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Electromotive Force for Solid Oxide Fuel Cells Using Biomass Produced Gas as Fuel

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The electromotive force (e.m.f.) of solid oxide fuel cells using biomass produced gas (BPG) as the fuels is calculated at 700-1,200 K using an in-house computer program, based on thermodynamic equilibrium analysis. Tour program also predicts the concentration of oxygen in the fuel chamber as well as the concentration of equilibrium species such as H_2, CO, CO_2 and CH_4. Compared with using hydrogen as a fuel, the e.m.f. for cells using BPG as the fuels is relative low and strongly influenced by carbon deposition. To remove carbon deposition, the optimum amount of H_2O to add is determined at various operating temperatures. Further the e.m.f. for cells based on yttria stabilized zirconia and doped ceria as electrolytes are compared. The study reveals that when using BPG as fuel, the depression of e.m.f. for a SOFC using doped ceria as electrolyte is relatively small when compared with that using Yttria stabilized zirconia.

Key words: Biomass produced gas, Electromotive force, Solid oxide fuel cells, Thermodynamic equilibrium

I. INTRODUCTION

Solid oxide fuel cells (SOFCs) have been developed rapidly in recent years due to their all-solid-state components, high efficiency, low pollution, and variety of fuels available. At cell operating temperature, any gaseous oxidable species can be fundamentally used as fuel. Thus various hydrocarbon fuels e.g. methane [1], *n*-butane [2], dimethyl ether [3] and methanol [4] have been tested in fueling SOFCs. It is generally accepted that using hydrocarbon fuels will make SOFCs more flexible and efficient than other fuel cell variants.

A biomass is a kind of organic material that has stored sunlight in the form of chemical energy. Through thermochemical, chemical or biochemical processes, a biomass can be converted to convenient solid, liquid, or gaseous fuels to meet a variety of energy needs. Biomass produced gas (BPG) comes from gasification, pyrolysis, or anaerobic digestion of a biomass [5]. BPG is a complex and variable mixture of hydrogen, carbon monoxide, methane, carbon dioxide, nitrogen and other gases. It is cheap and readily available and can be considered as an underexploited energy reserve. BPG is difficult to use in conventional power systems because of its low calorific capacity, which is neglected in electrochemical oxidation. It can therefore be considered a possible source of fuel for SOFCs. It has been demonstrated that gases with composition similar to BPG, such as synthesis gas and biogas, can produce significant power in SOFCs running at intermediate temperatures (<800 °C) [6,7].

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A SOFC is essentially an oxygen concentration cell where an electromotive force (e.m.f.) is produced due to the electrochemical potential gradient of oxygen between the anode and the cathode of the cell. When BPG is applied to SOFCs, the e.m.f. is determined by the gas composition in thermodynamic equilibrium on the anode side. The open circuit voltage (o.c.v.), determined by the e.m.f., is considered to be an important parameter of cell performance. Previous calculations were based on SOFCs using hydrogen or hydrocarbons as fuel [8,9]. The aim of this work is to calculate the e.m.f. for SOFCs using BPG as fuel. Gases produced by gasification of rice husks in a fluidized-bed reactor [10] and pine sawdust in a bubbling fluidized bed [11], respectively, are used as examples. The results reveal the optimal operational parameters such as gas composition, operational temperature, and steam-to-carbon ratios (S/C).

II. THEORY

The e.m.f. for SOFC using fluorite structure oxide as an electrolyte is given as the following equation [9]

$$E = \frac{RT}{F} \ln \frac{P_{O_2}^{*1/4} + P_{O_2}'^{1/4}}{P_{O_2}^{*1/4} + P_{O_2}''^{1/4}} \tag{1}$$

where F is the faradaic constant, R is the gas constant, T is the absolute temperature, P_{O_2}' and P_{O_2}'' are the oxygen partial pressures at the cathode and the anode, respectively, and $P_{O_2}^*$ corresponds to an oxygen partial pressure at which the ionic transference number of electrolyte becomes 0.5. In the ideal case of a pure ionic electrolyte, such as yttria stabilized zirconia

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(YSZ), Eq.(1) can be simplified as:

$$E = \frac{RT}{4F} \ln \frac{P'_{O_2}}{P''_{O_2}} \qquad (2)$$

which is the same as the formulation obtained from the Nernst equations.

The cathode is fed with pure oxygen, as typically done in a fuel cell, so P'_{O_2} is assumed to be 101 kPa. P''_{O_2}, oxygen partial pressure in the complex chemical system of BPG can be determined thermodynamically. The composition of a mixture at equilibrium is calculated by means of the so-called Gibbs free energy minimization method. The total Gibbs free energy of the system is expressed by

$$G(n_i) = \sum_1^k n_i \mu_i \qquad (3)$$

where n_i is the molars of species i, μ_i is the partial molar Gibbs free energy, and k is the species number. It is minimized with respect to n_i at constant temperature and pressure.

$$d(G_{\text{system}})_{T,P} = 0 \qquad (4)$$

There are many different algorithms to obtain a set of n_i that satisfies Eq.(4). Here Lagrange's method of undetermined multipliers is applied for the calculation. Based on the method we can construct a set of equations to solve n_i.

$$\mu_i + \sum_1^m \lambda_j a_{ji} = 0, \qquad \sum_1^m a_{ji} n_i - b_j = 0 \qquad (5)$$
$$(i = 1, 2, 3, \cdots, k; \quad j = 1, 2, 3, \cdots, m)$$

where a_{ji} is the amount of the atomic species j in the chemical formula of species i, b_j is the total molars of the atomic species j in the system, λ_j is the undetermined multiplier and m is the number of atomic species. The partial molar Gibbs free energy μ_i has two expressions for gas and solid, respectively:

$$\mu_{i(\text{gas})} = \mu^*_{i(T)} + RT \ln \left(\frac{n_i}{n_T} P \right) \qquad (6)$$
$$\mu_{i(\text{solid})} = \mu^*_{i(T)}$$

where $\mu^*_{i(T)}$ is the enthalpy of formation of pure species i at temperature T, and P is the standard pressure. $\mu^*_{i(T)}$ is calculated at different temperatures based on the basic thermodynamic data in Lange Handbook of Chemistry. For the convenience of solving this equation set, they are linearized by performing Taylor expansion. Newton iteration is then used to find a solution between temperatures of 700 and 1,200 K.

Because of strong reducing property of the BPG system, the oxygen partial pressure is quite low ($<10^{-13}$ kPa). So the five gas species H_2, CH_4, CO,

CO_2 and H_2O excepting oxygen and one solid species (graphite) which exist in noticeable amounts are selected for this calculation. The amounts of the mixture supplied to the anode are normalized to 1 mol. Finally, P_{O_2} is derived from the following chemical equilibrium:

$$2H_2 + O_2 = 2H_2O \qquad (7)$$
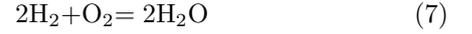
The calculations are carried out using the program developed with MATLAB® software in our laboratory.

III. RESULTS AND DISCUSSION

A. The e.m.f. for BPG SOFCs

In this section, the e.m.f for SOFC based on the YSZ electrolyte is calculated using gas produced in a fluidized-bed reactor in our lab [10], simplified as BPG-I. The e.m.f. is compared with those using humidified (3% H_2O) methane and hydrogen as fuels. The compositions of the fuels are listed in Table I.

TABLE I The composition (%) of biomass produced-gas [10,11] at the room temperature

	H_2	CH_4	CO	CO_2	H_2O	N_2
BPG-I	10.70	9.75	1.05	15.44	0	63.06
BPG-II	9.5	13.5	4.5	18	0	54.5

The mol numbers of the equilibrium species obtained from BPG-I at temperatures between 700 and 1,200 K are shown in Fig.1. It is clear that carbon deposition thermodynamically occurs below 900 K. The amount of graphite decreases with temperature. Above 900 K no graphite is thermodynamically formed. It should be noted that carbon deposition is also a function of starting composition. Figure 2 shows the oxygen partial pressure at various temperatures for BPG-I, humidified H_2 and humidified CH_4. The oxygen partial pressure in BPG-I increases with temperature from 10^{-28} kPa at
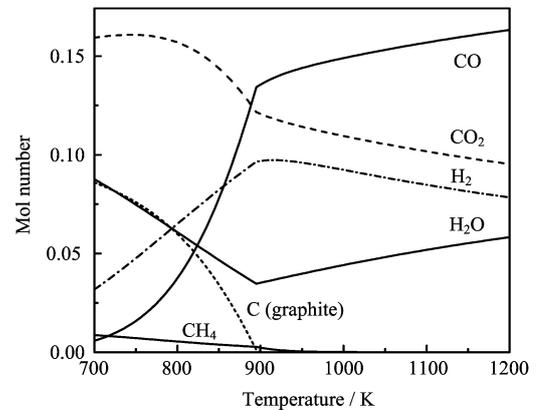

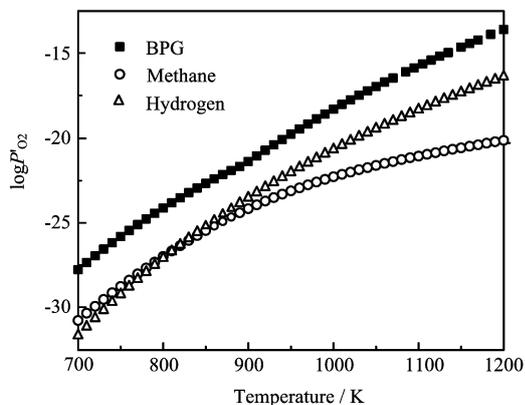FIG. 1 Equilibrium species for BPG-I at 700-1200 K.

FIG. 2 Variation of oxygen partial pressure with temperature for BPG-I, humidified CH_4 and humidified H_2.

700 K to 10^{-14} kPa at 1,200 K. It is much higher than that in the systems of humidified H_2 and CH_4. Figure 3 shows the temperature dependence of e.m.f. for SOFCs with BPG-I, humidified H_2 and humidified CH_4 as fuels. The e.m.f. at 700 K is 1.05, 1.16 and 1.19 V for cells with BPG-I, methane and hydrogen as fuels, respectively. It is shown that the e.m.f. for hydrogen and methane varies with temperature monotonically, while the e.m.f. for BPG-I increases from 1.05 V at 700 K to 1.065 V at 900 K, after which it decreases to 0.955 V at 1,200 K. The increase of e.m.f. with temperature is mainly due to the carbon deposition. Although the e.m.f. for BPG-I is approximately 0.1 V lower than that of hydrogen, it is higher than 1.0 V at temperatures below 900 K. This indicates that operating SOFCs with BPG-I is feasible.
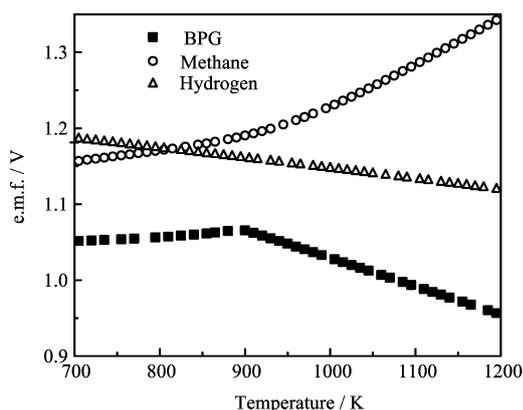

FIG. 3 Calculated e.m.f. for BPG-I, humidified CH_4 and humidified H_2 as a function of temperature.

B. Composition effect on e.m.f

The composition of BPG varies with the gasification condition and source of biomass. For example, gasification of pine sawdust in a bubbling fluidized bed is 4.5%CH_4, 13.5%CO, 18%CO_2 and 9.5%H_2 as reported

by Narvaez et al. [11], hereinafter referred to as BPG-II. The comparison of e.m.f. for cells with BPG-I and BPG-II as fuels is shown in Fig.4. It can be seen that their e.m.f. are almost equal below 900 K. However the e.m.f for BPG-II is higher than that for BPG-I by approximately 0.05 V above 1000 K, due to the higher methane and carbon monoxide content in BPG-II. The temperature, below which graphite is formed, is about 970 K for BPG-II, much higher than that for BPG-I, which consisted of gases with low carbon loading. It seems very likely that the temperature dependent behaviors of e.m.f. for different BPGs are similar.
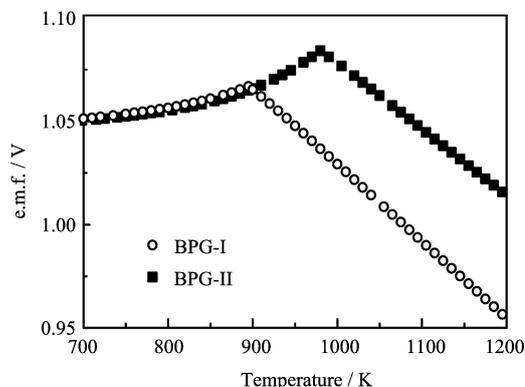

FIG. 4 Calculated e.m.f. for the two kinds of BPG as a function of temperature.

C. Humidification effect on e.m.f.

Under operating conditions an SOFC's fuel is usually moisturized for fuel reforming and stable operation. Figure 5 shows the e.m.f. for BPG-I with different stream content with 20% addition. The temperature related to the inflexion point in the plots and to carbon removal is coincident, and decreases from 900 K without H_2O addition to 700 K with increasing humidity. The e.m.f. at the temperature above inflection point decreases by approximately 0.05 V when the humidity increases to 20%. Therefore, from a thermodynamic
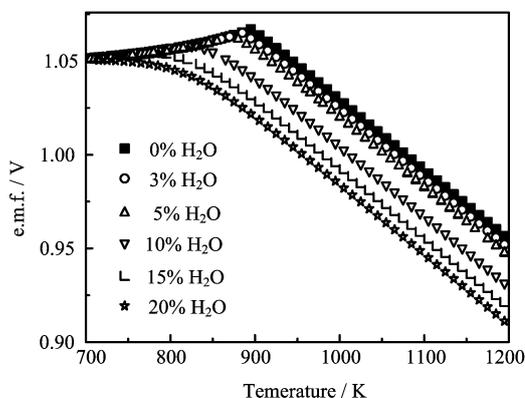

FIG. 5 E.m.f. as a function of temperature for the BPG mixed with H_2O in different percentage.

viewpoint, fuel humidification inhibits the carbon deposition, and depresses the e.m.f.. The optimum operating temperature and humidity can be roughly predicted by this calculation to be about 900 K and 5%H_2O.

D. Electrolyte effect on e.m.f.

YSZ, a pure anionic conductor over a wide range of oxygen partial pressures, is always used as an electrolyte for conventional high temperature SOFCs. Doped CeO_2, with higher conductivity than YSZ, is considered to be a potential electrolyte for SOFCs that operate at intermediate and low temperatures, although the presence of electronic conducting may cause depression of cell performance. In this section, e.m.f. for SOFCs using a doped CeO_2 electrolyte is compared with that using YSZ. In Eq.(1) $P_{O_2}^*$ of $(CeO_2)_{0.9}(Gd_2O_3)_{0.1}$ is determined from experimental results by the equation as follows [12]:

$$P_{O_2}^* = 1.25 \times 10^{12} \exp\left(\frac{-578}{RT}\right) \tag{8}$$

The e.m.f for SOFC using a mixed conductor as the electrolyte is calculated by Eq.(1) combined with Eq.(8).

The effect of electrolyte on e.m.f. for cells with humidified H_2 and BPG-I as fuels is shown in Fig.6. This result coincided with the experimental value measured in our lab [13]. The e.m.f. for SOFCs using hydrogen and BPG is quite different when the electrolyte is changed. The difference between the e.m.f for hydrogen and BPG operated on GDC (Gd doped CeO_2) based cells is much smaller than that of YSZ. At temperature above 800 K, the difference in e.m.f. can be neglected for the GDC based cell. The oxygen partial pressure P_{O_2}'' in BPG-I and humidified hydrogen is much lower than the critical value $P_{O_2}^*$ at temperatures above 800 K. For example, at 1,000 K, P_{O_2}'' in BPG-I and humidified hydrogen is 2.137×10^{-20} and 7.445×10^{-22} kPa respectively, but $P_{O_2}^*$ is 8.020×10^{-17} kPa. Eq.(1) can

be simplified as below:

$$E \approx \frac{RT}{4F} \ln \frac{1}{P_{O_2}^{*1/4}} \tag{9}$$

So the e.m.f. is not dependent on the fuel types but rather on $P_{O_2}^*$.

IV. CONCLUSION

The compositions in thermodynamic equilibrium of BPG systems between 700 and 1,200 K are calculated using Gibbs free energy minimization method. The e.m.f. of SOFCs using BPG as fuel is also derived. The e.m.f. of SOFCs using BFG as fuels is lower than that of those using hydrogen and methane as fuels, and is strongly influenced by carbon deposition. Humidification for BPG can prevent the formation of solid carbon however it lowers the e.m.f.. Through our calculations we selected BPG as a fuel for a SOFC, used a mixed conductor such as doped CeO_2 as an electrolyte, and made operation at a reduced temperature more feasible than what would be possible for a conventional SOFC.

V. ACKNOWLEDGMENT

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FIG. 6 e.m.f. as a function of temperature for YSZ and doped ceria as electrolyte.