



Modelling of a high-temperature polymer electrolyte membrane fuel cell integrated with a methanol steam reformer cell



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HIGHLIGHTS

- Development of 3D non-isothermal simulator of a combined MSR/HT-PEMFC unit.
- Implementation of CO poisoning model for HT-PEMFC and a mechanistic model for MSR.
- Performance and thermal sustainability evaluation of a combined MSR/HT-PEMFC unit.
- Proposal of a novel integrated MSR/HT-PEM stack with ten cells.

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ABSTRACT

A 3-dimensional non-isothermal simulator comprising a high temperature polymer electrolyte membrane fuel cell (HT-PEMFC) and a methanol steam-reforming cell (MSR-C) was developed in Fluent (Ansys™). The simulator takes into account most of the significant physical processes, including the electrochemical reactions and carbon monoxide poisoning effect on the electro-catalytic activity of the FC; it also considers the methanol steam reforming (MSR), water gas shift (WGS) and methanol decomposition (MD) reactions in the MSR-C. The developed model for the integrated MSR-C/HT-PEMFC unit was simulated between 443 K and 473 K and validated with experimental results reported in the literature, showing always a very good agreement. The thermal sustainability of the MSR-C/HT-PEMFC unit was assessed, and the role of the thermal insulation and air intake (cathode) stoichiometry in the thermal equilibrium of the device were analysed. A novel integrated MSR-C/HT-PEM stack with ten cells was proposed and simulated, showing a performance above the reported in the literature for similar devices. The results indicated that the proposed stack operates at currents between 4.5 A (0.1 A cm⁻²) and 54 A (1.2 A cm⁻²) without any external heat source. To minimize the degradation of the components the stack should adapt the operating temperature to the current density.

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1. Introduction

High temperature polymer electrolyte membrane fuel cells (HT-PEMFCs) operate at temperatures between 393 K and 453 K and can be directly fed with a methanol reformat stream without purification, due to its high tolerance to carbon monoxide (<3000 ppm) [1–3]. The great challenge of the HT-PEMFC devices is the heat recovery using a simple approach, avoiding heat exchangers, evaporators and chemical reactors [4]. A HT-PEMFC wastes ca. 50% of the input chemical energy in the form of heat, more energy than the required for fuel vaporization and MSR

reaction combined. To increase the energy efficiency, the thermal integration is mandatory. Several studies have been reported concerning the heat integration of HT-PEMFCs with *in-situ* hydrogen production systems, mostly focusing their attention to the thermal coupling with catalytic combustors and reformers [5–12]; where the heat losses to the environment are considered a critical factor to the overall efficiency of the system, mainly in the small scale applications [11,12]. The heat integration of a HT-PEMFC and a reformer operated at the same temperature (<473 K) was only considered by a few authors [13–17]. Pan et al. integrated a two-cell HT-PEMFC stack with a MSR, operating both devices at the same temperature, between 453 K and 473 K [13]. The results showed high voltage losses (160–200 mV) even at 473 K and low current densities, due to insufficient fuel supply from the reformer and

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the presence of residual methanol in the reformat stream. Avgouropoulos et al. incorporated the methanol reforming catalyst in the HT-PEMFC anodic compartment, naming this approach internal reforming methanol fuel cell (IRMFC) [14,15]. The results showed very low fuel cell performance due to insufficient fuel supply and catalyst poisoning by methanol. Nevertheless, Weng et al. using a two-stage temperature reformer integrated with a HT-PEMFC at 473 K obtained comparable results to a HT-PEMFC feed with pure hydrogen [17]. The first stage of the reformer was operated at 473 K using the heat release by the HT-PEMFC, while the second stage was operated at 513 K using a burner, running with the wasted hydrogen from the fuel cell. Compared to one-stage reformer, the two-stage reformer allowed higher methanol conversion and lower fluctuations in the reformat flow rate caused by the water/methanol evaporation. The authors reported recently a combined methanol steam reformer cell (MSR-C) and a HT-PEMFC, running at the same temperature, 453 K, and displaying rather high current densities ($>0.5 \text{ A cm}^{-2}$) [18,19]. To assemble the combined unit (MSR-C/HT-PEMFC) two novel bipolar plates were used, featuring the fuel cell flow field in one side and the reformer flow field in the other. In the first study a membrane electrode assembly (MEAs) based on pyridine type structure membrane from Advent TPS[®] [18] was used, while in the second study a MEA based on PBI phosphoric acid doped membrane from BASF [19] was used. The combined unit assembled with the MEA from BASF showed higher performance and long term stability than the MEA from Advent TPS[®]. Moreover, the performance of the combined unit assembled with the MEA from BASF was similar to the FC fed with pure hydrogen.

Several numerical studies simulating combined fuel cell/reformer units/combustors have been reported [4,20–22]. Sahlin et al. [4] investigated numerically and experimentally a 5 kW fuel cell system using a thermal fluid. The device used two separate circuits, where the heat was transferred between the reformer and the burner operating at high temperature and between the fuel cell and evaporator operating at low temperature. The authors obtained an efficiency of the system of 28–30%. Lotric et al. [23] used Aspen Plus[®] to study the thermal integration of all endothermic and exothermic processes present in a power supply based on PEMFC stack and a methanol reformer. The authors considered a low-temperature PEMFC (working at 343 K), a conventional high-temperature PEMFC (working at 453 K); in the latter case, the authors considered the presence of a novel nanocomposite polymer membrane with a water-insoluble solid proton conducting electrolyte operating at 528 K, matching the operating temperature of the reformer. The results indicate that operating both systems at the same temperature increases more than ten percentage points the overall efficiency. Moreover, operating at the same temperature increases the simplicity of the system and eliminates the need to burn methanol to heat up the system, which can produce dangerous exhaust gases such as formaldehyde and CO [24]. Avgouropoulos et al. [25] assessed experimentally and by simulation the concept of a 70 W IRMFC stack. The IRMFC stack was operated at 473 K; the maximum current density was rather low and stability of the combined unit was not assessed. Most of these numerical studies of combined HT-PEMFC/fuel processor units are one-dimension [20–23,25], modelling micro-combined heat and power (CHP) plants [4,20–23]. However, sophisticated numerical models of HT-PEMFCs based on PBI membrane doped with phosphoric acid are also available in the literature [26–36] and were summarized by Li et al. [26]. These models for HT-PEMFC focus on the effect of the cell design and operating conditions [27,28], the effect of temperature [29,30], the CO poisoning effect [31–33], the gas crossover through the membranes [34], the gas humidification [35],

mechanical and thermal stress-deformation [36] on the polarization curves of the HT-PEMFC. However, these sophisticated numerical models have never been applied to study the heat integration of HT-PEMFC and MSR.

In the present work the heat integration of a HT-PEMFC with a methanol steam reformer cell (MSR-C) was studied by simulation and validated with experimental data published by the authors [19]. The physical model considers an integrated unit (MSR-C/HT-PEMFC) using a novel bipolar plate designed to feature a fuel cell anode flow field in one side and the reformer flow field in the other. The mathematical model considers the electrochemical reactions at the anode and cathode catalyst layers, the temperature, the CO content in the anode fuel, the phosphoric acid doping level and the influence of the water content on the membrane proton conductivity. The CO poisoning model was based on the work developed by Springer et al. [37] and adapted to HT-PEMFC [31–33]. This model accounts for the electrochemical oxidation of CO, as well as the adsorption/desorption processes of CO and hydrogen on Pt catalyst surface. In the reformer, it was considered the kinetic model developed by Peppley et al. [38] and adapted by the authors for the commercial catalyst BASF RP60 [39]. The kinetic model is based on a Langmuir–Hinshelwood model with an overall reaction network comprising methanol steam reforming (MSR) reaction, reverse water-gas-shift (RWGS) and methanol decomposition (MD). The simulation results were analysed and validated based on the performance of the HT-PEMFC and MSR separated and combined. The effect of the reformat contaminants (CO, CO₂, CH₃OH and H₂O) and operating temperature on the performance of the MSR-C/HT-PEMFC combined unit was assessed. The thermal sustainability of the combined unit was also analysed, focusing on the level of thermal insulation and temperature control required for real applications. A MSR-C intercalated with a HT-PEMFC in a combined stack arrangement operating at similar temperature would simplify the heat integration and maximize the overall energy efficiency. Therefore, a novel integrated MSR-C/HT-PEM stack with ten cells is proposed; the simulations show that this stack can achieve high current densities (1.2 A cm^{-2}), above the reported in the literature for similar devices [13,17,25], without external heating. The stack operating conditions such as temperature, water/methanol flow rate, hydrogen and air flow rate, current density, potential or heat produce/consumed are studied.

2. Experimental

To achieve the heat integration between the MSR-C and the HT-PEMFC, a novel bipolar plate made of gold plated aluminium was designed, featuring a fuel cell flow field in one side and a reformer flow field in the other (Fig. 1). A Celtec P2200N membrane electrode assembly (MEA) from BASF with an active area of 45 cm² was used. The reforming reaction was carried out using 40 g of commercial catalyst (CuO/ZnO/Al₂O₃) from BASF (RP-60). The MSR-C performance was determined at different space-time-ratios (m_{cat}/F_{MeOH}) and operating temperatures (between 443 K and 473 K). The HT-PEMFC characterization was performed with λ_{Air} of 2 and λ_{H_2} of 1.2, between 433 K and 473 K; the anode was fed with different fuels: pure hydrogen, gas mixture with volume fractions of 75% of H₂ and 25% of CO₂ and reformat supplied directly from the MSR. A more detailed description of the MSR-C/HT-PEMFC combined unit can be found in the literature [19].

An unused Celtec P2200N MEA was characterized by field emission scanning electron microscopy (SEM) in order to determine the thickness of the membrane, anode and cathode catalyst layer and anode and cathode gas diffusion layer.

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