



A self-sustained, complete and miniaturized methanol fuel processor for proton exchange membrane fuel cell



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HIGHLIGHTS

- A self-sustained, complete and miniaturized methanol fuel processor was developed.
- The fuel processor can start up in 10 min at RT without any external heating.
- A H_2 production rate of $1 \text{ m}^3 \text{ h}^{-1}$ with CO content below 25 ppm was achieved.
- The thermal efficiency of whole processor can reach above 86%.

GRAPHICAL ABSTRACT



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ABSTRACT

A self-sustained, complete and miniaturized methanol fuel processor has been developed based on modular integration and microreactor technology. The fuel processor is comprised of one methanol oxidative reformer, one methanol combustor and one two-stage CO preferential oxidation unit. Micro-channel heat exchanger is employed to recover heat from hot stream, miniaturize system size and thus achieve high energy utilization efficiency. By optimized thermal management and proper operation parameter control, the fuel processor can start up in 10 min at room temperature without external heating. A self-sustained state is achieved with H_2 production rate of $0.99 \text{ Nm}^3 \text{ h}^{-1}$ and extremely low CO content below 25 ppm. This amount of H_2 is sufficient to supply a 1 kW_e proton exchange membrane fuel cell. The corresponding thermal efficiency of whole processor is higher than 86%. The size and weight of the assembled reactors integrated with microchannel heat exchangers are 1.4 L and 5.3 kg, respectively, demonstrating a very compact construction of the fuel processor.

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1. Introduction

Proton exchange membrane fuel cell (PEMFC) is considered as one of the most promising fuel cell technologies due to its high energy density, instant power output and low emission [1,2]. It can be potentially used as portable and small-scale stationary power generator at a range of scales, acting as an alternative to secondary

batteries [3,4]. Unfortunately, PEMFC encounters many technical challenges that need to be solved in the commercial process, such as durability, cost and hydrogen storage and distribution. Conventionally, the most popular strategy for hydrogen storage is storing hydrogen in pressurized vessels. However, this method is not suitable for supplying hydrogen to PEMFC because of large volume, low energy density and particularly poor safety. Therefore, it is very necessary to develop new approaches for hydrogen storage which are matched to portable and small-scale stationary PEMFC. One of the practical solutions is on board/site hydrogen generation from hydrocarbons based on the fuel processor. Methanol is one of the

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most popular hydrocarbons due to its high H/C ratio, no C–C bond, low reforming temperature, easy storage and transportation, etc. Generally, there are three ways to generate hydrogen from methanol, including steam reforming, partial oxidation and oxidative reforming. In fact, methanol oxidative reforming, namely auto-thermal reforming, is a combination of steam reforming and partial oxidation. At a proper molar ratio of O₂ to CH₃OH, methanol oxidative reforming has a reaction enthalpy change of zero, and thus needs no external heating after the reaction temperature is reached [5]. Though the addition of O₂ results in a decrease in H₂ yield, it is beneficial for fast start-up and quick dynamic response of the methanol fuel processor. From a series of the open literatures dedicated to methanol fuel processor, methanol steam reforming and oxidative reforming are both widely employed to produce hydrogen, showing different advantages.

Generally, CO concentration in the reformat should be reduced below 50 ppm due to the poison effect of CO on the anode catalyst of PEMFC [6]. Therefore, a desired methanol fuel processor is composed of five components, including combustor, vaporizer, reformer, CO eliminator and heat exchanger. From the practical point of view, it is highly desirable to develop a fuel processor with compact volume, lightweight and high thermal efficiency. In order to fulfill the above goals, active catalyst development, system integration and miniaturization are the main challenges to be overcome. For catalyst development, numerous catalysts which can be classified as Cu, noble metal and metal oxide based catalysts have been developed, providing a solid foundation for the construction of methanol fuel processor [7–11]. For system integration and miniaturization, considerable efforts have been made in the past decades. Thereinto, microreactor technology offers the unlimited possibility for the size reduction of methanol fuel processor due to its high heat and mass transfer rate, large surface-to-volume ratio, and many other virtues resulting from its characteristic scale of submillimeter [12–14]. Park et al. developed a microchannel methanol processor which consisted of a vaporizer and steam reformer with the catalysts coated on the microchannels [15]. The processor powered by electric heaters had a dimension of 70 mm × 40 mm × 30 mm and generated hydrogen for power output of 15 W_e. Afterward, methanol combustor was employed to heat the vaporizer and reformer instead of external heaters [16]. Kim also developed a micro methanol reformer combined with a hydrogen combustor [17]. The production rate of hydrogen was 50 ml min⁻¹ with an average composition of 74.4% H₂, 24.36% CO₂ and 1.24% CO. Reuse et al. fabricated a two-pass reactor which was used to couple methanol steam reforming and total oxidation [18]. The axial temperature profiles of methanol steam reforming never exceeded 2.5 °C. Evidently, these works all demonstrated the superior advantages of microreactor technology in methanol fuel processor development. Nevertheless, these works all focused on single methanol reformer heated by methanol/hydrogen combustor, and did not pay attention to CO elimination and energy recovery, which were nearly mandatory for the practical applications.

Compared to the researches focusing on methanol reformer combined with combustor, the public literature devoting to a complete methanol fuel processor is relatively scarce. Holladay et al. demonstrated a sub-watt miniature fuel processor which consisted of two vaporizer/preheaters, a steam reformer, a heat exchanger and a methanation reactor [19]. The CO concentration was in some cases below 100 ppm with a thermal efficiency of 19%. Ogura et al. developed a multi-layered microchannel reactor integrated with a methanol combustor, a reformer, a CO remover and two vaporizers for a 2.5 W_e PEMFC system [20]. An external heater was needed to help the combustor start up. Men et al. developed a complete miniaturized electrically heated methanol fuel processing

system, which consisted of an evaporator, a reformer, and two-stage PrOx reactors [21]. The generated H₂-rich reformat with CO less than 20 ppm could sustain electrical power output of 20 W_e. Pan et al. developed a compact integrated methanol fuel processor based on plate-fin reactor, which included a combustor, a reformer, and a four-stage PrOx unit [22]. The fuel processor was capable of reforming 70 ml min⁻¹ mixture of methanol and water and reduced CO level down to 50 ppm. Although great efforts have been put in and big advances have been obtained so far, there is still plenty of room to improve the performance of methanol fuel processor in terms of size, start-up behavior, dynamic response, product distribution, thermal efficiency and stability, etc.

This paper demonstrated our efforts on the development and performance evaluation of a self-sustained, complete and miniaturized methanol fuel processor based on modular integration and microreactor technology. Design concept, thermal management, operation parameter control, start-up strategy and stability of the methanol fuel processor were discussed in detail.

2. Experimental

2.1. Catalyst preparation and performance evaluation of whole methanol fuel processor

Three types of monolithic catalysts for the methanol oxidative reforming, methanol combustion and CO preferential oxidation (CO PrOx) were prepared by washcoating with the respective self-developed catalysts. One was Pt/γ-Al₂O₃ for methanol combustion. The other two were ZnO–Cr₂O₃/CeO₂–ZrO₂/γ-Al₂O₃ for methanol oxidative reforming and Rh–K/γ-Al₂O₃ for CO PrOx, respectively. Details of the catalyst preparation can be found in previous studies [23,24]. These three catalysts were all prepared by the first washcoating of γ-Al₂O₃ over the ceramic monolith with 400 cells per square inch followed by the impregnation with the active components. Taking ZnO–Cr₂O₃/CeO₂–ZrO₂/γ-Al₂O₃ as an example, a typical catalyst preparation procedure described as follows. Firstly, γ-Al₂O₃ layer was wash-coated on the ceramic monolith as the supporting layer of the catalytic activity component. A slurry composed of γ-Al₂O₃ and deionized water was prepared via mechanically milling overnight. Then the slurry was placed in a container with enough depth which allowed the ceramic monolith to immerse in the slurry. The ceramic monolith was dipped into the slurry for several times, and the excess slurry was allowed to drain off. The coated ceramic monolith was dried at room temperature for 12 h and at 120 °C for 6 h, and calcined in air at 500 °C for 4 h. Subsequently, the ceramic monolith with γ-Al₂O₃ layer was impregnated by aqueous solution of Ce(NO₃)₃·6H₂O and Zr(NO₃)₄·5H₂O (CeO₂:ZrO₂ = 4:1 in weight ratio). The impregnated sample was then dried in air and calcined at 500 °C for 4 h. The calcined sample was further impregnated by Zn(NO₃)₂·6H₂O and Cr(NO₃)₃·9H₂O (ZnO:Cr₂O₃ = 4:1 in weight ratio). The ZnO–Cr₂O₃/CeO₂–ZrO₂/γ-Al₂O₃ monolithic catalyst was finally formed after calcined at 500 °C for 4 h. The weight ratios of ZnO–Cr₂O₃, CeO₂–ZrO₂, γ-Al₂O₃ layers in the catalyst samples were 6, 8 and 15%, respectively. The preparation of Rh–K/γ-Al₂O₃ and Pt/γ-Al₂O₃ monolithic catalysts followed the similar procedure.

In the performance evaluation of the whole methanol fuel processor, the catalytic reaction was initiated by introducing reactant feed regulated by respective mass flow controller and liquid pump. After catalytic reaction, the reactor effluent passed through a condenser with a mixture of ice and water to trap the unreacted methanol and water. The flow rate of the dry reformat was measured by a soap bubble flow meter. The dry reformat were analyzed by an on-line gas chromatograph (GC 4000A, Beijing East & West Analytical Instruments Inc) equipped with a thermal

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