

Non-galvanic hydrogen production by water splitting using cermet membranes

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The mixed ion-electron conducting Cu-cermet membranes are suggested for hydrogen production by water splitting at moderate temperature (873-1173°C) because of their good de-catalyzing carbon-formation reactions. The logarithmic hydrogen production rates with p_{H₂O} in the oxidizing gas and with p_{H₂} in the reducing gas were investigated. Cu-based cermet membranes should be further studied to enhance their relatively poor thermal stability, with severe agglomerates of the Cu phase observed following operation at 1173K.

Key words: water splitting, cermet membranes.

Introduction

In recent years, hydrogen has received intensive attention both directly as a fuel and indirectly in the synthesis of fuels to meet demanding environmental regulations. Several different approaches have been made to produce sufficient hydrogen for use as a clean-burning fuel. Among them, the way of extracting hydrogen from natural gases, nonrenewable resources is inevitably generating carbon dioxide and needs a further sequestration process.[1] To circumvent carbon dioxide forming issues, hydrogen production from water has been considered as an alternative strategy. Hydrogen production by water splitting using mixed conducting membranes[2,3] has been recognized as a practical choice due to the advances in the area of membrane technology.

Because the equilibrium constant for water dissociation into oxygen and hydrogen is small, the concentration of hydrogen generated is very low even at 1000°C as shown in Fig. 1. However, it has been reported that significant amounts of hydrogen could be produced at moderate temperatures if the equilibrium were shifted toward dissociation by removing either the oxygen or hydrogen using a mixed-conducting membrane with the advantage of no electric power or electrical circuitry.

Recently, a two-phase (metal: Ni, oxide: Gd-doped CeO₂) oxygen transmitting membrane was successfully applied to water splitting reactors.² Cermet membranes have several particular advantages, because hydrogen production in this case is a direct result of oxygen permeation through membranes, factors affecting the hydrogen production rate are; (i) ambipolar (oxygen ion

and electron) conductivity; (ii) oxygen partial pressure gradient; (iii) temperature; (iv) membranes thickness; (v) surface oxygen exchange kinetics. However, while methane has been used to establish the oxygen potential gradient across the membrane, carbon formed on the Ni surface under the measurement conditions where it was predicted to be thermodynamically stable.

Experimental

In this report, as an alternative for avoiding carbon formation on the Ni surface, Cu was chosen because it does not catalyze carbon-forming reactions. Cu-Ce_{0.8}Gd_{0.2}O_{1.9-d} cermet membranes were prepared by mixing Cu powder (Alfa Aesar, 40 vol.%) and Ce_{0.8}Gd_{0.2}O_{1.9-d} powder (purchased from Praxair Surface Technologies Specialty Ceramics, 60 vol.%) for 24 h in a ball mill.

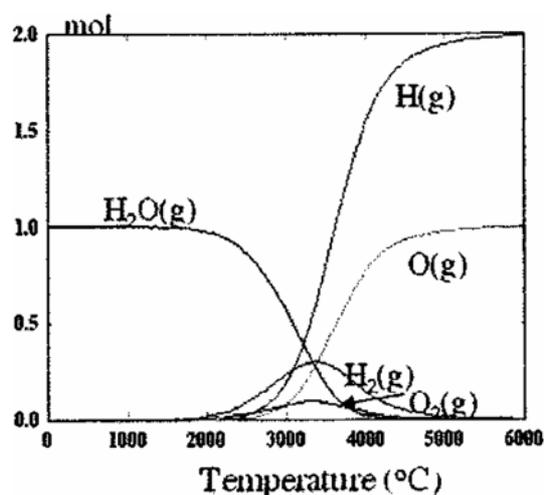


Fig. 1. Calculated equilibrium concentration profiles of water dissociation as a function of temperature.

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The mixed powders were pressed into pellets at 200 MPa and sintered at 1323 K for 10 h in 200 ppm H₂/balance N₂ gas. X-ray diffraction spectra confirmed a two phase structure cermet.

The hydrogen production rate was measured on dense disks ($\approx 96\%$ theoretical, 12 mm in diameter of various thicknesses). The planar surface of each disk was polished with 600-grit SiC paper and then affixed to an alumina tube. A seal formed when the assembly was heated to 900°C and spring-loaded rods squeezed a copper ring between the membrane and the alumina tube. To establish the oxygen potential gradients across the membranes, a “reducing” gas (a hydrogen-helium mixture) was flowed into the reducing side of the membrane. Nitrogen with 100 ppm hydrogen, “oxidizing gas”, was bubbled through a water bath (EX-35D1 heating bath, Fisher Scientific). The hydrogen production rate at the oxidizing side was analyzed with an Agilent 6890 gas chromatograph.

Results and Discussion

The logarithmic dependence of hydrogen production rate as a function of p_{H_2} in the reducing gas is shown in Fig. 2. For the measurements, the p_{H_2O} in the oxidizing gas was 0.04 atm. The hydrogen production rate increased with increasing p_{H_2} because of a decrease in p_{O_2} , which leads to an increase in the driving force for oxygen permeation from the oxidizing to the reducing side.

The dependence of hydrogen production rate on p_{H_2O} (0.03–0.49 atm) at 900°C in the oxidizing gas with dry 80% H₂/balance He as the reducing gas is shown in Fig. 3. A p_{H_2O} increase in the oxidizing gas leads to an increase of the p_{O_2} gradient across the membrane. Because the logarithmic increase of hydrogen production rate from water splitting in Fig. 3 is a direct result of oxygen permeation from the oxidizing side, the results can also be interpreted by a logarithmic dependence of the oxygen permeation rate on the p_{O_2}

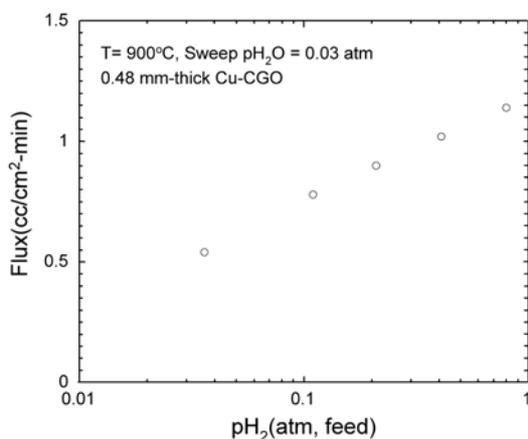


Fig. 2. Dependence of hydrogen production rates on p_{H_2} in the reducing gas. Membrane thickness = 0.48 mm.

gradient, leading to the fact that the hydrogen production rate investigated is dominated by bulk oxygen diffusion under the measured conditions.

The hydrogen production rate at 0.49 atm of p_{H_2O} was 2.3 cm³/minute-cm², comparable to the hydrogen production rate of Ni-CGO in the same measurement conditions. The Cu loading (40 vol. %) instead of Ni may be expected to provide a qualitative performance enhancement due to good chemical resistance to carbon forming without losing the performance in hydrogen production.

Figure 4 shows the dependence of hydrogen production rate on temperature with $p_{H_2} = 0.04$ atm in the reducing gas and $p_{H_2O} = 0.07$ atm in the oxidizing gas. The hydrogen production rate increased with temperature and showed Arrhenius-type behavior, with an average apparent activation energy of 0.82 eV.

Back scattered electron images in scanning electron microscope (in Fig. 5) showed dense and randomly distributed copper phase in the oxide matrix (Gd doped

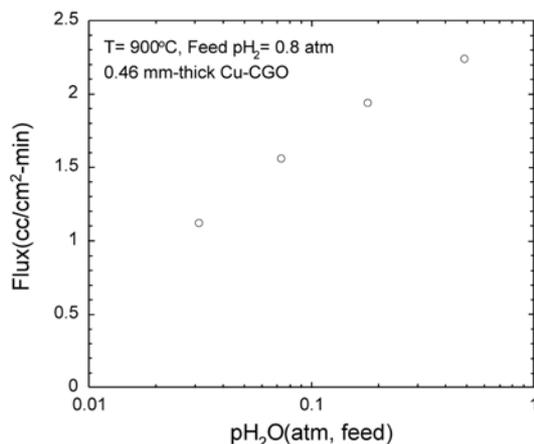


Fig. 3. Dependence of hydrogen production rate on p_{H_2O} in the oxidizing gas; reducing side $p_{H_2} = 0.8$ atm.

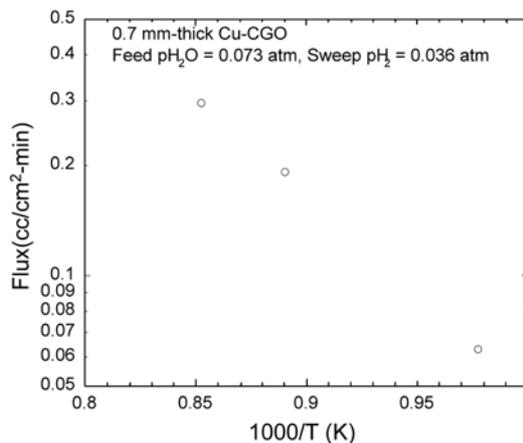


Fig. 4. Dependence of hydrogen production rate on temperature with $p_{H_2} = 0.04$ atm in the reducing gas and $p_{H_2O} = 0.07$ atm in the oxidizing gas.

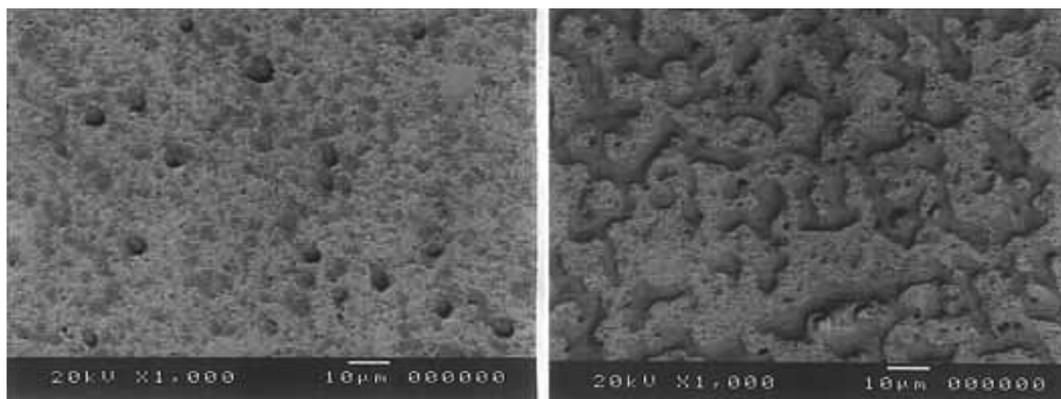


Fig. 5. SEM (Scanning Electron Micrograph) images after measurements at (a) the reducing gas side, (b) the oxidizing gas side.

Ceria). Copper agglomerates are shown at the oxidizing side in the post-run membrane image.

Even though Cu-base cermet membranes do not promote significant carbon formation during the water splitting operation, Cu-based cermet membranes should be further studied to enhance their relatively poor thermal stability, with severe agglomerates of the Cu phase observed following operation at 1173K.

Conclusions

To summarize, the mixed ionic-electronic conducting Cu-cermet membranes are suggested for hydrogen production by water splitting at moderate temperature (873-1173°C) because of their good de-catalyzing carbon-formation reactions. Logarithmic hydrogen production rates with p_{H_2O} in the oxidizing gas and with p_{H_2} in the reducing gas were shown.

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