An electrochemical steam pump using a proton conducting ceramic

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An electrochemical steam pump was operated at temperatures of 700–900 °C using a high-temperature type protonic conductor, $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$, as a solid electrolyte. When wet air and dry air were introduced into the anode and cathode, respectively, and direct current was applied to the solid electrolyte, the partial pressure of water vapour decreased at the anode, while it increased at the cathode. At low current densities, the pumping rate of water vapour was increased by decreasing the operating temperature and increasing the partial pressure of water vapour at the anode. This is due to the change in proton transport number in $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ which depends on the operating condition. At high current densities, the pumping rate was limited by the diffusion rate of water vapour through the porous anode.

1. Introduction

High-temperature type protonic conductors are of considerable industrial interest because of their applications in solid oxide fuel cells, steam electrolysers to produce hydrogen and steam or hydrogen gas sensors [1, 2]. Furthermore, an electrochemical hydrogen pump is possible using proton conductors as a solid electrolyte, the concept of which is illustrated in [3]. On introducing hydrogen and argon into the anode and the cathode, respectively, and on applying direct current to the cell, hydrogen evolves at the cathode according to Faraday's law.

On the other hand, if wet air and dry air are supplied to the anode and the cathode, respectively, of the proton conductor cell shown in Fig. 1, water vapour at the anode will be electrolysed into protons, which migrate from the anode to the cathode. These then react with oxygen molecules to form water molecules at the cathode. Outwardly, this phenomenon appears to be a kind of steam pump, which pumps water vapour selectively, and the humidity in various systems can be controlled using this type of electrochemical device. In the present study, we constructed an electrochemical steam pump and demonstrated the above-mentioned concept using $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ ceramic as a proton conductor. In addition, we discuss the effect of the operating conditions on the pumping characteristic.

2. Experimental details

$SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ ceramic was prepared by a solid state reaction of $SrCO_3$, CeO_2 and Yb_2O_3, followed by a sintering. Further details of the preparation were described in [2]. The structure of the test cell

was as follows:

$$gas\ I,\ Pt\,|\,SrCe_{0.95}Yb_{0.05}O_{3-\alpha}\,|\,Pt,\ gas\ II \qquad (1)$$
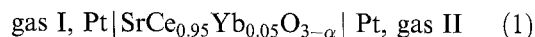
The ceramic was cut into a disc of 12 mm diameter and 0.5 mm thickness. Porous Pt electrodes were attached on both faces of the disc by baking a Pt-paste at 900 °C. Each electrode was connected with two platinum lead wires for the current and voltage output terminals. Two gas compartments were made by sandwiching the disc between sections of two alumina tubes which stood vertically and were sealed by a glass ring gasket. Wet air and dry air were used as gas I and II, respectively. The flow rate was 20 ml min^{-1}. The partial pressure of water vapour was controlled by saturating water vapour at temperatures of 20 $\sim$ −78 °C. Direct current was applied from a galvanostat (Nikko Keisoku, model NPGS-2501). The operating temperature was in the region of 700 $\sim$ 900 °C. The partial pressure of water vapour in the outlet gas was analyzed by a humidity sensor (Osaka Sanso Kogyo, model DPO-2DP). The overpotential of each electrode was measured by a current interruption method. In this case, porous platinum metal was coated on side of the disc as a reference electrode.

3. Results and discussion

3.1. *Electrochemical steam pump*

When wet air ($P_{H_2O} = 737\ Pa$) and dry air ($P_{H_2O} = 105\ Pa$) were introduced into two gas compartments, at 700 °C, the test cell gave a stable e.m.f. of 36.0 mV, the electrode with higher P_{H_2O} being the negative pole. This is a type of steam concentration cell, the theoretical e.m.f. of which may be
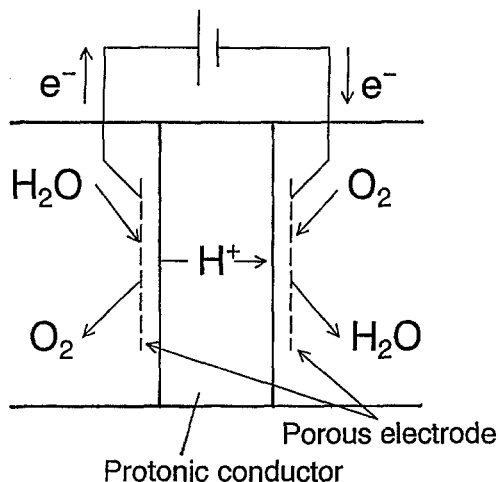
Fig. 1. The schematic illustration of the steam pump using a high-temperature type protonic conductor.
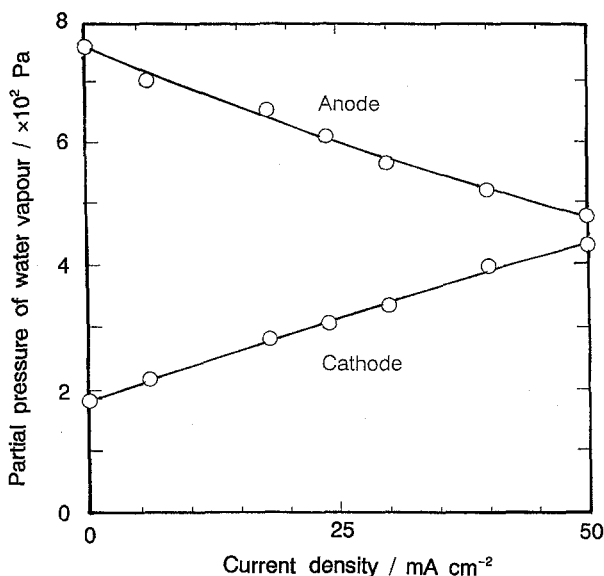

Fig. 2. Changes in partial pressure of water vapour at the anode and at the cathode by passing a direct current (700 °C): these values were measured at each outlet.
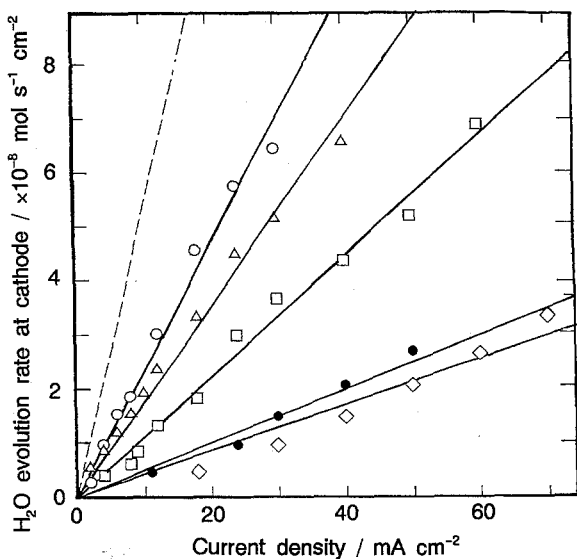

Fig. 3. The effect of the operating temperature on pumping characteristics: partial pressures of water vapour in wet air and in dry air were 2.3×10^3 and 0.1×10^3 Pa, respectively; the broken line indicates theoretical values calculated from Faraday's law. Temperatures: (O) 700, (△) 750, (□) 800, (●) 850 and (◇) 900 °C.
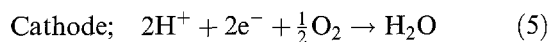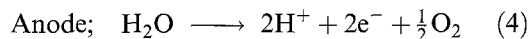
expressed as

$$E_0 = \frac{RT}{2F} \ln \left\{ \left(\frac{P_{H_2O}(I)}{P_{H_2O}(II)} \right) \left(\frac{P_{O_2}(II)}{P_{O_2}(I)} \right)^{1/2} \right\} \quad (2)$$

where R, F and T have their usual meanings. In the case of $P_{O_2}(I) = P_{O_2}(II)$, E_0 is further simplified as follows:

$$E_0 = \frac{RT}{2F} \ln \frac{P_{H_2O}(I)}{P_{H_2O}(II)} \quad (3)$$

The proton transport number, which was determined from E/E_0, was 0.44. In this case, other conducting species are mainly electron holes, as reported in the previous papers [4, 5].

Figure 2 shows the change in P_{H_2O} in each gas compartment when the direct current is applied to the above cell. P_{H_2O} at the anode decreased with increasing current density, and P_{H_2O} at the cathode increased. These results suggest the following electrode reactions:

$$\text{Anode;} \quad H_2O \longrightarrow 2H^+ + 2e^- + \tfrac{1}{2}O_2 \quad (4)$$

$$\text{Cathode;} \quad 2H^+ + 2e^- + \tfrac{1}{2}O_2 \rightarrow H_2O \quad (5)$$

Hence, water vapour is apparently pumped from the anode to cathode via the migration of protons through the solid electrolyte. This conclusion was supported by the fact that, when argon was used in place of dry air, the hydrogen evolution was observed at the cathode.

3.2. Pumping characteristics under various conditions

To understand the pumping characteristics, the steam pump was run under various conditions. Figure 3 shows the evolution rate of water vapour at the cathode in the region of $700 \sim 900$ °C. At any temperature, the evolution rates were lower than values calculated from Faraday's law, and the evolution rate became gradually smaller as the operating temperature was raised. These results can be explained by the fact that the proton transport number is not unity and that this value decreases with increasing temperature. Similar behaviour was observed in the dependence of the water vapour evolution rate at the cathode on P_{H_2O} at the anode, as shown in Fig. 4. The decrease in P_{H_2O} caused the proton transport number to decrease, resulting in the lower evolution rate. Thus, pumping characteristics of the present cell are closely related to the operating condition, which determines the proton transport number in $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$.

Pumping characteristics were evaluated at higher current densities. As shown in Fig. 5, the evolution rate of water vapour at the cathode increased with increasing current density up to $50\,mA\,cm^{-2}$, but then reached a limited value. The lower the P_{H_2O} at the anode, the lower the current density at which the evolution rate was saturated. On the other hand, anodic overpotentials became larger as P_{H_2O} at the anode decreased. These results suggest that the limiting
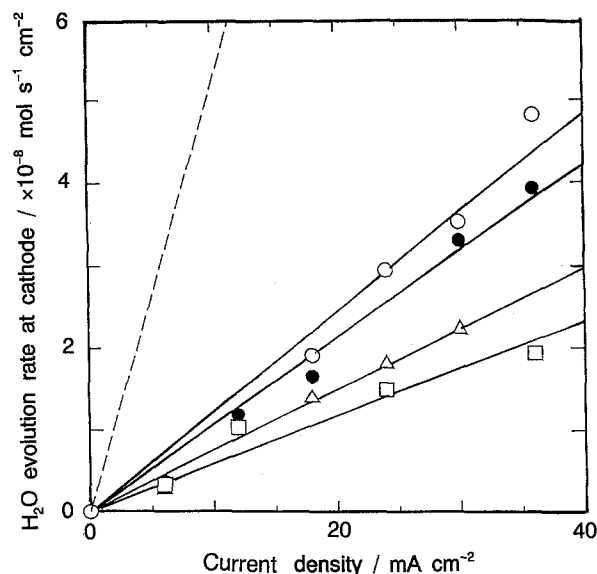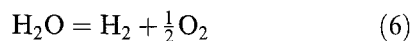
Fig. 4. The effect of partial pressure of water vapour in wet air on pumping characteristics (700 °C); the partial pressure of water vapour in dry air was 0.1×10^3 Pa; the broken line indicates theoretical values calculated from Faraday's law. Key: (□) 200, (△) 600, (●) 1200 and (○) 2300 Pa.

Fig. 6. The effect of the anode thickness on pumping characteristics (700 °C); partial pressures of water vapour in wet air and in dry air were 1.2×10^3 and 0.1×10^3 Pa, respectively. Key: (○) thin; (●) thick.

3.3. Other applications

current behaviour at higher current densities is associated with the electrode reaction at the anode. To clarify which step is rate determining, the steam pump was run using a test cell, whose porous anode layer was three times thicker than that of the previous cell. The result is shown in Fig. 6. Evidently, the pump characteristics depend on the thickness of the anode material, indicating that the rate-determining step is the diffusion of water vapour through the porous anode. In this case, it is not necessary to consider hydrogen molecules as the diffusion species since the equilibrium partial pressure of hydrogen arising from the thermal dissociation equilibrium given by Equation 6 is too small (4.57×10^{-13} atm at 700 °C and 613 Pa P_{H_2O}).

$$H_2O = H_2 + \tfrac{1}{2}O_2 \qquad (6)$$

Detailed studies on pumping characteristics at higher current densities are in progress.

The present steam pump will be applied to control the humidity in various systems. Furthermore, this function offers additional applications for a separator of H_2O from H_2O-D_2O mixed gas and for a membrane reactor for the oxidative coupling of methane. The possibility of the former has been reported elsewhere [6]. Thus, we attempted to achieve the oxidative coupling of methane by means of the removal of water vapour from the reaction system using the steam pump. In this case, a methane–oxygen mixture ($CH_4 : O_2$ mole ratio = 3:1) was supplied to the anode at 750 °C, and porous Ag metal was used as an anode material. The result is shown in Fig. 7. Under open circuit condition, the silver electrode slightly catalysed the oxidative coupling of methane to ethane
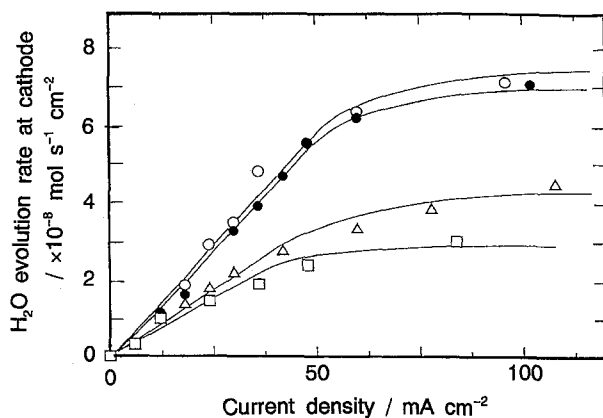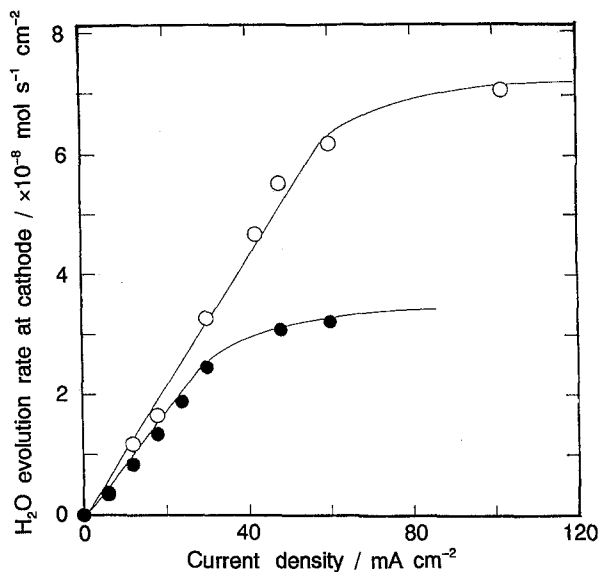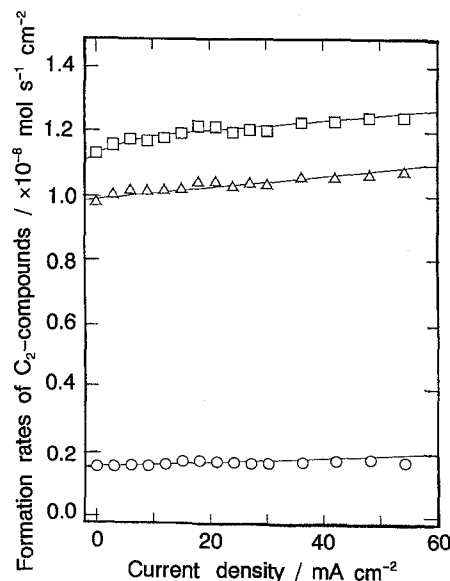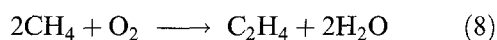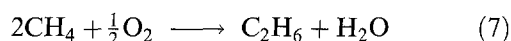

Fig. 5. Pumping characteristics at high current densities (700 °C); the partial pressure of water vapour in dry air was 100 Pa. Key: (□) 200, (△) 600, (●) 1200 and (○) 2300 Pa.

Fig. 7. The oxidative coupling of methane using the steam pump: (750 °C); $CH_4 : O_2 = 3:1$, porous Ag metal was used as an anode material. Key: (□) C_2-products; (△) C_2H_6 and (○) C_2H_4.

and ethylene:

$$2CH_4 + \tfrac{1}{2}O_2 \longrightarrow C_2H_6 + H_2O \qquad (7)$$

$$2CH_4 + O_2 \longrightarrow C_2H_4 + 2H_2O \qquad (8)$$

On supplying direct current to the test cell, the formation rate of C_2-hydrocarbons, especially ethane, was gradually enhanced with increasing current density. Simultaneously, the generation of water vapour at the cathode was observed. Thus, the steam pump from the anode to the cathode shifts the equilibria of Equations 7 and 8 to the right, resulting in the acceleration of C_2-formation.

4. Conclusion

The main conclusions of the present study are:

(i) The steam pump may be used as an electrochemical humidity controller.

(ii) The proton transport number in $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$, which determines the pumping characteristics, was changed by operating condition such as temperature and partial pressure of water vapour.

(iii) A limiting current behaviour was observed at high current densities, because the diffusion of

water vapour through the pores at the anode was the rate-determining step under such conditions.

(iv) The steam pump is also effective for the acceleration of C_2-formation in the oxidative coupling of methane.

Acknowledgement

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