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Steam Reforming of Hydrocarbons and Water Gas Shift Reaction Through a Wall of Stabilized Zirconia Used as Hydrogen Separator

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Steam reforming of CH_4 and C_2H_4 or water gas shift reaction was allowed to occur through a wall of stabilized zirconia acting as hydrogen separator. The reactions proceed *via* transport of oxygen ions in the zirconia lattice from cathode to anode of the wall, accompanying an electron transfer in the reverse direction through the outer lead wire. Hydrogen without CO_2, CO, or hydrocarbons can be obtained directly by each reaction at the cathode side. The rate of hydrogen production increases exponentially with a rise in applied potentials *via* chromel-constantan thermocouples. The presence of reducing gas such as CO, CH_4, or H_2 at the anode side will decrease considerably the applied potential required to produce hydrogen at the same rate. A tentative reaction mechanism is proposed on the basis of kinetic information of the reaction.

Steam reforming or partial oxidation of hydrocarbons is at present the most efficient and economical process for hydrogen manufacture. The product gas, often called synthesis gas, is converted to high-content hydrogen through water gas shift reaction with simultaneous production of carbon dioxide. Removal of carbon dioxide, carbon monoxide, and hydrocarbons from make-gas is indispensable for getting high-purity hydrogen, which will inevitably raise the hydrogen cost. Under these circumstances, it is desired that high-purity hydrogen should be obtained directly by steam reforming of hydrocarbons or by water gas shift reaction without any removal processes for carbon dioxide, unreacted hydrocarbons, and carbon monoxide. We describe in this report a simple method to obtain pure hydrogen without carbon dioxide, carbon monoxide, or hydrocarbons by running water gas shift reaction or steam reforming of methane and ethylene with the aid of stabilized zirconia. The calcia-stabilized and yttria-stabilized zirconia used in this work are well known as solid electrolytes in which conduction is due almost entirely to oxygen ion transport in a lattice with anion vacancies.[1)]

The basic concept of the method will be explained by Fig. 1. At the anode, CH_4, C_2H_4, and CO are oxidized by oxygen ion as follows:

$$\text{Anode:}\quad CH_4 + 4O^{2-} \rightarrow CO_2 + 2H_2O + 8e^-, \tag{1}$$

$$C_2H_4 + 6O^{2-} \rightarrow 2CO_2 + 2H_2O + 12e^-, \tag{2}$$

$$CO + O^{2-} \rightarrow CO_2 + 2e^-. \tag{3}$$

The electrode works not only as an accepter of electrons liberated but also as a catalyst for the reaction. The electrons are transported through the lead wire connecting both the electrodes of anode and cathode. At the cathode, water vapor is reduced by the electrons transported from the anode, producing only hydrogen:

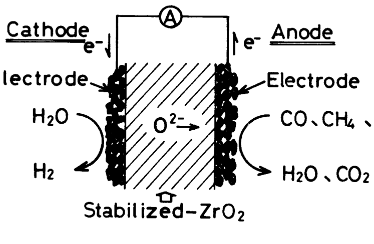


Fig. 1. Schematic model of reactions proceeding through the wall of stabilized zirconia.

$$\text{Cathode:}\quad H_2O + 2e^- \rightarrow H_2 + O^{2-}. \tag{4}$$

The overall reactions can be written as follows:

From Eqs. 1 and 4,

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2. \tag{5}$$

From Eqs. 2 and 4,

$$C_2H_4 + 4H_2O \rightarrow 2CO_2 + 6H_2. \tag{6}$$

From Eqs. 3 and 4,

$$CO + H_2O \rightarrow CO_2 + H_2. \tag{7}$$

Equations 5 and 6 represent steam reforming of methane and ethylene, respectively. Equation 7 is water gas shift reaction. By the method described above, we can get pure hydrogen directly by steam reforming of hydrocarbons or water gas shift reaction without any separation processes for CO_2, CO, and hydrocarbons.

Experimental

The calcia-stabilized zirconia (CSZ) and yttria-stabilized zirconia (YSZ) used were obtained from Nippon Kagaku Togyo Company. The contents of CaO and Y_2O_3 were 11 and 8 mol%, respectively. The geometry of the reactor used is illustrated in Fig. 2. The outer diameter of the zirconia tube was 21 mm and its thickness was 2.5 mm. The length of the tube was 300 mm. The outer diameter of the reactor was 30 mm. The electrodes were affixed on to the zirconia tube by wetting the tube with a suspension of powders of metal oxide in acetone followed by evaporation of the acetone. The metallic electrodes were prepared by decomposition or reduction of the oxides at 873 K in a flow of helium or hydrogen before use. The apparatus employed was a glassmade flow reactor system operated at atomospheric pressure. The reaction temperatures were 873—1273 K. Water vapor (usually 2.7 kPa) carried by helium was fed into the reactor. The feed rate of water vapor was usually 23 μmol min^{-1}. Pure H_2, CH_4, CO, and C_2H_4 were used as anode gases usually without dilution. The flow rate of anode gas was 0.22—2.2 mmol min^{-1}.

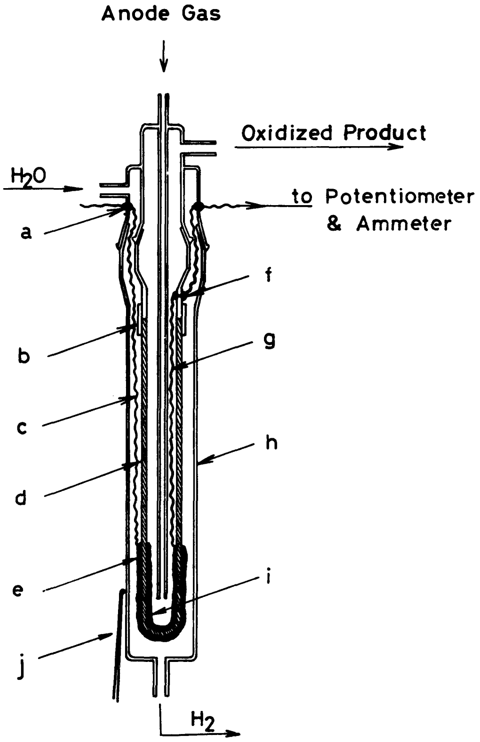


Fig. 2. The geometry of reactor; a and f: silicone seals, b: silicone rubber, c and g: lead wires, d: CSZ or YSZ, e: electrode (cathode), i: electrode (anode), h: quartz glass, j: thermocouple.

Results and Discussion

Electrode Material. Table 1 shows the efficiency of electrode materials for either the cathode or anode of CSZ. The reactivity test on electrode materials was carried out by using aged silver (Ag*), which had been used for reaction at 973 K for more than 20 h, on one side of the electrodes. The geometric area of the zirconia surface coated with Ag* was 80.1 cm². The areas of the electrode materials tested were 52.8 cm². Hydrogen was used as a test anode gas. For every electrode pair given in Table 1, hydrogen was produced according to the theory described above. This was confirmed by the fact that the amount of hydrogen produced at the cathode side (analyzed by gas chromatography) corresponded well to those calculated from currents measured with the ampere meter A in Fig. 1. Moreover, the reaction ceased and resumed in correspondence to disconnecting and connecting the lead wires for both the electrodes, respectively.

The results in Table 1 indicate that Ag, Ni, Pt, Pd, and In_2O_3-SnO_2 are all good electrodes as far as the efficiency of hydrogen formation is concerned. However, Ni, Pt, Pd, and In_2O_3-SnO_2 could not be attached firmly to the zirconia tube by the method described in the experimental section. In contrast, the silver electrode may be ascribed to a solid contact of silver particles on the zirconia surface.

The high efficiency of hydrogen production for the fresh silver pair (Ag–Ag) decreased considerably after 20 h reaction at 973 K (Ag*–Ag*) probably because of the sintering of silver particles during the reaction. After 20 h, however, the electrode pair Ag*–Ag* showed a reproducible activity when the reaction had been run below 973 K. Hence, the following studies were carried out with the electrode pair of Ag*(cathode)–Ag*(anode).

Table 1. Comparison of efficiencies of electrode materials on CSZ at 973 K

Electrode material		Rate of H_2 formation at cathode/μmol min^{-1}
Cathode	Anode	
Ag	Ag	2.62
Ag	Ag*	1.88
Ag*	Ag*	0.68
In_2O_3-SnO_2	Ag*	0.15
Ni	Ag*	1.34
Pt	Ag*	1.22
Pd	Ag*	1.11
Ag*	In_2O_3-SnO_2	1.12
Ag*	Ni	1.59
Ag*	$PrCoO_3$	0.81
Ag*	Pt	0.75
Ag*	Pd	0.75

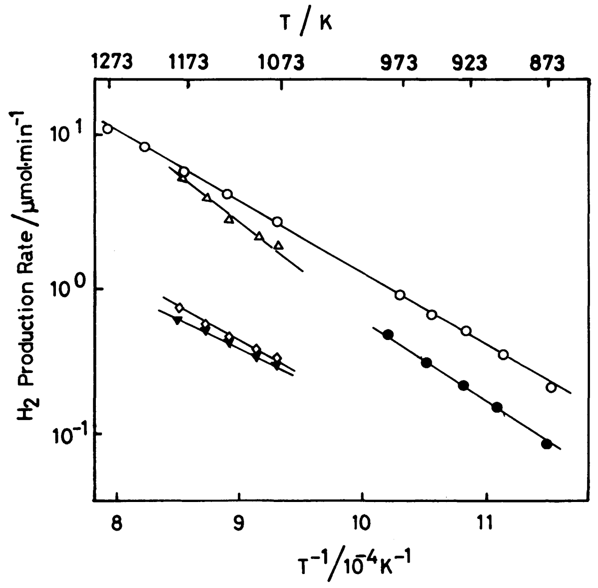


Fig. 3. The rates of hydrogen formation as functions of temperature for different anode gases. The flow rate of anode gas was 0.63 mmol min^{-1}. Anode gas; ○: H_2(using YSZ), ●: H_2(using CSZ), △: C_2H_4(YSZ), ◇: CO(YSZ), ▼: CH_4(YSZ).

Comparison of Efficiencies of Anode Gases for YSZ and CSZ. The effect of anode gases on the rate of hydrogen formation was examined for both YSZ and CSZ. Rates of hydrogen production using different reducing gases on the anode side are plotted in Fig. 3. as a function of reaction temperature. The results in Fig. 3 show that there are large differences among the efficiencies of the anode gases for the production of hydrogen in both the cases of YSZ or CSZ used. The apparent activation energies calculated from the slopes in Fig. 3 are 79 (YSZ; anode gas, H_2), 94 (YSZ; C_2H_4), 77 (YSZ; CO), and 70 kJ mol^{-1} (YSZ; CH_4). The activation energy for CSZ with H_2 as anode gas (closed circles) is 80 kJ mol^{-1} which is very close to that for the YSZ-H_2 system (open circles). Moreover, there are not so much differences between the rates for YSZ (open circles) and for CSZ (closed circles); the ratio of the rates is less than 2.6.

Effect of Applied Potential from Thermocouples. The maximum rate of hydrogen formation observed in this work (Fig. 3; YSZ at 1273 K with anode gas of H_2) is 10.8 μmol min^{-1} corresponding to a current density of 0.72 mA cm^{-2}. This value is far too low for the application of the method to practical use. Therefore, in order to enhance the rate of hydrogen formation, we attempted to apply an electric potential between both the electrodes. Electric energy was supplied on the Seebeck effect from the heat stored in the furnace of reactor *via* 30 pairs of chromel-constantan thermocouples connected in series. Figure 4 shows a sharp increase in the rate of hydrogen formation as a function of effective applied potentials from the thermocouples. The rate increases exponentially with a rise in the applied potential for all the cases using different anode gases. Although the efficiency of thermoelectric generation of electricity is still low,[2,3] the method can easily be applied and utilization of waste heat from chemical plants may be feasible. Whatever the primary energy source of electricity may be or whatever the method for final conversion of energy into electricity may be, the results of Fig. 4 suggest that the applied potential required to yield the same rate of hydrogen formation is caused to decrease when a reducing gas is present at the anode side of the stabilized zirconia, as compared with the value in the case of helium as anode gas (the arrows in Fig. 4 indicate an example of differences in the potentials required). From a viewpoint of electrochemical decomposition of water vapor, the results are taken to indicate that the reducing gas would favorably reduce the consumption of electric power.

Although the efficiency of hydrogen production is still far low for practical use, we have been able to demonstrate that the method proposed in this work can be used for the production of pure hydrogen. Higher temperatures, higher pressures of steam and anode gas, greater electric applied potentials, thinner thicknesses of stabilized zirconia, and higher surface areas of zirconia and electrodes, must improve the efficiency remarkably.

Effects of Concentrations of Gases at Anode and Cathode. Effects of concentrations of anode gases are shown in Fig. 5. The conversion of water to hydrogen depends strongly on the concentration of anode gas irrespective of the presence or absence of electric potential applied. On the other hand, the rate of water decomposition does not depend on the concentration of water vapor (cathode gas) as shown in Fig. 6. The conversion of anode gases is in the range 0.02—0.92% depending on reaction conditions as seen from Figs. 5 and 6. The conversion of water vapor to hydrogen does not depend much on the flow rate of anode gas in the range between 2.2 and 0.22 mmol min^{-1}. Thus, the conversion of pure hydrogen as anode gas increases from 0.26 to 2.4% when the flow rate of anode gas has been decreased from 2.2 to 0.22 mmol min^{-1}.

The rate of hydrogen formation, *viz.*, the current during reaction, increases exponentially with a rise in the applied potential (Fig. 4). If the diffusion of oxygen ion is the rate determining step, Ohm's law should be observed. Hence, the results in Fig. 4 suggest that the rate determining step is of electrochemical reaction. The results that the conversion of water vapor depends on the kind of anode gas (Fig. 3)

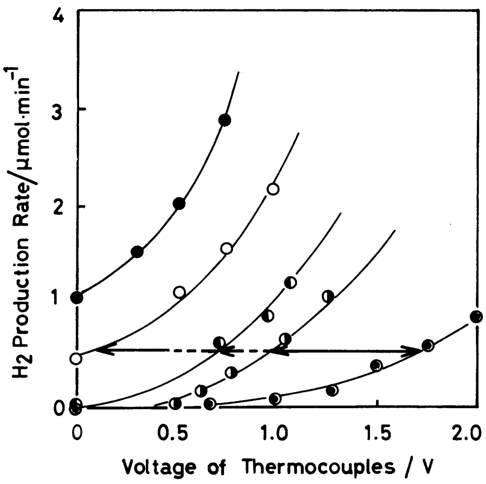


Fig. 4. Rate of hydrogen formation as functions of applied potential from thermocouples using different anode gases. The reactions were carried out at 973 K. The flow rate of anode gas was 0.63 mmol min^{-1}. Anode gas; ●: H_2(using YSZ), ○: H_2(CSZ), ◐: CO(CSZ), ◑: CH_4(CSZ), ⊙: He(CSZ).

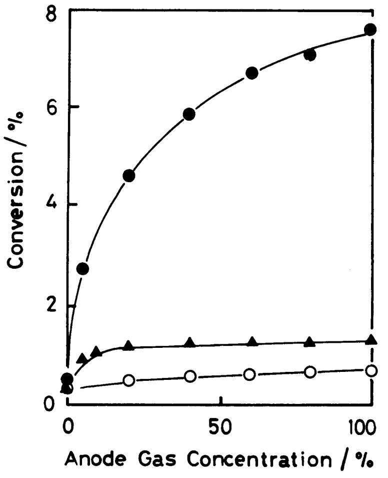


Fig. 5. Effect of the concentration of anode gas on the conversion of water vapor. The reaction at 973 K using CSZ. Anode gases were diluted with He. The flow rate of the gas mixture of He and anode gas was 50 ml min^{-1}. Anode gas; ●: H_2(with applied potential, E=1.0 V), ▲: CO(E=1.0 V), ○: H_2(without applied potential).

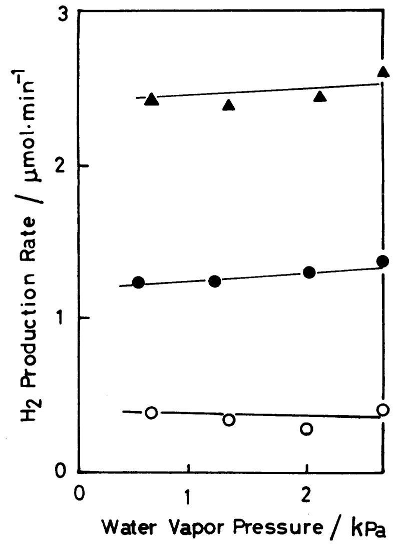
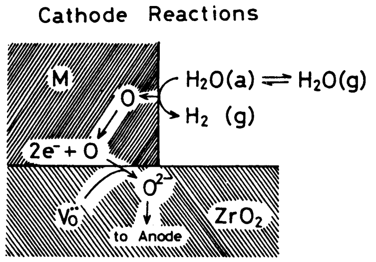


Fig. 6. Effect of the pressure of water vapor at cathode on the rate of water decomposition. The reaction at 973 K using CSZ. Flow rate of anode gas was 2.2 mmol min^{-1}. Anode gas and the value of applied potential; ▲: H_2(with applied potential, $E=1.0$ V), ●: CO($E=1.2$ V), ○: H_2($E=0$ V).

and on the concentration of anode gas (Fig. 5), suggest that the rate determining step is the oxidation process of anode gas by oxygen at the surface of silver electrode. The oxygen is transported from the cathode through the stabilized zirconia. The ion conductivity of oxygen in YSZ is 9 to 11 times as high as that in CSZ in the temperature range between 873 K and 973 K.[4] However, the rate of hydrogen formation on YSZ is no more than 2.6 times that on CSZ (Fig. 3). This obsevation together with the results in Figs. 3, 4, and 5 excludes the possibility that the diffusion of the oxygen ion is the rate determining step under the reaction condition in this work. The diffusion may become the rate determining step when the rate of overall reaction has been increased remarkably.

The reaction mechanism which we have in mind is shown in Fig. 7. At the cathode side, the oxygen atom formed through decomposition of the adsorbed water (Eq. II) on silver electrode (M) diffuses through the surface or bulk of the electrode (Eq. III). The oxygen atom is transfered into the stabilized zirconia through the reaction with anion vacancies (Vö) and electrons which have been supplied from the anode *via* the outer circuit (Eq. IV). The reactions of Eqs. V to VIII occur at the anode side. Equations V and VI are the reverse reactions of Eqs. IV and III, respectively. Equation VII is the reaction when carbon monoxide is used as anode gas. Similar reactions can be considered when hydrogen, ethylene, or methane instead of carbon monoxide is used. The oxidation of anode gas by the adsorbed oxygen atom (Eq. VII) is assumed to be the rate determining step. The applied potential between the anode and cathode would increase the activity of oxygen at the anode, thus enhancing the rate of hydrogen production exponentially (Fig. 4). Further studies are needed to confirm the mechanism proposed in Fig. 7.

In conclusion, the method examined in this work can be used in principle for the production of pure hydrogen. However, much more improvement in the efficiency of hydrogen production is needed for practical application of the method.



<u>Cathode</u> ($H_2O(g) + 2e^-(M) \longrightarrow H_2(g) + O^{2-}(ZrO_2)$)

$$H_2O(g) \rightleftharpoons H_2O(a)(M) \tag{I}$$

$$H_2O(a)(M) \longrightarrow H_2(g) + O(a)(M) \tag{II}$$

$$O(a)(M) \xrightarrow{\text{diffusion}} O(M/ZrO_2) \tag{III}$$

$$O(M/ZrO_2) + 2e^-(M) + V\ddot{o} \longrightarrow O^{2-}(ZrO_2) \tag{IV}$$

<u>Anode</u> ($CO(g) + O^{2-}(ZrO_2) \longrightarrow CO_2(g) + 2e^-(M)$)

$$O^{2-}(ZrO_2) \longrightarrow O(M/ZrO_2) + 2e^-(M) + V\ddot{o} \tag{V}$$

$$O(M/ZrO_2) \xrightarrow{\text{diffusion}} O(a)(M) \tag{VI}$$

$$O(a)(M) + CO(g) \not\longrightarrow CO_2(a)(M) \tag{VII}$$

$$CO_2(a)(M) \rightleftharpoons CO_2(g) \tag{VIII}$$

Fig. 7. The reaction mechanism.

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