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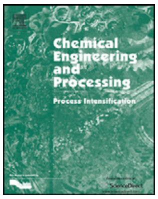

Performance of biogas-fed solid oxide fuel cell systems integrated with membrane module for CO_2 removal

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ABSTRACT

Two SOFC systems with CO_2 capture, i.e., SOFC with CO_2 capture from biogas feed (biogas-cap SOFC) and SOFC with CO_2 capture from reformed gas (reformed gas-cap SOFC) have been investigated. Employing the sweep gas to increase the gas separation capability, both systems offered higher power density but lower electrical efficiency than those of the SOFC without CO_2 capture (non-cap SOFC). The installation of a vacuum pump can improve the electrical efficiency of the biogas-cap SOFC but not for the reformed gas-cap SOFC. Economic analysis revealed that the biogas-cap SOFC with vacuum pump installation is superior to the other SOFC systems.

1. Introduction

In view of current and foreseeable energy shortage and environmental scenario, the exploitation of a renewable energy sources has attracted much attention in recent literature. Biogas is one of the renewable energy sources derived from the processing of the waste streams with variable nature, e.g., farm residues, industrial effluents and landfill. Compared to fossil fuel, biogas offers advantages of being renewable and free of non-methane hydrocarbon. A general problem found in the utilization of biogas for electricity generation is that most of biogas is derived from small-scale sources, e.g., farm and municipal wastes, therefore, biogas can only be employed in a small size power generator (5–100 kW) [1]. Furthermore, the biogas composition fluctuates markedly depending on its sources [2]; it generally contains methane (40–65%) and carbon dioxide (30–40%) with small amount of H_2S as an impurity.

The solid oxide fuel cell (SOFC) is a promising electricity generation technology owing to its high performance and environment friendly operation. SOFC fuelled by biogas can offer high efficiency (30–40%) even in small size power generations (<20 kW) [1]. Additionally, it can achieve reasonable performance even at low methane contents in biogas. Laboratory tests suggest that, the SOFC electrical efficiency drops only 5% when the methane contents in biogas diminish from 70 to 30 mol% [3]. Moreover, biogas can be internally reformed in SOFC stack due to the typical high stack temperature (1073–1273 K). However, if biogas is directly fed into the SOFC stack, carbon deposition can easily occur [4], in addition, a large temperature gradient is also a major problem for the SOFC stack fed directly by biogas due to a strong cooling effect caused by the fast reforming reaction [5,6]. A fuel processor is normally installed in the biogas-fuelled SOFC system to relieve these problems. Our recent work has shown that the addition of excess steam, CO_2 or air can inhibit the carbon formation in the fuel processor [7]. The use of steam as the reforming agent in the fuel processor (steam reforming) offers higher performance for SOFC system compared with the use of air (partial oxidation) [8]. Nevertheless, with an increase in CO_2 content in biogas, the H_2 yield of the pre-reformer reduces due to the reaction between CO_2 and H_2 generated from the steam reforming reaction via Reverse water gas shift reaction, RWGS. The decrease in H_2 concentration in the reformed gas can diminish the power density and the investment cost also increase due to the enlargement in the SOFC stack size [9]. Furthermore, the presence of large amounts of CO_2 in the pre-reforming product can decrease the cell potential. Suwanwarangkul et al. [10] studied the performance of SOFC fuelled by the mixture of H_2 and CO_2 gases with several H_2/CO_2 ratios. They reported that when H_2 concentra-

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tion decreases from 100 to 20%, the SOFC cell potential decreases by 20% due to the impact of the RWGS reaction. Hence, the separation of CO_2 from the biogas feed or from the reformed gas is the interesting way to increase the biogas-fuelled SOFC system performance.

Currently, there are various available CO_2 separation technologies, e.g., chemical absorption, adsorption and membrane technology. Membrane technology has been widely tested and presently applicable in the capture of CO_2 in natural gas [11]. Compared with CO_2 absorption technology which is conventionally used, membrane technology offers the advantages of operational flexibility in handling feed streams with variable flow rates and compositions. Polymeric membrane is one of the interesting choices due to its low capital investment costs compared with other types of membrane [12]. Moreover, the process equipment for the polymeric membrane operation is also simple and easy to handle. Selection of polymeric membrane for gas separation is based on two parameters; permeability and permselectivity. Polyimide membrane is the more attractive gas separator because it offers higher permselectivity and permeability compared to membranes derived from other polymers [13]. The use of capillary module with polyimide membrane for the CH_4 enrichment in biogas mixtures (CH_4, CO_2 and H_2S) was also investigated and the results showed that CH_4 concentration in biogas increases from 55–85% up to 91–94.4% [14]. Poly(dimethylsiloxane) (PDMS) and poly(1-trimethylsilyl-1-propyne) (PTMSP) can be utilized in the separation of acid gases (CO_2 and H_2S) from syngas at room temperature due to their high CO_2/H_2 selectivity. Nonetheless, H_2 permeance increases at elevated temperature [15]. It should be noted that a common problem arising from the use of these polymeric membranes is the instability of the membranes at high operating temperature [16].

In the present study, an integration of a biogas-fuelled SOFC system and CO_2-selective membrane technology was investigated. The improvement in the SOFC power density following to the installation of CO_2-selective membrane was considered. Two configurations are applied in this study: (1) SOFC with the capture of CO_2 from the biogas feed (biogas-cap SOFC) and (2) SOFC with the capture of CO_2 from the reformed gas (reformed gas-cap SOFC). Furthermore, two available operation modes in the permeation side of membrane, i.e., the exploitation of sweep gas and the exploitation of vacuum pump were also investigated. Thermodynamic analysis was performed to evaluate the performance indicators (overall electrical efficiency and power density) of these configurations and operations and to compare them with those of the SOFC system without CO_2-selective membrane installation. Lastly, an economic analysis was employed to identify whether the CO_2-selective membrane should be installed into the SOFC system.

2. Modeling

2.1. Fuel processor

The key steps are the dry reforming (Eq. (1)) and the steam reforming (Eq. (2)) reactions.

$$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO \tag{1}$$

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO \tag{2}$$

Due to the high CO_2 concentration in biogas feed, the mildly endothermic reverse water gas shift reaction (RWGS) (Eq. (3)) also takes place in the fuel processor inhibiting the generation of hydrogen.

$$CO_2 + H_2 \leftrightarrow H_2O + CO \tag{3}$$

To simplify the calculations, the fuel processor is assumed to operate isothermally with the exit gas reaching equilibrium composition.

2.2. SOFC stack model

Electrochemical reactions taking place in the SOFC stack convert the chemical energy of the fuel directly to electricity. At the cathode section, oxygen is reduced to oxygen ions (Eq. (4)) which migrates through the solid electrolyte to react with the fuel (Eq. (5)) at the anode section. Only hydrogen is assumed to react electrochemically with oxygen ions since the H_2 electro-oxidation is much faster than the CO electro-oxidation [17] and the rate of WGS reaction is fast at high temperatures [18–20]. It is also assumed that methane remaining from the fuel processor is consumed via the steam reforming and that the anode gas compositions are always at their equilibrium along the cell length due to the fast kinetics particularly at high temperature of SOFC. It is noted that Ni-YSZ, YSZ and LSM-YSZ are chosen as the materials for the anode, electrolyte and cathode of the SOFC stack, respectively.

$$\tfrac{1}{2}O_2 + 2e^- \rightarrow O^{2-} \tag{4}$$

$$H_2 + 2O^{2-} \rightarrow H_2O + 2e^- \tag{5}$$

The open circuit voltage (E) of the cell can be calculated from the following Nernst equation:

$$E = E^0 + \frac{RT}{2F} \ln\left(\frac{P_{H_2} P_{O_2}^{1/2}}{P_{H_2O}}\right) \tag{6}$$

The voltage (V) (Eq. (7)) is always less than the open circuit voltage (E) due to the existence of various losses; i.e., ohmic loss (η_{ohm}), activation loss (η_{act}) and concentration loss (η_{Conc}).

$$V = E - \eta_{\text{ohm}} - \eta_{\text{act}} - \eta_{\text{Conc}} \tag{7}$$

2.2.1. Ohmic loss (η_{Ohm})

The ohmic loss is the resistance to flow of electron through the electrodes and the interconnectors as well as resistance to the flow of ions through electrolyte. This voltage drop is the vital one in all types of cells and is linearly proportional to current density (i). It also varies with the electrical conductivity (σ) as expressed in Eq. (8). Due to the higher electrical conductivity of the electrodes and interconnectors compared to the electrolyte, only ohmic loss in the electrolyte is considered. The electrical conductivity increases with the cell operating temperature as expressed in Eq. (9) [21].

$$\eta_{\text{ohmic}} = \frac{iL}{\sigma} \tag{8}$$

$$\text{where} \quad \sigma = 3.34 \times 10^4 \exp\left(-\frac{10300}{T}\right) \tag{9}$$

It should be noted that although the ohmic loss in current collector could be high depending on type of material used, it is assumed negligible in this study.

2.2.2. Activation loss (η_{Act})

Activation loss is controlled by the kinetics at the electrode surface. For SOFC, due to the high temperature, the electrode reaction rate is fast, resulting in low activation polarization. The activation loss in electrodes can be expressed by the Butler–Volmer equation,

$$i = i_0 \left[\exp\left(\frac{\alpha z F \eta_{\text{act}}}{RT}\right) - \exp\left(-\frac{(1-\alpha) z F \eta_{\text{act}}}{RT}\right)\right] \tag{10}$$