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Design and Analysis of HT-PEMFC Systems with Different Fuel Processors for Stationary Applications

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Abstract. Due to its high CO tolerance, the high-temperature polymer electrolyte membrane fuel cell (HT-PEMFC) has a simpler fuel processing than a low-temperature polymer electrolyte fuel cell (LT-PEMFC) system. In this study, a performance of the HT-PEMFC integrated with a glycerol steam reformer system with/without a water gas shift reactor is examined and compared with the LT-PEMFC system. The HT-PEMFC system shows good performance over the LT-PEMFC system at the operational condition of high current density condition (>6000 A/m^2). The presence of high CO concentration is the main problem of operation of HT-PEMFC system without the water gas shift reactor at high current density. At the same time, the LT-PEMFC suffers from CO poisoning and low oxygen concentration at high current density as well. Considering the system efficiency, the HT-PEMFC system with the water gas shift reactor in the glycerol processor shows the highest overall system efficiency.

Key words

HT-PEMFC, LT-PEMFC, System Efficiency, Glycerol Reforming

1. Introduction

Due to the need for clean energy and efficiency technology, many researchers have paid attention to study and develop fuel cells for electricity generation. The high current density, low operating temperature and rapid start up of a polymer electrolyte membrane fuel cell (PEMFC) make it the major, interesting fuel cell type for uses in transportation and stationary power generation.

In general, a conventional PEMFC, which is operated at temperatures below 100 ^{o}C, has a flooding problem especially at dry operating condition and requires pure hydrogen fuel with low CO content to avoid catalyst poisoning. To overcome some limitations of the low-temperature PEMFC (LT-PEMFC), a high-temperature PEMFC (HT-PEMFC) has been developed. Due to a lower CO coverage on the surface of a platinum catalyst at a operating temperature of the HT-PEMFC, it is possible to use directly the reformate gas from a fuel processor with simple purification processes. In the case of LT-PEMFC, the reformate gas obtained needs to be treated by water gas shift and preferential oxidation processes. As a result, the HT-PEMFC system is less complicate than the LT-PEMFC system.

At present, a reformate gas derived from fuel processors is the preferred fuel for PEMFC operation before hydrogen transport and storage are readily available. Among the various types of fuel, glycerol is considered a potential feedstock for producing hydrogen [1]. It is a by-product of biodiesel process via the transesterification of vegetable oil and alcohol. The use of glycerol to produce high-value added products can also reduce the biodiesel production cost.

In general, a design task for fuel cell systems depends on their applications and desired efficiency. This study focuses on the development of a HT-PEMFC system for a stationary power generation. The efficiency of the HT-PEMFC system with different fuel processors is investigated and compared with a LT-PEMFC system. The HT-PEMFC system considered here can be divided into two cases. The first one involves the HT-PEMFC and a glycerol reformer without a CO removal process, whereas in the second one, a water gas shift reactor is included in the HT-PEMFC system to further improve its overall system efficiency. To examine the performance and efficiency of LT-PEMFC and HT-PEMFC system, reformate gas from glycerol fuel processor is used as fuel and the effect of CO poisoning is also incorporated in the simulation model of PEMFCs.

2. PEMFC Systems for Stationary Applications

A fuel steam reforming (SR) is regarded as a suitable process to produce hydrogen in the stationary application of fuel cells because it provides high hydrogen yield. In addition, for this fuel cell application, size and weight of the system seem to be not a critical issue. However, the heat integration of a fuel processor and a fuel cell is preferred to enhance the overall efficiency of stationary power systems. As shown in Fig. 1 (a)-(c), the unreacted hydrogen and oxygen from the anode and cathode sides of HT-PEMFC and LT-PEMFC are sent to a burner to supply heat for a glycerol steam reforming.

Due to a high CO tolerance of HT-PEMFCs, it is possible to use the reformate gas obtained directly from the glycerol reformer without the requirement of CO removal processes. This process system is presented in Fig. 1(a). Generally, to increase hydrogen yield in endothermic steam reforming processes, high reforming temperature and excess steam feed are required. However, the content of CO increases with increasing the reforming temperatures. With the aim at direct use of the reformate gas, the operating temperature of the steam reformer needs to be reduced to satisfy the operational constrain of the HT-PEMFC, while excess steam is still required to shift the equilibrium of the steam reforming reaction toward the product side. However, this causes the higher requirement of energy to preheat excess steam, which is necessary to enhance the hydrogen yield at the low-temperature operation of the reformer. To improve the HT-PEMFC performance, the fuel processing subsystem, i.e., a water gas shift reactor (WGS), is added to the steam reformer (Fig. 1(b)) to maximize the hydrogen content and eliminate CO before being fed to the HT-PEMFC. It should be noted that a large size of the water gas shift reactor is the main problem of PEMFC systems for automotive applications, but not for stationary applications.

For LT-PEMFCs, they are operated at low temperatures and requires the reformate fuel with less CO to avoid catalyst poisoning. The content of CO in a hydrogen feed for LT-PEMFC is limited to be less than 10 ppm. Therefore, both water gas shift and preferential oxidation (PROX) processes are added to the fuel reforming process for the LT-PEMFC system. Typically, the fuel processing system for LT-PEMFCs is demonstrated in Fig. 1(c). In the WGS reactor, CO is reduced and at the same time, more hydrogen is also generated. Nonetheless, the reformate gas obtained from this process still has CO exceeding the acceptable level of LT-PEMFC. Therefore, the reformate gas should be further treated by the PROX reactor to reduce the concentration of CO to a satisfactory level. However, the oxidation reaction occurred in this process is the cause of hydrogen loss and parasitic loss from a compressor for feeding air to the reactor.

Apart from the CO purification process, the main difference between the LT-PEMFC and HT-PEMFC systems involves the use of a humidifier unit. Due to the fact that HT-PEMFC can be operated at dry condition, the humidification is unnecessary for this type of PEMFC, but the reactant feed needs to be humidified in the case of LT-PEMFC to prevent drying out of a Nafion membrane. However, the humidifier can be removed from the anode side of LT-PEMFC when operated by using the reformate gas because the reformate gas from the reforming process is saturated with water.

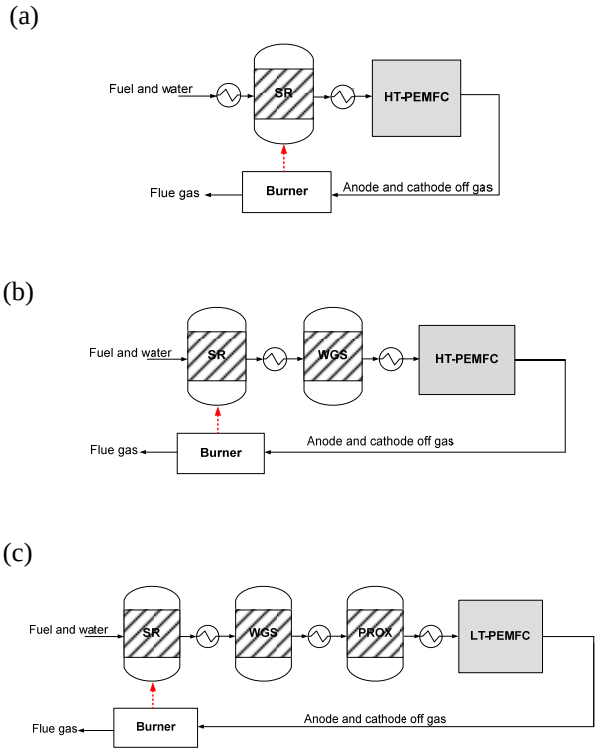


Fig. 1 PEMFC system integrated with a fuel processing process for stationary application: (a) HT-PEMFC with only a steam reformer (case 1), (b) HT-PEMFC with a steam reformer and a water gas shift reactor (case 2) and (c) LT-PEMFC with a steam reformer, a water gas shift reactor and a preferential oxidation reactor (case 3).

The target power output of both the LT-PEMFC and HT-PEMFC systems for stationary application is about 3 kW. The main purpose is to produce electricity for small household.

3. Modeling of PEMFC Systems

In this study, the thermodynamic model of a reforming process and the electrochemical model of PEMFCs are employed to investigate the performance and efficiency of combined glycerol fuel processor and PEMFC systems.

A. Fuel Processing

The equilibrium composition of a reformate gas obtained from the steam reforming of glycerol is calculated from the direct minimization of Gibbs free energy. The external heat used to maintain the glycerol reformer at isothermal condition is determined by considering the enthalpy change between reactants and products of the reformer when inlet and outlet temperatures are equal to the

reforming temperature. The WGS reactor is also modelled as an equilibrium reactor and its operating temperature is specified at 473.15 K. The reaction occurring in the WGS reactor involves a water gas shift reaction. For PROX process, the conversion reactor is chosen to model this reactor. It is operated at the oxygen to CO ratio of 1.5 and temperature of 423.15 K. The CO conversion is fixed at 95% [2] and the remaining oxygen will react with hydrogen. In addition, the sequentially two stages of the PROX reactor are applied, for this work, to reduce the CO concentration lower than 10 ppm in case of the LT-PEMFC system.

B. PEMFC

The basic relation of a fuel cell voltage and current density for PEMFCs is described by Eq. (1). The cell voltage (E_{cell}) can be calculated by subtracting the reversible cell potential (E_r), the maximum voltage that can be achieved by a fuel cell at specific operating condition, by various voltage losses.

$$E_{\text{cell}} = E_r - \eta_{\text{act,a}} - \eta_{\text{act,c}} - \eta_{\text{ohmic}} \quad (1)$$

where $\eta_{\text{act,a}}$ is the activation loss at the anode, $\eta_{\text{act,c}}$ is the activation loss at the cathode and η_{ohmic} is the ohmic loss.

The reversible cell potential is described by Nernst equation (Eq. (2)):

$$E_r = -\left(\frac{\Delta H_T}{nF} - \frac{T\Delta S_T}{nF}\right) + \frac{RT}{nF}\ln\left[\frac{(RT)^{1.5} C_{\text{H}_2-\text{Pt}} C_{\text{O}_2-\text{Pt}}^{0.5}}{a_{\text{H}_2\text{O}}}\right] \quad (2)$$

where $a_{\text{H}_2\text{O}}$ is the water activity defined by the ratio of water partial pressure to its saturation pressure.

It is noted that details of the model describing the voltage losses used in this study can be found in the references [3,4]. Due to the fact that the fuel used at the anode is a reformate gas from the fuel processor section, the effect of CO poisoning is included in the anode activation loss model of both the HT-PEMFC and LT-PEMFC. The CO poisoning model of LT-PEMFC, which is proposed by Bhatia et al. [5], is used in this work. For HT-PEMFC, the exchange current density of hydrogen oxidation in the presence of CO is i_0^{CO} instead of i_0 (for pure hydrogen). The i_0^{CO} can be calculated from CO coverage (θ_{CO}) assuming the bridge model of CO adsorption on Pt as follows:

$$i_0^{\text{CO}} = i_0\left(1 - \theta_{\text{CO}}\right)^2 \quad (3)$$

The CO coverage as given in Eq. (4) is developed from experimental data reported by Li et al. [6] to explain a CO poisoning effect on the HT-PEMFC in case of using the reformate gas containing high CO content (3-10%) and can be described as follows:

$$\theta_{\text{CO}} = a * \ln\frac{[\text{CO}]}{[\text{H}_2]} + b * \ln(i) * \ln\frac{[\text{CO}]}{[\text{H}_2]} + c \quad (4)$$

a = -0.00012784*T^2 + 0.11717499*T - 26.62908873

b = 0.0001416*T^2 - 0.12813608*T + 28.852463626

c = -0.00034886*T^2 + 0.31596903*T - 70.11693333

The power output of the fuel cell (P_{FC}) can be calculated from the current density (i) and E_{cell} as follows:

$$P_{\text{FC}} = i \cdot A \cdot n \cdot E_{\text{cell}} \quad (5)$$

where A is the cell active area and n is the number of cells. The required power for these two units, i.e., fuel processor and PEMFC, is taken into account for calculating the system efficiency. The efficiency of pump and compressor are specified at 0.7. The heat management in the integrated systems is carried out by using heat exchanger and burner. The heat from product streams of the reformer and the energy from anode and cathode off gases are recovered by heat exchanger and burner. The recovered heat will be utilized to preheat and vaporize water for the glycerol reformer as well as it will be used to maintain reaction temperature of reformer at isothermal operation.

C. System Efficiency

For stationary applications, a required energy for the reforming process is partially supplied by the heat recovered from the anode and cathode off gases. The system efficiency is calculated by Eq. (6).

$$\eta_{\text{sys}} = \frac{P_{\text{FC}} - P_{\text{parasitic}}}{\dot{m}_{\text{glycerol}} \cdot LHV_{\text{glycerol}} + Q_{\text{ref}} - Q_{\text{rec}}} \quad (6)$$

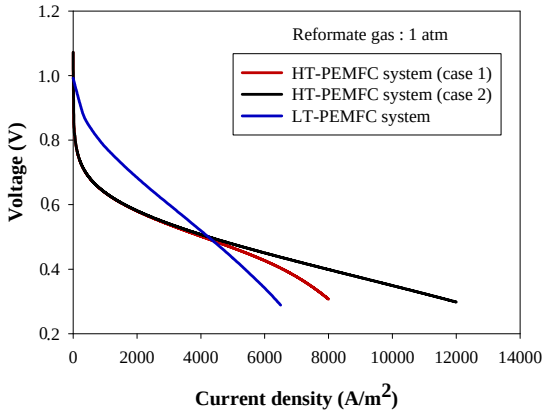
where $\dot{m}_{\text{glycerol}}$ is the molar flow rate of glycerol used for producing hydrogen, LHV_{glycerol} is the lower heating value of glycerol, Q_{ref} is the energy required for the steam reforming process accounting for the heat of vaporization, the sensible heat to heat up the reactants to the desired temperature and the heat needed for maintaining the reformer at an isothermal operation level, Q_{rec} is the heat recovered from the anode and cathode off gases as well as the high temperature product gas coming out from the glycerol reformer, $P_{\text{parasitic}}$ is the required power used in auxiliary units, namely, compressor and pump.

Furthermore, due to the fact that the fuel processor consumes water, while the fuel cell produces some, the water balance between recovered water from the fuel cell exhaust gas and the required water of reforming process is calculated in this work.

Table I Operating condition of reformer and PEMFC

System	S/C	Reformer Temperature (K)	Fuel Cell Temperature (K)
HT-PEMFC (case 1)	4	900	448.15
HT-PEMFC (case 2)	2	950	448.15
LT-PEMFC	2	950	353.15

(a)



(b)

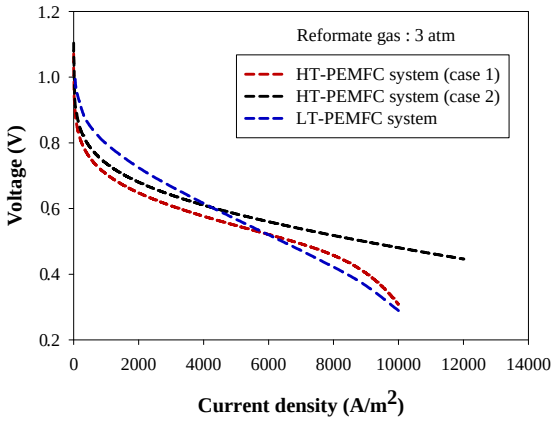


Fig. 2 Polarization curve of different PEMFC system at different pressure operations when reformate gas from a glycerol processor is fed to PEMFCs: (a) 1 atm and (b) 3 atm.

4. Results and Discussion

A. HT-PEMFC and LT-PEMFC Performance

The performance of HT-PEMFC and LT-PEMFC is studied by using a reformate gas from the glycerol steam reforming process as fuel. The reformate gas contains H_2, CO, CO_2, CH_4, H_2O and some trace of N_2 (in case of applying a PROX unit in the glycerol processing unit). The operating condition of the glycerol processor is chosen by considering the operational constraints (i.e., CO contamination) of HT-PEMFC and LT-PEMFC, as shown in Table I. The CO fraction coming from PROX in the glycerol processor at a desired condition is lower than 10 ppm in case of LT-PEMFC system. For HT-PEMFC system without the WGS reactor (case 1), the optimal condition of the reformer providing the highest system efficiency is used in this study when CO fraction is about 7%. Considering the HT-PEMFC system including the WGS reactor (case 2), the reformer condition that provides the CO fraction lower than 0.1% after the reformate gas is treated by the WGS reactor, is applied. It is observed that the hydrogen fraction in the anode feed for each PEMFC system is of the order: HT-PEMFC (case 2) > HT-PEMFC (case 1) > LT-PEMFC.

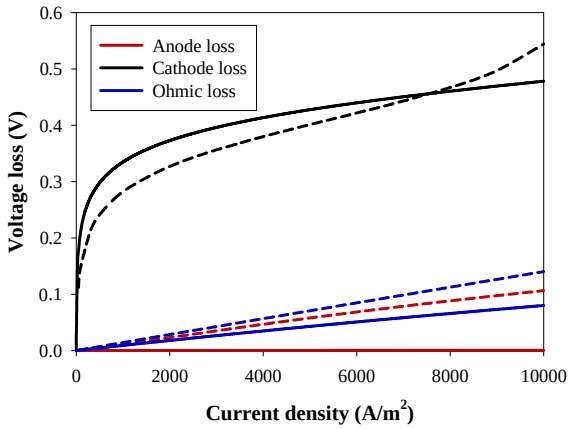


Fig. 3 Voltage losses in PEMFCs operated on a reformate gas (3 atm): HT-PEMFC system (case 2) (solid line) and LT-PEMFC (case 3) (dash line).

From the simulation results (Fig. 2), it is observed that when operated at pressure of 1 atm, the HT-PEMFC system without a WGS reactor (case 1) has the same performance as that with the WGS reactor (case 2) at a low current density operation. However, the performance of the HT-PEMFC without a WGS reactor drops at high current density because the high CO concentration in reformate gas enlarge CO poisoning effect at high current density. For LT-PEMFC system, the higher performance is obtained at current density < 4000 A/m^2 but the performance becomes drop after that point. Considering the operation of PEMFC systems at high pressure (3 atm), the HT-PEMFC with a WGS reactor shows the highest performance at high current density whereas LT-PEMFC system gives the lowest performance. The obtained low performance of the LT-PEMFC system at low and high pressure operations results from CO effect and oxygen starvation on anode and cathode activation loss, especially at high current density which is shown in Fig.3. In this figure, the individual voltage loss occurred in HT-PEMFC and LT-PEMFC operated on the reformate gas is given. It is found that the anode of LT-PEMFC is higher than that of HT-PEMFC, whereas the ohmic loss and cathode activation losses in HT-PEMFC are slightly more pronounced. However, the cathode activation loss of LT-PEMFC seems to be more than HT-PEMFC at high current density. This may be because a large amount of CO which reduce active site of Pt catalyst and low oxygen concentration at the catalyst layer. This can be explained that why the performance of HT-PEMFC is superior to LT-PEMFC at high current density.

B. Comparison of HT-PEMFC and LT-PEMFC System Efficiency

To compare the performance of HT-PEMFC and LT-PEMFC systems for small stationary application, the power output target is specified at 3 kW and the PEMFC systems is operated at pressure of 3 atm.

Table II System efficiency and water balance of PEMFC systems

Parameters	Full load	Partial load
Power (kW)	3	1.5
System efficiency (%)		
• HT-PEMFC system (case1)	27.55	30.96
• HT-PEMFC system (case2)	31.63	35.97
• LT-PEMFC system	28.43	34.73
Water balance (mole/s)		
• HT-PEMFC system (case1)	0.0074	0.0033
• HT-PEMFC system (case2)	0.0099	0.0043
• LT-PEMFC system	0.0128	0.0052

The efficiency of LT-PEMFC and HT-PEMFC systems is investigated at the same power output (3 kW) and voltage (0.65 V). The main purpose of developing LT-PEMFC and HT-PEMFC systems is to generate electricity for the small household application, which requires high system efficiency without having more regard for weight and size of the system. The system efficiency of individual integrated PEMFC system at full and partial loads is shown in Table II. It is found that the highest system efficiency is obtained by the HT-PEMFC system (case 2) in which the WGS reactor is employed to improve the quality of the reformate gas. The HT-PEMFC system (case 1) without the WGS reactor provides the efficiency lower than the HT-PEMFC system (case 2) and the LT-PEMFC system (case 3). This is due to its operation needs a higher steam to carbon ratio to reduce the fraction of CO in the reformate gas and thus, high energy is required to generate steam for this system. In addition, in the HT-PEMFC system (case 1), the reformate gas obtained from the glycerol processor contains a lower hydrogen fraction and a higher CO fraction, compared to the HT-PEMFC system (case 2). The high CO fraction results in a large anode activation loss. It is also found that the partial load condition of the PEMFC system provides higher efficiency than the full load condition. This is because the fuel cell is operated at higher voltage at partial load compared to full load and therefore the losses occurring at partial load are lower. In addition, the water balance of all the systems show a positive value that means a water recovery from the PEMFC system is high enough to support the amount of water required for the reformer and humidifier (in the case of LT-PEMFC system).

5. Conclusions

The system efficiency of HT-PEMFC systems with different fuel processors for small stationary application is investigated and compared with a LT-PEMFC system when the target power output of both the LT-PEMFC and HT-PEMFC systems is about 3 kW. The HT-PEMFC system integrated a glycerol reformer with/without a CO removal process using a water gas shift reactor is considered. The HT-PEMFC system with/without the water gas shift reactor provides higher performance than the LT-PEMFC system when a reformate gas from the glycerol processing section is used as a fuel and the fuel cell is operated at the current density of higher 6000 W/m^2. Considering the system efficiency, it is found that HT-PEMFC system with the water gas shift reactor shows the highest value, followed by the LT-PEMFC system and the HT-PEMFC system without the water gas shift reactor. The highest efficiency which is obtained from HT-PEMFC system is approximately 32% and 36% at full load and partial load conditions, respectively.

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