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Performance of yttria-stabilized zirconia fuel cell using H_2–CO_2 gas system and CO–O_2 gas system

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ABSTRACT

This paper reports the performance of an yttria-stabilized zirconia fuel cell (YSZ) using five kinds of gas systems. The final target of this research is to establish the combined fuel cell systems which can produce a H_2 fuel and circulate CO_2 gas in the production process of electric power. A large electric power was measured in the H_2–O_2 gas system and the CO–O_2 gas system at 1073 K. The formation process of O^{2-} ions in the endothermic cathodic reaction ($1/2O_2+2e^- \rightarrow O^{2-}$) controlled the cell performance in both the gas systems. The electric power of the H_2–CO_2 gas system, which allowed to change CO_2 gas into a CO fuel ($H_2+CO_2 \rightarrow H_2O+CO$) in the cathode, was 1/31–1/11 of the maximum electric power for the H_2–O_2 gas system. This result is related to the larger endothermic energy for the formation of O^{2-} ions from CO_2 molecules at the cathode ($CO_2+2e^- \rightarrow CO+O^{2-}$) than from O_2 molecules. The CO–H_2O gas system and the H_2–H_2O gas system was expected to produce a H_2 fuel in the cathode ($CO+H_2O \rightarrow H_2+CO_2$, $H_2+H_2O \rightarrow H_2+H_2O$). Although relatively high OCV values (open circuit voltage) were measured in these gas systems, no electric power was measured. At this moment, it was difficult to apply H_2O vapor as an oxidant to the cathodic reaction in a YSZ fuel cell.

1. Introduction

The decrease in the CO_2 concentration in atmosphere is an important target to stop the global warming [1]. To overcome this situation, many renewable energies such as wind power, solar energy, water power, geothermal energy, tidal power, and biomass energy have been developed instead of fossil fuels. The above energies are converted to electric power or in the form of clean H_2 molecules. The produced H_2 molecules are supplied as a fuel to several types of fuel cells [2]. The conversion efficiency from a chemical energy of H_2 molecules to an electric power is closely related to the structures and materials of electrolyte, anode and cathode of a fuel cell [2]. On the other hand, the research on the circulation of CO_2 gas or energy development using CO_2 gas has been scarcely reported as compared with the papers and patents on a H_2 fuel [3–7].

In our previous papers, (1) the electrochemical reforming of biogas (60% CH_4–40% CO_2) to produce a H_2–CO mixed fuel ($CH_4+CO_2 \rightarrow 2H_2+2CO$) [8–11], (2) the electrochemical shift reaction of CO gas to produce a H_2 fuel ($CO+H_2O \rightarrow H_2+CO_2$) [12,13] and (3) electrochemical decomposition of CO gas into solid carbon and O_2 gas ($2CO \rightarrow 2C+O_2$) [14,15] were investigated to achieve a complete closed system (Eq. (1)) of H_2 production and CO_2 decomposition from a biogas. Eq. (1) shows the ideal combined chemical process and proceeds by the supply of an external electric power.

$$\text{Biogas } (3CH_4 + 2CO_2) + CO_2 \text{ (circulated)} + H_2O \rightarrow 7H_2 + CO_2 \text{ (circulated)} + 5C + 5/2O_2 \quad (1)$$

Our next challenge is to establish the combined fuel cell systems which produce both the electric power and a H_2 fuel during the decomposition process of CO_2. As a first stage of this strategy, we analyze 6 reactions for H_2 and CO fuels in Table 1. In a usual fuel cell, Eq. (2) for the H_2–O_2 gas system is applied to produce an electric power. Eq. (5) for the CO–O_2 gas system is also possible in a solid oxide fuel cell to produce an electric power. CO gas in Eq. (5) is formed from Eq. (3) for the H_2–CO_2 gas system, which can also produce an electric power during the formation process of H_2O and CO gas. Eq. (7) for the CO–H_2O system is an attractive reaction

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Table 1
Possible fuel–oxidant gas systems for fuel cell.

Fuel	Oxidant	Chemical reaction	
H_2	O_2	$H_2 + 1/2O_2 \rightarrow H_2O$	(2)
H_2	CO_2	$H_2 + CO_2 \rightarrow H_2O + CO$	(3)
H_2	H_2O	$H_2 + H_2O \rightarrow H_2O + H_2$	(4)
CO	O_2	$CO + 1/2O_2 \rightarrow CO_2$	(5)
CO	CO_2	$CO + CO_2 \rightarrow CO_2 + CO$	(6)
CO	H_2O	$CO + H_2O \rightarrow CO_2 + H_2$	(7)

[12,13] which creates a H_2 fuel during the production of an electric power. The produced CO_2 gas is supplied to Eq. (3) to change again into CO gas during the production process of an electric power. Eqs. (4) and (6) do not seem to proceed in a fuel cell. Although the standard Gibbs free energy change (ΔG°) of Eq. (4) or (6) is 0 kJ/mol, the ΔG value of Eq. (4) or (6) becomes a negative value by controlling the partial pressures of H_2, H_2O, CO and CO_2 gases in the anode and cathode of a fuel cell. When the activation energy required for the decomposition of H_2O and CO_2 molecules is sufficiently low, Eqs. (4) and (6) are the possible reaction systems producing an electric power.

Fig. 1 shows two types of the combined reaction systems for the production of a H_2 fuel and the circulation of CO_2 gas in the production process of electric power. The combined system A uses Eqs. (3) and (7) in Table 1. The two reactions can produce two types of electric power and the formed CO and H_2 gases are circulated between Eqs. (3) and (7) as a closed system. Another combined system B includes Eqs. (3) and (5), and can produce two types of electric power. The produced CO_2 gas is treated in a closed system. In the combined system B, a H_2 fuel produced in another process is to be supplied. As shown in Fig. 1, the combined system

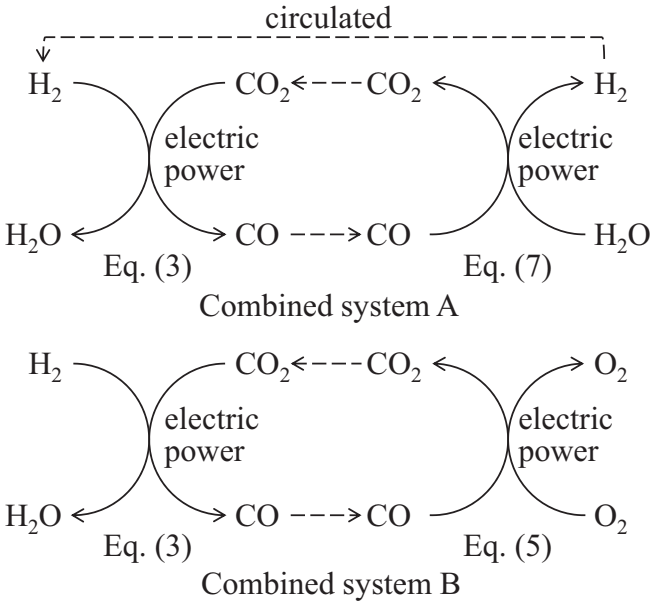

Fig. 1. Combined reaction systems for the production of a H_2 fuel and the circulation of CO_2 gas in the production process of electric power.

of possible chemical reactions produces electric power in addition to the useful chemical product which can be supplied as an active starting gas in the neighbor electric power generation process. The circulation of CO_2 gas in the above combined system provides an ideal solution for both the global warming and clean energy development. In this paper, the evaluation of electric power was experimentally studied using an yttria-stabilized zirconia cell (YSZ) for the basic reactions of Eqs. (2)–(5) and (7) in Table 1 at 1073 K.

2. Standard Gibbs free energy change

Fig. 2(a) shows the temperature dependence of the standard Gibbs free energy change of Eqs. (2), (3), (5) and (7) in Table 1. Eqs. (2) and (5) have the large negative ΔG° values in a wide temperature range of 273–1273 K. The corresponding emf (electromotive force, E°) is higher than 1 V ($E^\circ = -\Delta G^\circ/2F$, F: Faraday constant). These chemical reactions are used to produce a great

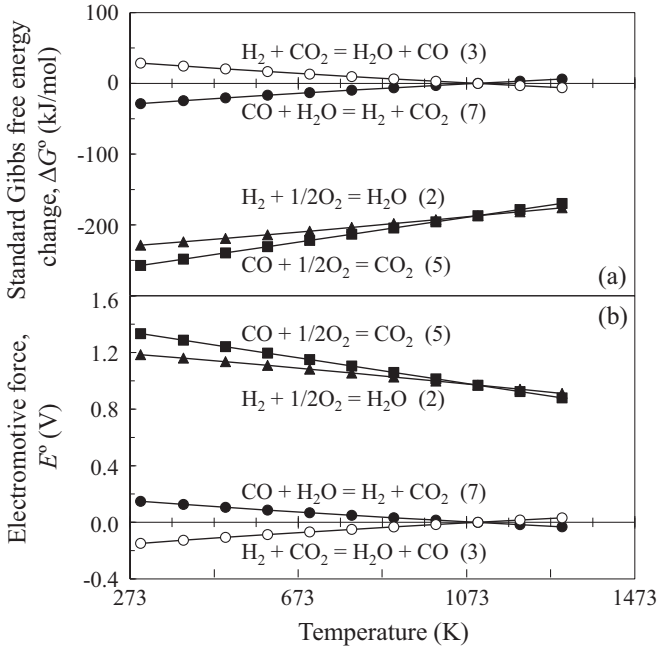

Fig. 2. (a) Standard Gibbs free energy change of Eqs. (2), (3), (5) and (7), and (b) the corresponding electromotive force (emf, E°).

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