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Effectiveness of heat-integrated methanol steam reformer and polymer electrolyte membrane fuel cell stack systems for portable applications

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HIGHLIGHTS

- A concept of compact, heat integrated system of PEMFC stack and methanol steam reformer (MSR) is proposed.
- Three separate systems are designed based on different types of PEMFC stacks.
- Proposed novel HT PEMFC (nHT PEMFC) stack operates at 255 °C which matches the MSR operating at 250 °C.
- Systems are compared using mass and energy balances model coupled to a physical model.
- Highest efficiency is attained by the system with nHT PEMFC stack operating at 255 °C.

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ABSTRACT

Efficiently combining proton exchange membrane fuel cell (PEMFC) stack with methanol steam reformer (MSR) into a small portable system is still quite a topical issue. Using methanol as a fuel in PEMFC stack includes a series of chemical processes where each proceeds at a unique temperature. In a combined MSR—PEMFC-stack system with integrated auxiliary fuel processors (vaporizer, catalytic combustor, etc.) the processes are both endothermic and exothermic hence their proper thermal integration can help raising the system efficiency. A concept of such fully integrated and compact system is proposed in this study. Three separate systems are designed based on different PEMFC stacks and MSR. Low-temperature (LT) and conventional high-temperature (cHT) PEMFC stack characteristics are based on available data from suppliers. Also, a novel high-temperature (nHT) PEMFC stack is proposed because its operating temperature coincides with that of MSR. A comparative study of modelled systems is performed using a mass and energy balances zero-dimensional model, which is interdependently coupled to a physical model based on finite element method (FEM). The results indicate that a system with nHT PEMFC stack is feasible and has the potential to reach higher system efficiencies than systems with LT or cHT PEMFC stacks.

1. Introduction

Although PEMFC technology is already quite mature a number of key obstacles still remain for their successful realization as a high-energy density standalone portable or stationary power sources. One of the major constraints for the PEMFCs is that they use hydrogen as a fuel which has a very low energy density per volume at conditions of standard ambient temperature and pressure (SATP). Therefore, pure hydrogen is stored either as gas at very high pressures (up to 800 bar) or as liquid at very low temperatures below −253 °C. Hydrogen is not a naturally occurring energy source on Earth; it is actually just an energy carrier and it has to be produced from other sources using various processes (e.g. electrolysis, gasification or reforming). As energy carrier methanol is also showing promise because at SATP, compared to hydrogen at 800 bar, it still has more than 2.6 times higher energy density per volume and is in liquid form which greatly facilitates its storage and transportation.

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Methanol as a fuel can be used in PEMFC directly in a so-called direct methanol fuel cell (DMFC) or it can be transformed into hydrogen rich gas using an on-site reformer. Although systems using DMFCs are simpler comparing to combined systems with methanol reformer and PEMFCs, far greater energy densities are archived with combined systems. Methanol steam reforming is more attractive than methanol auto-thermal reforming because of its higher attainable hydrogen concentration and smaller amount of carbon monoxide (CO) in the reformate stream. Unfortunately even a small amount of CO in the incoming stream presents a severe limitation for LT PEMFC. At operating temperatures around 80 °C CO tends to strongly adsorb onto the active sites of platinum (Pt) and thus poisons the catalyst. Cleaning processes like water-gas shift (WGS) and/or preferential oxidation (PROX) are needed to reduce the concentration of CO. Typical operating temperatures for PROX are somewhere between 100 and 200 °C although sometimes they are even outside this range [1]. There are several approaches to overcoming the CO poisoning of electrocatalysts [2]. With Pt–Ru catalyst around 10 ppm of CO can be tolerated in the stream [3] or with air-bleeding technique even up to 200 ppm [4].

The phenomenon of CO adsorption on Pt is far less pronounced at higher temperatures [5]. That is why cHT PEMFC based on polybenzimidazole (PBI) polymer doped with phosphoric acid (H_3PO_4) can still operate reasonably unaffected at temperatures above 160 °C and can tolerate up to several percent of CO in hydrogen rich gas stream. Several studies have confirmed that [6–8]; also datasheets from commercial suppliers are available [9,10]. Other advantages of cHT PEMFCs over LT PEMFCs are simplified water management because no humidification is necessary and during operation only water vapour is present in the system which eliminates the possibility of flooding the cathode channels. Heat is produced at a higher temperature level and can be used to preheat gases, vaporise water–methanol mixture or to produce hot water and/or steam in industrial or home applications.

Despite higher tolerance of cHT PEMFC to CO a major drawback is the adsorption of acid anions ($H_2PO_4^-$) on the active sites of the Pt catalyst [11]. In spite of higher temperatures this slows down the oxygen reduction reaction (ORR) kinetics more than in the case of LT PEMFC, hence, lower power density is achieved. Phosphoric acid is also highly soluble in water and can leach out from the membrane especially if the fuel cell is exposed to frequent start–stop cycles because liquid water can be present in the system. Its vapour pressure is highly temperature and concentration dependent [12] (e.g. at atmospheric pressure an 85% concentrated H_3PO_4 starts boiling at 158 °C while 100% concentrated H3PO4 at 261 °C). The lower temperature limit of cHT PEMFC is about 130 °C at which temperature water is in vapour phase. At temperatures higher than 155 °C an equilibrium is established between orthophosphoric acid and highly water-soluble pyrophosphoric acid:

$$2H_3PO_4 \leftrightarrow H_4P_2O_7 + H_2O \qquad (1)$$

At higher temperatures further condensation of phosphoric acid leads to polyphosphoric acid. Steady decline in conductivity at long-term operation of H_3PO_4/PBI membranes is explained in terms of influence of water concentration (activity) formed on cathode side, which leads to the hydrolysis of polyphosphoric acid and leaches out water-soluble orthophosphoric and pyrophosphoric acids. On the other side, at temperatures higher than 180 °C, the vapour pressure of phosphoric acid becomes prohibitively high, which again leads to losses of acid from the fuel cell [13].

The main challenge of every energy system is to recuperate heat available within the system to maximize its efficiency. Since some unit reactions in combined PEMFC systems are exothermic (catalytic combustion, PROX) and others endothermic (vaporisation,

MSR) the goal is to direct the heat from sources to sinks within the system (see also Fig. 1). The most obvious step that applies such action is the direct thermal coupling of the MSR and the HT PEMFC stack which can be done in two ways. One is to use existing, cHT PEMFCs and develop a new catalyst that would allow the MSR to operate at temperatures below 200 °C and still achieve near to 100% conversion rate of methanol. First results on development of LT MSR have already been published by a research group claiming to achieve 100% conversion at 195 °C [14,15]. The second way is the use of conventional catalyst in the MSR which enables to attain practically full conversion of methanol between 250 °C–300 °C. This however depends on the geometry, flow characteristics, catalysts loading, and steam-to-carbon ratio (S/C). Typically, conversions above 95% are achieved at 250 °C with $S/C \leq 2{:}1$ [16–20] while some researches also achieved 100% conversion with $S/C \leq 1.5{:}1$ [21,22]. Since all conventional PEMFCs operate at lower temperature as the MSR there is a need for development of nHT PEMFC that could operate at temperatures higher than 250 °C and consequently enable direct thermal coupling of the nHT PEMFC stack and the MSR. Some research efforts in this direction have been published recently with development of so-called solid acid fuel cell (SAFC) [23,24] although first publications on this topic date back several years ago [25–27].

There are researches devoted to thermal coupling of the catalytic combustor and the MSR [17,19,20,22]. One research even tried coupling the stack of cHT PEMFCs and the MSR [21]. Some studies on the integrated systems where all of fuel processing reactors are combined together in the system are available. There are numerical studies of such systems but they are more focused on the implementation [28] and dynamics [29,30] of the whole system. A related numerical study [31] on stationary integrated system for a small household with glycerol reforming process and PEMFC stack showed that a system with LT PEMFC stack has lower electric efficiency than the system with cHT PEMFC stack when a WGS process is used in both cases. If heat generated in the PEMFC stack is used to produce hot water at 50 °C for household usage the combined efficiencies of both systems are increased to 60%. More in-depth insight to the design of small compact systems was presented in Ref. [32] although the PEMFC stack was excluded from the analysis. Beside numerical calculations also an experimental system was constructed by the same authors in their previous work [33]. Concept and experimental data of compact, highly integrated system was presented in Refs. [34,35] although in experiments the stack of cHT PEMFCs was not thermally coupled to the fuel processing units. Another research group published the experimental
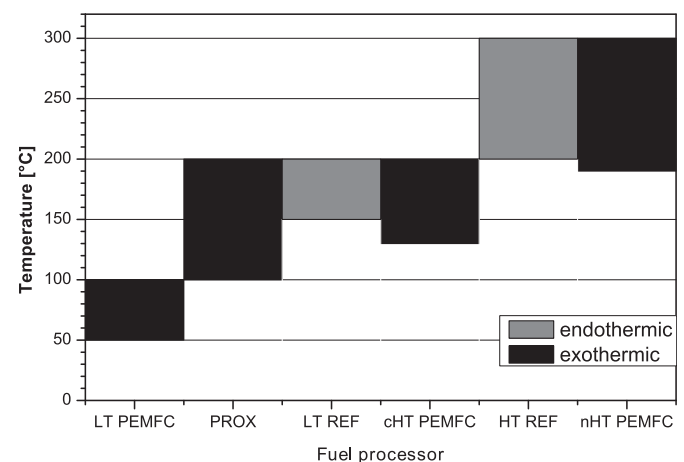

Fig. 1. Fuel processors sorted according to their operating temperature range.