydrogen concentration and the downstream concentration of H_2O (which is the difference between the initial and consumed H_2O concentration). The p_{O_2} on the feed side was estimated from the concentration of formed H_2O on the feed side and the concentration of downstream H_2 (which is the difference between the initial and consumed H_2 concentration). As can be seen in Fig. 4, the increase of the p_{H_2} in the feed gas corresponds to the increase of p_{O_2} gradient, and the hydrogen production rate shows a logarithmic dependence on this p_{O_2} gradient. A similar result was also observed for the dependence of hydrogen production rate on the sweep $p_{\text{H}_2\text{O}}$ (Fig. 2): the $p_{\text{H}_2\text{O}}$ increase in the sweep gas corresponds to an increase of p_{O_2} gradient. These results show that the hydrogen production rate is dependent on the p_{O_2} gradient across the membrane. In mixed oxygen ion-electron conductors, the logarithmic dependence of oxygen permeation rate on the p_{O_2} gradient is taken as evidence for a process that is limited by the bulk

diffusion of oxygen (2-4). Notice that the hydrogen production from water splitting is a direct result of oxygen removal, or oxygen permeation, from the sweep side. Therefore, the hydrogen production rate for the 0.97-mm-thick ANL-1b membrane is mainly limited by bulk oxygen diffusion under the measured conditions. However, as shown in the following subsection, the importance of surface kinetics becomes significant as membrane thickness decreases.

Dependence on Temperature and Membrane Thickness

The temperature and thickness dependences of hydrogen production rate were measured with 80% H₂/balance He feed and 49% H₂O/balance N₂ sweep gases. Hydrogen production rate was measured between 700 and 900°C at constant sweep and feed gas flow rates. The production rates of three membranes (0.97-, 0.46-, and 0.28-mm-thick) are shown in Fig. 5. as a function of temperature. Production rate increased with temperature and showed Arrhenius-type behavior, with an average apparent activation energy of 0.85 eV.

Figure 6 shows the membrane thickness dependence of hydrogen production rate at 900°C with 80% H₂/balance He feed gas and 49% H₂O/balance N₂ sweep gas. Measurements were made with membrane thicknesses between 1.68 and 0.10 mm. Hydrogen production rate increased with decreasing membrane thickness, but the increase declined as membrane thickness decreased. A maximum production rate of 4.4 cm³/min-cm² (STP) was obtained with a 0.10-mm-thick membrane. This result clearly shows that surface kinetics plays an important role as membrane thickness decreases. Therefore, to increase the hydrogen production rate further, surface kinetics should be increased by either increasing the surface area of the membrane (10,11) or applying active catalysts at the surfaces. Further study of surface kinetics is in progress.

CONCLUSIONS

Novel mixed oxygen ion-electron conducting cermet membranes can be used to produce hydrogen through water splitting. We obtained a maximum hydrogen production rate of 4.4 cm³/min-cm² (STP) with a 0.10-mm-thick membrane at 900°C, using 50 vol.% water vapor in the sweep side. Because of the increased driving force for oxygen permeation from the sweep side to the feed side, the hydrogen production rate increased with the p_{H₂O} in the sweep gas and with the p_{H₂} in the feed gas. The hydrogen production rate also increased with decreasing membrane thickness, but surface kinetics began to dominate the process at a membrane thickness of <0.3 mm.

ACKNOWLEDGMENTS

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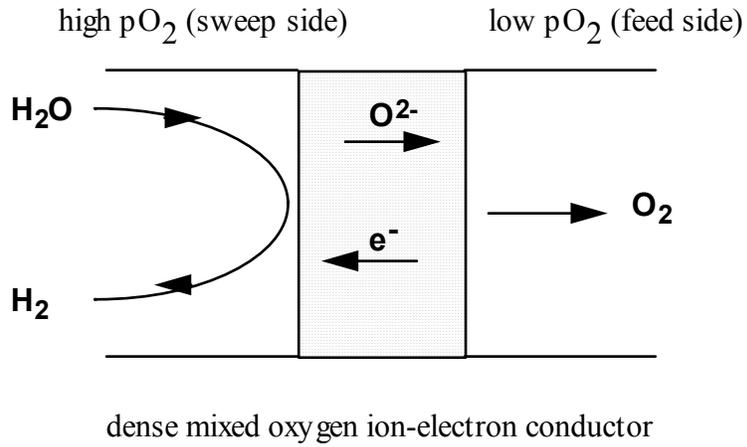


Fig. 1. Hydrogen production from water splitting with a mixed oxygen ion-electron conducting membrane.

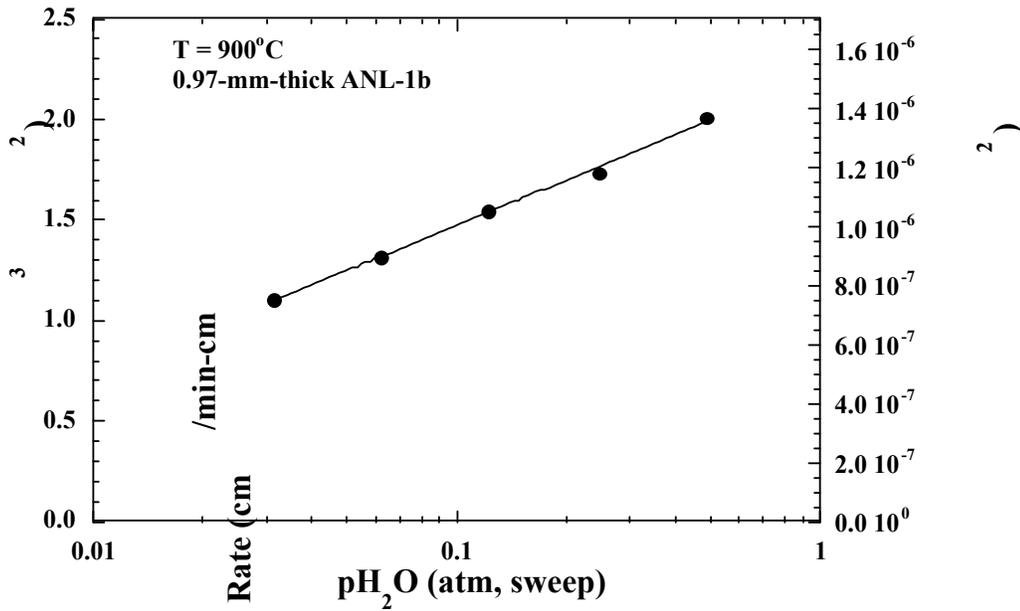


Fig. 2. Dependence of hydrogen production rate on water partial pressure.

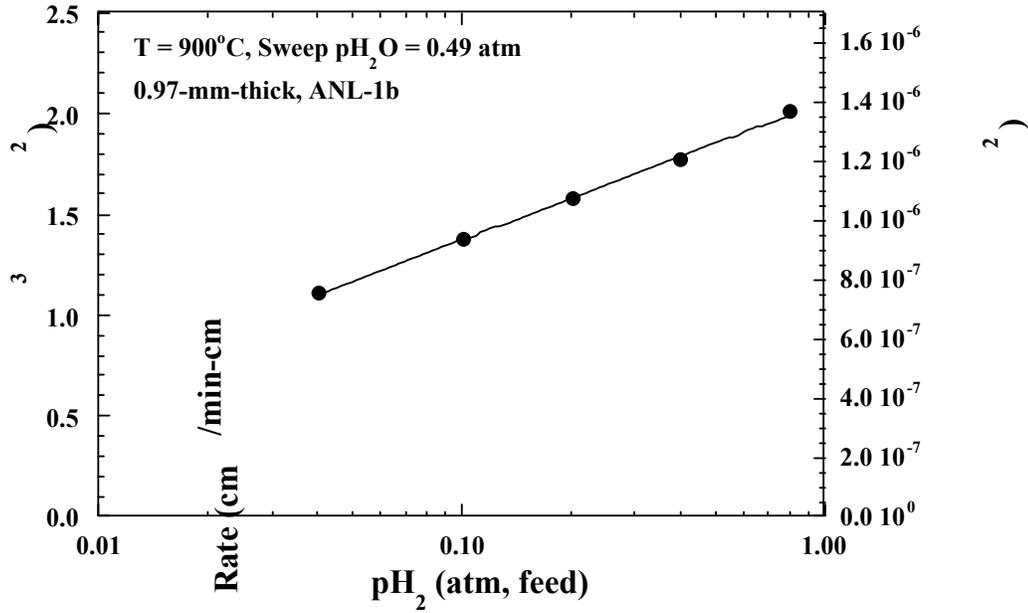


Fig. 3. Dependence of hydrogen production rate on hydrogen partial pressure.

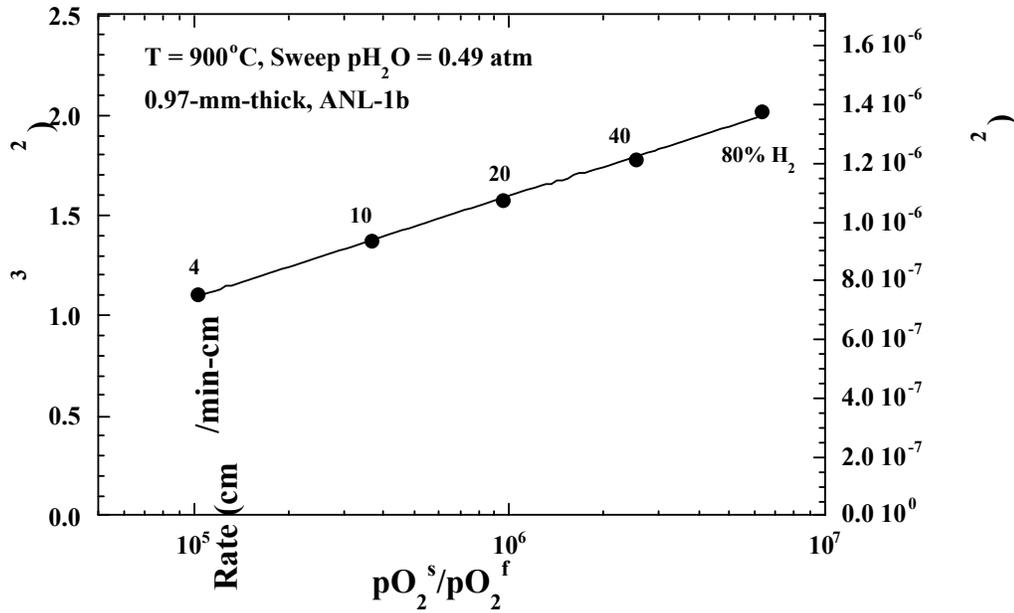


Fig. 4. Dependence hydrogen production rate on pO_2 gradient across the membrane. pO_2^s and pO_2^f indicate estimated sweep and feed pO_2 , respectively.

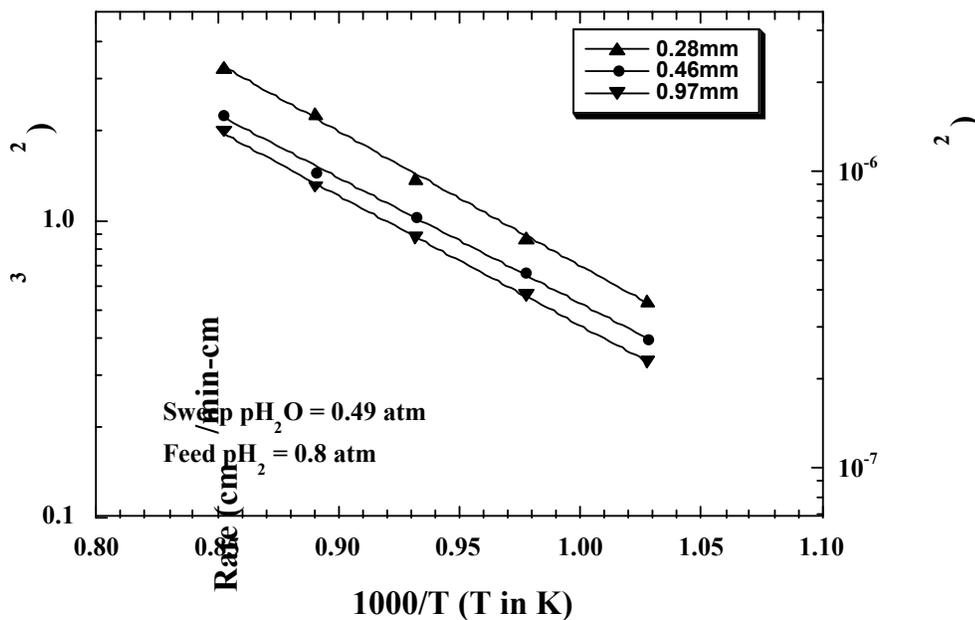


Fig. 5. Dependence of hydrogen production rate on temperature, with 80% H_2 feed gas and 0.49 atm sweep $p_{\text{H}_2\text{O}}$. Membrane thicknesses are indicated on inset.

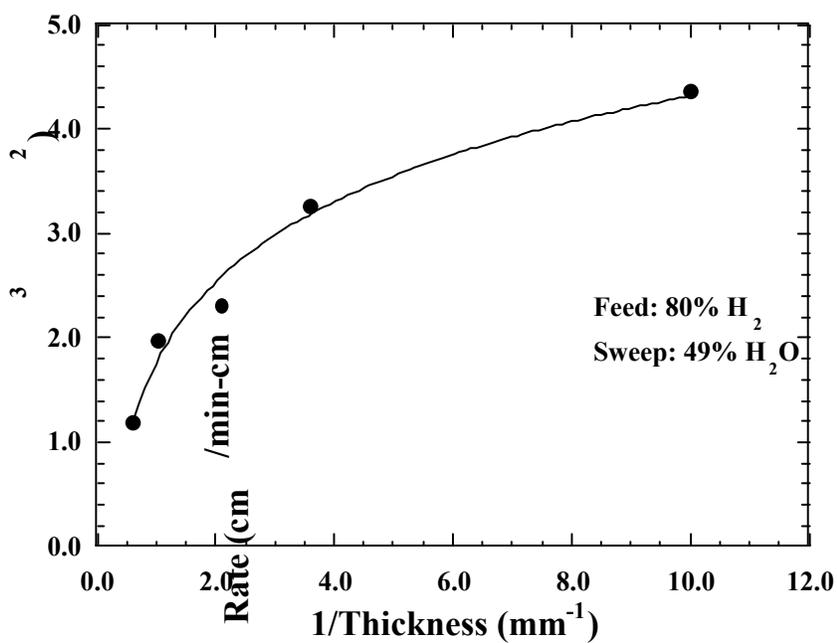


Fig. 6. Dependence of hydrogen production rate on the membrane thickness. Rate is plotted against inverse of membrane thickness.

