Reforming of Dimethyl Ether to Hydrogen-Rich Gas for HT PEM Fuel Cells

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Experimental results on the performance of the catalysts for DME steam reforming (DME SR) to hydrogen-rich gas and on HT PEMFC operation with pure hydrogen and reformate gas have been analyzed. Electric efficiency of the DME fuelled HT PEM FC system has been estimated. It has been found that expected electric efficiency of the system equals 38 – 41.5% (LHV).

1. Introduction

In recent years, the development of power plants on the base of various type fuel cells fed by hydrogen-rich gas has been attracting much attention. The hydrogen-rich gas for fuel cell feeding is produced by catalytic conversion of hydrocarbons – benzene, methane, ethanol, methanol, dimethyl ether (DME), etc. Among these hydrocarbons, conversion of DME and methanol to hydrogen-rich gas proceeds with the best performance and selectivity at low temperatures (250-300°C). Direct synthesis of DME is more profitable, than methanol synthesis (Shikada et al., 1998). Physicochemical characteristics of DME are similar to those of LPG; DME is safe for transportation and storage (Dybjaer et al., 1997). Besides, DME seems to be a promising diesel fuel alternative (Fleisch et al., 1997) that will obviously lead to stimulation of respective infrastructure. Hydrogen-rich gas produced by DME steam reforming (Galvita et al., 2001; Matsumoto et al., 2004; Mathew et al., 2005; Semelsberger et al., 2006; Kawabata et al., 2006) shows good promises for fuel cell and other applications. In the present paper, we report on the performance of the catalysts for DME steam reforming (DME SR) to hydrogen-rich gas, on HT PEMFC operation with pure hydrogen and reformate gas and on the calculation results of electric efficiency of DME fuelled HT PEM FC system.

2. DME SR to Hydrogen-Rich Gas

The most preferable way for hydrogen-rich gas production from DME is the reaction of catalytic steam reforming:

$$(CH_3)_2O + 3H_2O = 6H_2 + 2CO_2 \tag{1}$$

According to present-day understanding, the reaction proceeds by two-step scheme including DME hydration to methanol (reaction 2) and methanol SR to hydrogen-rich gas (reaction 3):

$$CH_3OCH_3 + H_2O = 2CH_3OH \tag{2}$$
$$CH_3OH + H_2O = CO_2 + 3H_2 \tag{3}$$

Besides, during DME SR carbon monoxide is formed by the reaction of CO_2 hydrogenation:

$$CO_2 + H_2 = CO + H_2O \tag{4}$$

DME hydration is known to proceed on the catalysts containing acidic centers, while methanol SR is catalyzed by copper-based systems. In this regard, two approaches to DME SR catalysts designing are used:
- mechanical mixing of a DME hydration catalyst and a methanol SR catalyst;
- synthesis of a bifunctional catalyst containing on its surface both acidic centers and copper-based centers.
Among the known DME SR catalysts, mechanical mixture of WO_x/ZrO_2 (DME hydration catalyst) and $CuZnAlO_x$ (methanol SR catalyst) (Badmaev et al., 2007a), as well as bifunctional $Cu-CeO_2/\gamma-Al_2O_3$ system (Badmaev et al., 2007b) are the most active and selective for hydrogen-rich gas production. Consider their catalytic performance. As an example, Fig. 1(a, b) demonstrates the effect of temperature on the product distribution over the optimal mechanically mixed $WO_x/ZrO_2 + CuZnAlO_x$ and bifunctional $Cu-CeO_2/\gamma-Al_2O_3$ catalysts. H_2, CO, CO_2 were the main reaction products. Methanol concentration in the whole temperature interval was insignificant ($\leq 10^{-2}$vol.%) at $T \geq 250°C$. Methane was observed only at $T \geq 350°C$; its concentration was below 1 vol.%. Fig. 1 presents also the equilibrium composition of the reaction products in DME SR. The equilibrium composition was calculated on the assumption that all three reactions (2, 3 and 4) proceed in the system.
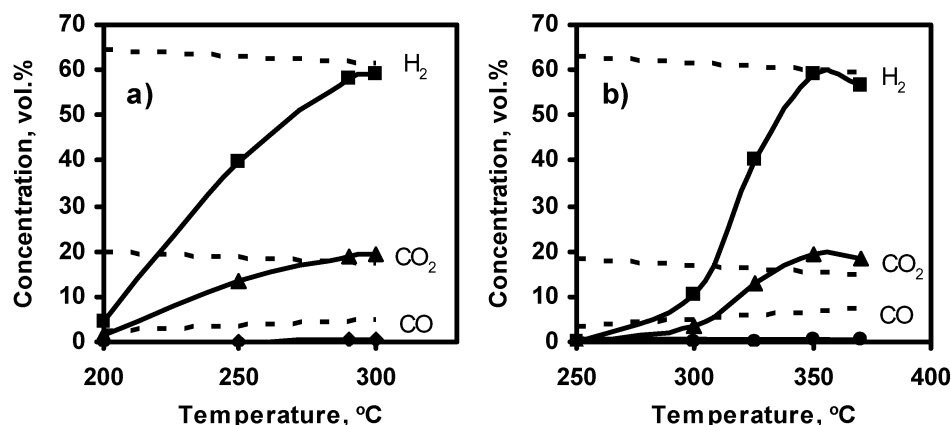
Fig. 1. Effect of temperature on the H_2, CO, CO_2 concentrations in DME SR over mechanically mixed WO_x/ZrO_2 + $CuZnAlO_x$ (a) and bifunctional $Cu-CeO_2/\gamma-Al_2O_3$ (b) catalysts. Experimental conditions: GHVS = 10000 h^{-1}, atmospheric pressure, feed composition: DME : H_2O : N_2 = 20:60:20 (vol.%). Solid lines – experiment; dotted lines – thermodynamic equilibrium values.

As Fig. 1 shows, the H_2, CO_2 and CO concentrations increase with temperature over both catalysts. At 300°C for mechanically mixed catalyst and at 350°C for bifunctional catalyst, the H_2 concentration is close to the equilibrium value, while the CO_2 concentration exceeds the equilibrium value. The CO concentration over both catalysts in the whole temperature range was below equilibrium and equalled an insignificant value of ca. 0.5-0.7 vol.% at 300-350°C. This occurred most likely due to reaction 4 which did not attain equilibrium under the experimental conditions.

The results obtained prove WO_x/ZrO_2 + $CuZnAlO_x$ and $Cu-CeO_2/\gamma-Al_2O_3$ to be efficient catalysts for DME SR to hydrogen-rich gas with low CO content. With the use of diluent-free reaction mixtures, hydrogen productivity on these catalysts attains 0.25- 0.6 mol $H_2/(g \cdot h)$ at 300-350°C, atmospheric pressure and molar ratio $H_2O/DME \sim 3$. In this case, DME conversion reaches 100%, reformate gas (hydrogen-rich gas) contains up to ~70 vol.% H_2, less than 1 vol.% CO, the rest – steam and CO_2. That gas is quite acceptable for HT PEM FC feeding without humidifying and CO removal.

3. Performance of HT PEM FC stack

HT PEMFC is a relatively new type of fuel cells. Electrolyte in these fuel cells is a membrane made of thermostable polymer (polybenzimidazole) impregnated with phosphoric acid. Compared to conventional PEM FC, HT PEM FCs operate at a higher temperature (160-180°C) and show obvious advances (Calundann et al., 2006) – hydrogen-rich gas fed to the anode compartment of HT PEM FC needs neither humidifying nor CO cleanup. In particular, HT PEM FC can tolerate 1-3 vol.% CO in

the hydrogen-rich feed gas. The data presented in Fig. 2 confirm these advantages. Fig. 2 illustrates the performance of a 12-cell-HT PEM FC stack fed by pure hydrogen or reformate gas.
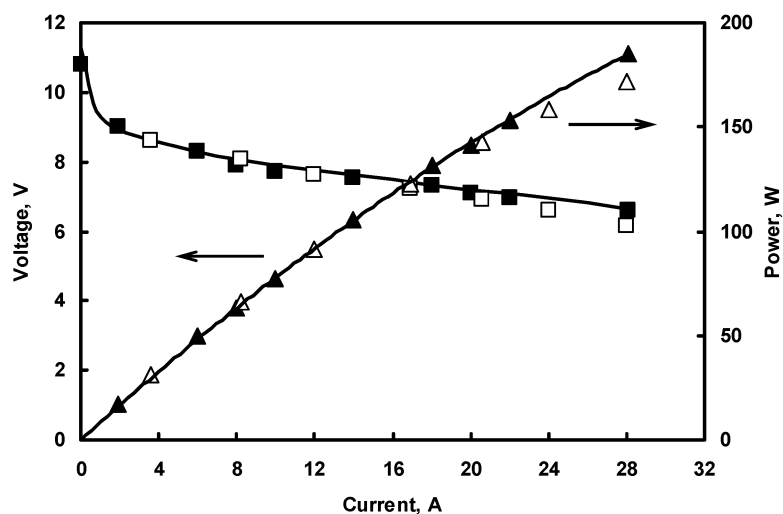

Fig. 2. Performance of 12-cell HT PEM FC stack with pure hydrogen (▲,■) and reformate (△,□) at 160°C and atmospheric pressure. Experimental conditions: cathode compartment - air flow rate 12 l/min; anode compartment - reformate (75 vol.% H_2, 1 vol.% CO, 24 vol.% CO_2) flow rate 5.0 l/min, pure hydrogen flow rate 3.5 l/min; no humidification.

The stack was manufactured by ZBT gGmbH (Duisburg, Germany) using PEMEAS GmbH (Frankfurt, Germany) Celtec®-P100 MEAs. Active surface of each MEA was 50 cm^2. It is seen that with both fuels – pure hydrogen or reformate gas containing ~1 vol.% CO – the stack demonstrated practically the same performance.

In general, the above results suggest that in the DME fuelled HT PEM FC design both water management and CO cleanup systems can be neglected that would obviously simplify the system and reduce its cost, as compared to conventional PEM FC systems. In this regard, it seemed reasonable to estimate an electric efficiency of the DME fuelled HT PEM FC system.

4. Electric efficiency of DME fuelled HT PEM FC system

Fig. 3 shows principle scheme of the DME fuelled HT PEM FC system. It includes the DME, water and air supply systems, four heat-exchangers (HE), HT PEM FC stack and a heat-coupled DME SR reactor.
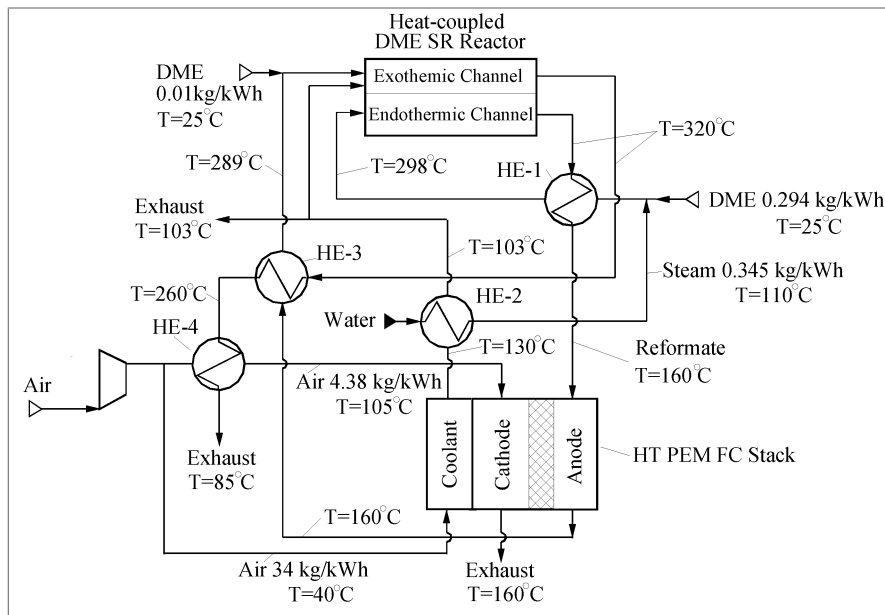
Fig. 3. Schematic diagram of a DME fuelled HT PEM FC system.

The heat-coupled reactor comprises exothermic and endothermic channels involved into intensive heat contact. Endothermic catalytic DME SR reaction proceeds in the endothermic channels. Catalytic combustion of DME and outlet anode gas from HT PEM FC stack proceeds in the exothermic channels.

Reformate (hydrogen-rich gas) is supplied to the HT PEM FC anode compartment; air – to the cathode compartment. HT PEM FC stack is cooled by air.

Analysis of the scheme of DME fuelled HT PEM FC system (Fig. 3), i.e. estimation of the system electric efficiency was performed on the following assumptions.

i) DME SR reactor operates at atmospheric pressure, temperature of 320°C, molar ratio $H_2O/DME\sim3$. Under these conditions, in accordance with the data reported in Section 2, the reactor produces reformate (hydrogen-rich gas) containing ~1 vol.% CO.

ii) HT PEM FC stack operates at atmospheric pressure, temperature of 160°C, hydrogen (reformate) utilization efficiency ≤80%; oxygen (air) utilization efficiency ≤50%. Calculation of the electric power generated by HT PEM FC stack based on the current-voltage characteristics presented in Fig. 2.

iii) Electric efficiency of the system was calculated by equation:

$$\eta = \frac{W}{\Delta H},$$

where W – generated electric power; ΔH – lower heating value (LHV) of DME consumed for the electric power generation.

It was found that as the HT PEM FC stack power ranges 50-70% of the maximum value, the system electric efficiency equals 38-41.5%

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