JOURNAL OF APPLIED ELECTROCHEMISTRY **24** (1994) 126–130

Recycling of carbon dioxide using a proton conductor as a solid electrolyte

T. HIBINO, S. HAMAKAWA, T. SUZUKI, H. IWAHARA

Synthetic Crystal Research Laboratory, School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464–01, Japan

Received 12 March 1993; revised 20 July 1993

Using a proton conductor based on $SrZrO_3$ or $CaZrO_3$ as a solid electrolyte, three attempts have been made to react CH_4 with CO_2 efficiently. When the mixture of CH_4 and CO_2 was used as a fuel gas for a SOFC, the cell provided stable electric power. Furthermore, the electrochemical hydrogen pump accelerated both the reforming of CH_4 with CO_2 and the oxidative coupling of CH_4 with CO_2.

1. Introduction

From the standpoint of the recycling of CO_2, the following reforming of CH_4 with CO_2 has recently been studied [1–3].

$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2 \qquad (1)$$

However, this reaction is endothermic and is thermodynamically impossible except at high temperatures. One approach to such a problem is the use of a high temperature type proton conductor as a solid electrolyte, in which three modes are proposed.

We have previously reported that a high temperature type proton conductor is applicable as a solid electrolyte for a hydrogen-air fuel cell [4]. In general, the fuel cell evolves heat due to the decrease in entropy of the reaction, the ohmic resistance of the cell and the overpotential of the electrode reactions [5]. If this thermal energy is used for an endothermic reaction such as Equation 1, a solid oxide fuel cell (SOFC) system with high energy efficiency can be constructed. Furthermore, in the case of the proton conductor, oxide ions do not penetrate into the anode, and the following electrode reactions take place:

$$\text{Anode:} \qquad \tfrac{1}{2}H_2 \longrightarrow H^+ + e^- \qquad (2)$$

$$\text{Cathode:} \qquad H^+ + \tfrac{1}{4}O_2 + e^- \longrightarrow \tfrac{1}{2}H_2O \qquad (3)$$

This means that CO produced at the anode is recovered without combustion. The above-mentioned SOFC system enables the cogeneration of chemicals and electric power as well as the recycling of CO_2 (Fig. 1(a)).

Furthermore, we have recently proposed the coupling of CH_4 by removing hydrogen electrochemically from the reaction system using a proton conductor as a membrane diaphragm [6]. When CH_4 and argon are introduced to the anode and cathode, respectively, and a direct current is sent to the proton conductor, hydrogen is pumped from the anode to the cathode, and hence the formation of C_2-hydrocarbons is promoted. Similarly, if the reforming of CH_4 with CO_2 is accelerated, the reaction temperature may be decreased and serious coking may be depressed (Fig. 1(b)).

As an alternative reaction using CH_4 and CO_2 as a reactant, the oxidative coupling of CH_4 with CO_2 has been reported [7, 8].

$$2CH_4 + CO_2 \longrightarrow C_2H_6 + CO + H_2O \qquad (4)$$

The proton conductor can also be applied to this reaction system. If CH_4 and CO_2 are introduced to the anode and cathode, respectively, CO_2 is reduced to CO with hydrogen which migrates from the anode to the cathode. This makes possible the acceleration of Equation 4 without the accompanying Equation 1 as a side reaction (Fig. 1(c)).

Although there are some applications of high temperature type proton conductors to catalytic reactions of hydrocarbons such as CH_4 and C_2H_6 [6, 9, 10], no attempt has so far been made to treat them with CO_2. In the present study, we apply the proton conductor to the reaction of CH_4 with CO_2. The proton conductors used here are $SrZr_{0.9}Yb_{0.1}O_{3-\alpha}$ and $CaZr_{0.9}In_{0.1}O_{3-\alpha}$ ceramics, which exhibit moderate proton conductivity as well as good stability to CO_2 [11, 12].

2. Experimental procedure

2.1. *Preparation of proton conductors*

$SrZr_{0.9}Yb_{0.1}O_{3-\alpha}$ was prepared by a solid state reaction, followed by sintering. The desired amounts of raw materials ($SrCO_3$, ZrO_2 and Yb_2O_3) were mixed with ethanol and calcined in air at 1623 K for 10 h. The oxide powder was ground in a ball mill and pressed into a cylindrical pellet at $2 \times 10^3\,\text{kg cm}^{-2}$.

The pellet was sintered in air at 1923 K for 10 h. The density of the sinter was larger than 95% of its theoretical value. The specimen obtained was sliced into a thin disc (thickness: 0.5 mm and diam.: 12 mm). $CaZr_{0.9}In_{0.1}O_{3-\alpha}$ was made in a similar manner as above, the oxide powder being moulded into a crucible (inside diam.: 5 mm, length: 15 mm and thick-

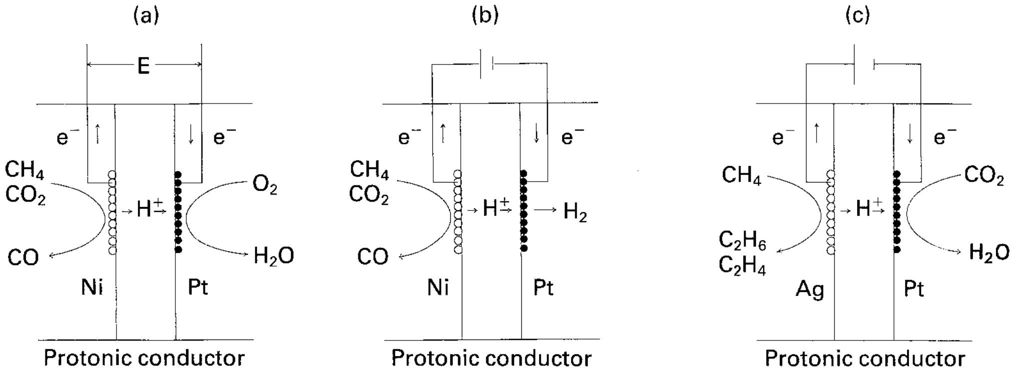

Fig. 1. Principles of the recycling of CO_2 using a proton conductor as a solid electrolyte: (a) fuel cell using the CH_4–CO_2 mixture as a fuel gas; (b) the reforming of CH_4 with CO_2; (c) oxidative coupling of CH_4 with CO_2.

ness: 1 mm) at 2×10^3 kg cm^{-2} and then being sintered in air at 1923 K for 10 h.

2.2. *Fuel cell*

The thin disc of $SrZr_{0.9}Yb_{0.1}O_{3-\alpha}$ was used as a solid electrolyte. The schematic structure of the test cell is shown in Fig. 2(a). NiO powder paste was baked at 1373 K to produce a porous nickel electrode. Then, platinum paste was baked at 1173 K. Each electrode was attached to two platinum wires for the current and potential leads in order to eliminate the ohmic resistance of the platinum lead wires from the cell. The mixture of CH_4 and CO_2 was introduced to the nickel electrode compartment at 1273 K. The flow rate of the mixture gas (CH_4/CO_2 ratio: 1) was 30 ml min^{-1}. The polarization characteristics of each electrode were studied by a current interruption method, in which a platinum wire was wound around the side of the solid electrolyte as a reference electrode.

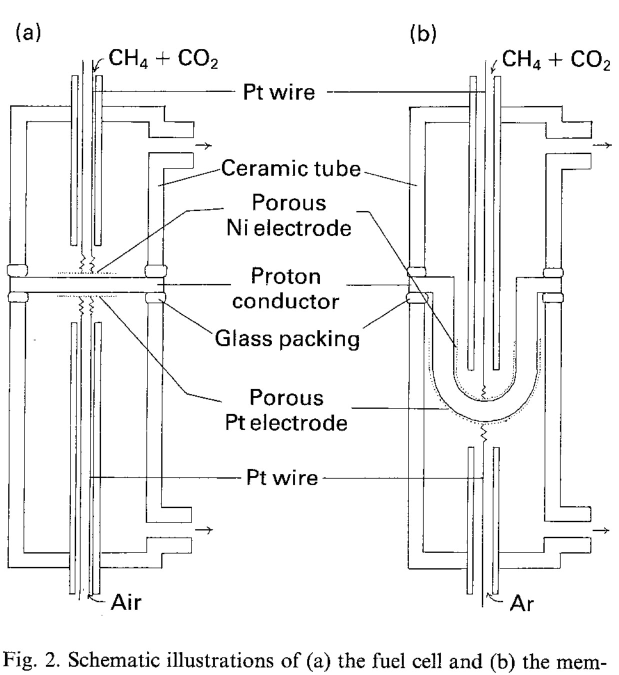

Fig. 2. Schematic illustrations of (a) the fuel cell and (b) the membrane reactor.

2.3. *Reforming of CH_4 with CO_2*

The crucible-type ceramic of $CaZr_{0.9}In_{0.1}O_{3-\alpha}$ was used as an electrolyte diaphragm, as shown in Fig. 2(b). Porous nickel and platinum electrodes were baked on the inner and outer sides of the crucible, respectively. These electrodes were connected to a galvanostat with a platinum wire. The reaction temperature was 1023 K, and the flow rate of the mixture of CH_4 and CO_2 (CH_4/CO_2 ratio: 1) was 30 ml min^{-1}. The effluent gas was analysed by gas chromatography with Porapak Q and molecular sieve 5 A columns.

2.4. *Oxidative coupling of CH_4 with CO_2*

The reaction cell was the same as shown in Fig. 2(b), except using a porous silver electrode instead of the porous nickel electrode. The reaction temperature was 1173 K, and the flow rates of both CH_4 and CO_2 were 20 ml min^{-1}.

3. Results and discussion

3.1. *Solid oxide fuel cell (SOFC)*

When the CH_4–CO_2 mixture gas was introduced to the nickel electrode compartment, the fuel cell gave rise to a stable e.m.f. of about 800 mV. The conversions of CH_4 and CO_2 to products were 34.3 and

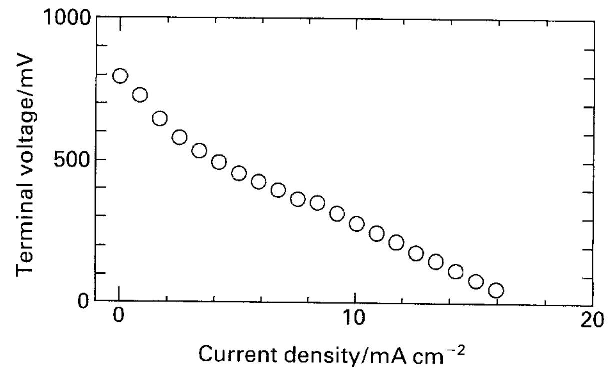

Fig. 3. Discharge characteristic of the fuel cell using the CH_4–CO_2 mixture as a fuel gas: $CH_4 + CO_2$, Ni||$SrZr_{0.9}Yb_{0.1}O_{3-\alpha}$||Pt, air; the electrolyte thickness was 0.5 mm; the CH_4/CO_2 molar ratio was unity; the operation temperature was 1273 K.

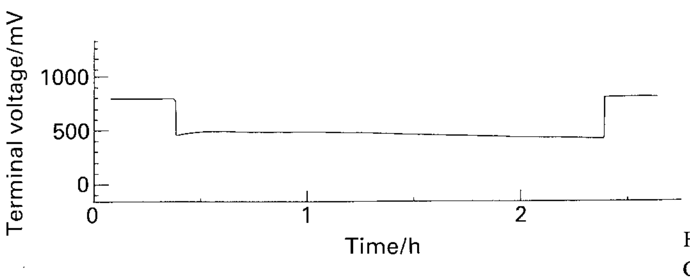

Fig. 4. Continuous discharge test of the fuel cell using the CH_4–CO_2 mixture as a fuel gas: the current density was 4 mA cm^{-2}.

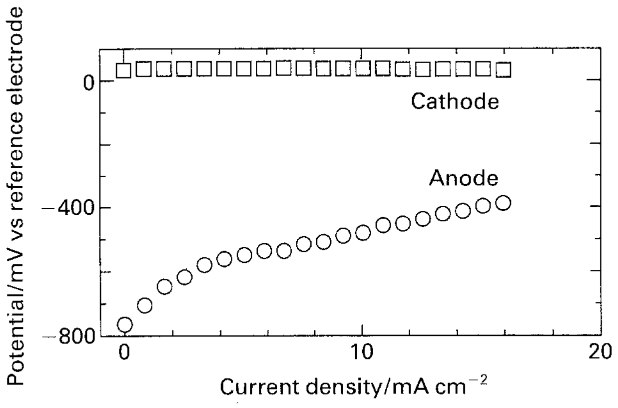

Fig. 5. Polarization characteristics (*IR* free) of nickel and platinum electrodes in the SOFC.

36.4%, respectively, suggesting that the reaction (Equation 1) was dominant. From the material balance of carbon before and after the reaction, it was found that coke deposited significantly.

The typical discharge performance is shown in Fig. 3. The relation between terminal voltage and current density was almost linear. In addition, the terminal voltage during the discharge of the cell did not deteriorate within 2 h, as shown in Fig. 4. These results mean that $SrZr_{0.9}Yb_{0.1}O_{3-\alpha}$ ceramic is applicable as a solid electrolyte for the present cell. However, due to the low conductivity of $SrZr_{0.9}Yb_{0.1}O_{3-\alpha}$ ceramic (7.7×10^{-3} S cm^{-1} at 1273 K) [11], the electric power is still low. Hence, it is necessary to reduce the thickness of the electrolyte further.

The overpotential of each electrode is shown in Fig. 5. The polarization at the cathode was very small, while that at the anode was rather large. This is probably due to carbon deposition, which inhibits the diffusion of hydrogen through the pores of the nickel electrode and thus depresses the rate of the electrode reaction. Hence, this reaction must be carried out using the reactant with an excess of CO_2 in which coking does not thermodynamically take place.

3.2. *Reforming of CH_4 with CO_2*

The membrane reactor was fabricated using $CaZr_{0.9}In_{0.1}O_{3-\alpha}$ ceramic tube as electrolyte diaphragm, as shown in Fig. 2(b). The CH_4–CO_2 mixture gas and argon were introduced to the nickel and platinum electrode compartments, respectively, at 1023 K. The conversions of both CH_4 and CO_2 were a few percent. Hydrogen, CO and water vapour were observed at the anode, but no product was detectable at the cathode. However, on applying direct current to the reaction cell, hydrogen was evolved at the cathode, as shown in Fig. 6(a). At low current densities, the rate of evolution of hydrogen was in agreement with the value calculated from Faraday's law, suggesting that the proton transport number was unity. However, at high current densities, the hydrogen evolution rate deviated from the theoretical value. This is probably due to either p or n-type electric conduction. These findings indicate that hydrogen is pumped electrochemically from the anode to the cathode.

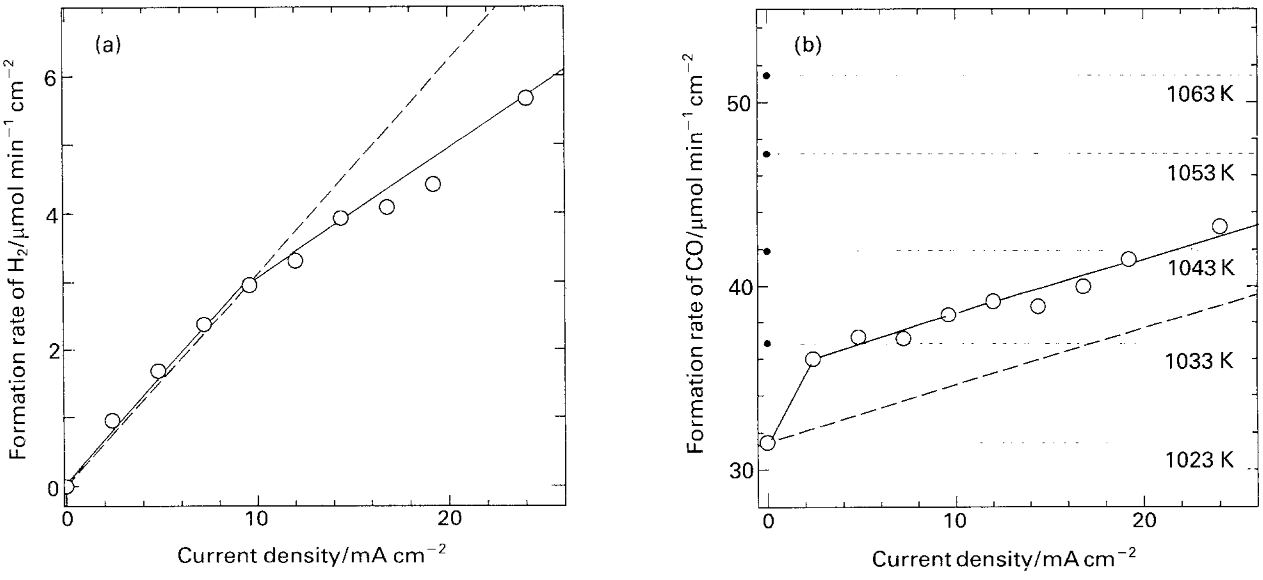

Fig. 6. Evolution rate of hydrogen at the cathode (a) and the formation rate of CO at the anode (b): the reaction temperature was 1023 K; the CH_4/CO_2 molar ratio was unity; the broken lines show the value calculated from Faraday's law.

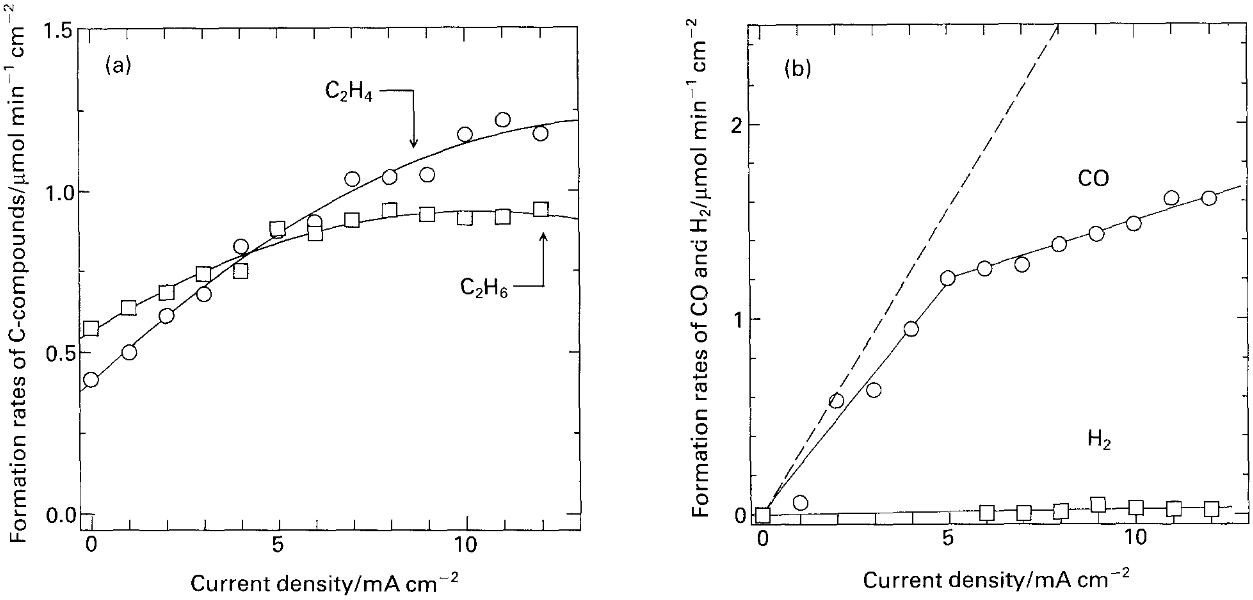

Fig. 7. Formation rate of C_2-hydrocarbons at the anode (a) and the formation rate of CO at the cathode (b): the reaction temperature was 1173 K; the broken line shows the value calculated from Faraday's law.

At the anode, the rate of formation of CO increased with increasing current density (Fig. 6(b)). The formation rate of CO at 24 mA cm^{-2} corresponded to the value under the open circuit condition at 1043 K. This means that the present cell can depress the reaction temperature by more than 20 K at 24 mA cm^{-2}. The resistive heating of the cell was found to raise the cell temperature experimentally by only 1.1 K at 24 mA cm^{-2}. This improvement is directly associated with the migration of hydrogen from the anode to the cathode.

As a mechanism for the activation of CO formation, it is considered that the electrochemical hydrogen pump shifts the equilibrium of the reaction (Equation 1) to the right. However, it should be noted that the formation rate of CO is larger than the faradaic value. This means that there is an additional effect on the activation of CO formation. On passing direct current through the cell, molecular or atomic hydrogen diffuses into the pores of the nickel electrode. This phenomenon may change the morphology of the electrode, for example, its pore volume. If so, the effective surface of the nickel metal increases and thus the CO formation is additionally enhanced.

3.3. *Oxidative coupling of CH_4 with CO_2*

CH_4 and CO_2 were introduced to the silver and platinum electrode compartments, respectively. Hydrogen, ethane, ethylene and a small deposition of coke were observed at the anode. The conversion of CH_4 was less than a few percent. On the other hand, no product was observed at the cathode.

On imposing direct current, the formation rates of C_2-hydrocarbons became progressively large as the current density increased, as shown in Fig. 7(a). This indicates that the dimerization of CH_4 is promoted by pumping hydrogen from the anode to the cathode. At the same time, CO was observed at the cathode, and its formation rate increased with increasing current density (Fig. 7(b)). Thus, CO_2 is reduced to CO with the pumped hydrogen. However, at high current densities, the increase in CO formation was small. Probably, either p or n-type electric conduction becomes dominant.

At less than 5 mA cm^{-2}, the current efficiencies for C_2 and CO-formations were 48.4 and 80.3%, respectively. This may be explained by the fact that hydrogen is produced at the anode, not only by the dimerization of CH_4, but also by coking. Hence, since both of these reactions are accelerated by the electrochemical hydrogen pump, the current efficiency for C_2-formation is low.

The oxidative coupling of CH_4 with CO_2 on PbO/MgO catalyst has been reported [7,8]. In this case, since the reaction (Equation 1) is accompanied as a side reaction, the selectivity to C_2-hydrocarbons is low. However, the present method excludes such a side reaction.

4. Conclusions

Three attempts have been made to recycle CO_2 effectively using a proton conductor as a solid electrolyte:

(i) The SOFC using a CH_4–CO_2 mixture as a fuel gas generates stable electric power. However, it is necessary to inhibit coking and reduce the resistance of the electrolyte further.

(ii) The electrochemical hydrogen pump effect makes it possible to accelerate the reforming of CH_4 with CO_2 so that the reaction temperature can be lowered by more than 20 K at 24 mA cm^{-2}.

(iii) The formation rate of both C_2-hydrocarbons and CO is raised by introducing CH_4 and CO_2 to the anode and cathode, respectively. In this case, the reforming of CH_4 with CO_2 does not occur as a side reaction.

References

[1] T. Sodesawa, A. Dobashi, and F. Nozaki, *React. Kinet. Catal. Lett.* **12** (1979) 107.

[2] Y. Sakai, H. Sato, T. Sodesawa, and F. Nozaki, *ibid* **24** (1984) 253.

[3] M. Masai, H. Kado, A. Miyake, S. Nishiyama, and S. Tsuruya, *Stud. Surf. Sci. Catal.* **36** (1988) 67.

[4] H. Iwahara, H. Uchida, and N. Maeda, *J. Power Sources* **7** (1982) 293.

[5] K. Kanamura, S. Yoshioka, and Z. Takehara, *J. Electrochem. Soc.* **138** (1991) 2165.

[6] T. Hibino, S. Hamakawa, and H. Iwahara, *Chem. Lett.* (1992) 1715; S. Hamakawa, T. Hibino, and H. Iwahara, *J. Electrochem. Soc.* **140** (1993) 459.

[7] K. Aika and T. Nishiyama, *J. Chem. Soc., Chem. Commun.* (1988) 70.

[8] K. Asami, T. Shikada, and K. Fujimoto, *Bull. Chem. Soc. Jpn.* **64** (1991) 266.

[9] P. Chiang, D. Eng. and M. Stoukides, *J. Electrochem. Soc.* **138** (1991) L11.

[10] L. S. Woldman and V. D. Sokolovskii, *Catal. Lett.* **8** (1991) 61.

[11] T. Yajima, H. Suzuki, T. Yogo and H. Iwahara, *Solid State Ionics* **51** (1992) 101.

[12] T. Yajima, H. Kazeoka, T. Yogo, and H. Iwahara, *ibid.* **47** (1991) 271.