Fuel Processing Technology 92 (2011) 166–174

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Integrated membrane system for pure hydrogen production: A Pd–Ag membrane reactor and a PEMFC

A. Brunetti [a], G. Barbieri [a,*], E. Drioli [a,b]

[a] Institute on Membrane Technology (ITM-CNR), National Research Council, c/o The University of Calabria, Cubo 17C, Via Pietro BUCCI, 87036 Rende CS, Italy
[b] Department of Chemical Engineering and Materials, The University of Calabria, Cubo 44A, Via Pietro BUCCI, 87036 Rende CS, Italy

ARTICLE INFO

Article history:
Received 17 May 2010
Accepted 17 September 2010

Keywords:
Integrated membrane plant
Pure hydrogen, Fuel processor
PEMFC

ABSTRACT

In this work, an integrated system consisting of single stage hydrogen production and a commercial PEMFC was investigated experimentally. The CO-free hydrogen fed to the PEMFC was produced in a Pd–Ag membrane reactor (MR), upgrading a syngas stream with a composition similar to that coming out of a reformer (CO 45%; H_2 50%; CO_2 4%; N_2 balance, on dry basis). The performance of the MR was evaluated in terms of CO conversion and H_2 recovery as a function of the feed pressure (up to 600 kPa) and space velocity; no sweep gas was used for promoting the H_2 permeation, since this role was assigned exclusively to the feed pressure.

Special attention was paid to the analysis of the integrated system, focusing on the influence of the Pd–Ag MR operating conditions on the electrical performance of the PEMFC. The PEMFC internal crossover was also considered to have an effect on the electrical performance and this was taken into account estimating the PEMFC actual efficiency. Furthermore, the chemical efficiency of the integrated membrane plant was evaluated, considering the H_2 converted into electricity with respect to the total amount of H_2 contained in the feed mixture. An interesting performance was shown by the integrated system since the PEMFC performance was close to the power nominal value.

1. Introduction

A polymeric electrolyte fuel cell (PEMFC) is an electrochemical device where a fuel globally reacts with oxygen, thereby generating electricity and producing combustion by-products. Generally, hydrogen is the preferred fuel for a PEMFC because of its high reactivity on the fuel cell electrode and the null environmental impact of the reaction product, the latter being only water. Unfortunately, there are no known sources of gaseous hydrogen on the planet Earth. It follows that the whole hydrogen has to be generated using available energy sources. Since hydrogen gas is difficult to store and transport, it should be generated, locally, close to the final user from available fuels, most commonly hydrocarbons or coal gasification. This device used in fuel cell applications must meet specific technical and marketing demands. It must be small and lightweight, processing feeds of varying composition to deliver hydrogen free from CO and other fuel cell poisons over a wide range of flow rates at a cost comparable to current market values [1,2]. The unit must be sufficiently rugged to withstand frequent shut downs and cold start up and it must operate for many years, unattended and with minimum service [3].

In the design of the fuel processor, some constraints must be observed: CO content in the hydrogen stream must be reduced under 10 ppm to avoid electrode poisoning and, thus, performance depletion. Also, inert dilution of the hydrogen fed to the cell reduces hydrogen utilization. The use of an upgrading membrane unit constituted of a Pd–Ag MR, where the water gas shift (WGS) reaction is performed, allows the removal of CO content from the reformate stream, producing, meanwhile, more hydrogen that can be easily recovered as pure stream in the permeate side. Typically, WGS units include high temperature and low temperature reactors operating at ca. 400 and 200 °C, respectively. The WGS catalyst must be highly active to reduce reactor volume and it must be stable in the fuel processor environment, which may include exposure to air and liquid water when the system is shut off [4].

A Pd-based MR allows the conversion achievable in a traditional reactor (TR) to be significantly exceeded and, contemporarily, a high-purity hydrogen stream to be recovered and fed directly to a PEMFC [5]. The membrane operates as molecular-scale filters separating H_2 from the rest of the gases when a pressure difference between the two membrane sides is applied.

Industrial hydrogen generation processes use polymeric membranes with a variety of permeation and selectivity specifications. However, producing high-purity, fuel cell grade hydrogen with those membranes may require two or more steps. Alternatively, more expensive but highly selective palladium-based membranes produce

* Corresponding author. Tel.: +39 0984492029; fax: +39 0984402103.
E-mail address: g.barbieri@itm.cnr.it (G. Barbieri).

0378-3820/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.fuproc.2010.09.023

high-purity hydrogen. They are an attractive option despite their cost [6], since they assure that the hydrogen produced is CO free [7].

In the past, palladium-alloy membranes were successfully used for hydrogen production/separation also for the WGS step [8–10]. However, the majority of these studies proposed the use of a sweep gas to promote H_2 permeation and a small minority combines the use of a low feed pressure at the sweep gas to improve the permeation. The use of sweep gas produces a diluted H_2 stream that, subsequently, needs further separation steps. In this work, moving in the logic of process intensification strategy, and the role of promoting the hydrogen permeation through the membrane was assigned only to the feed pressure. In this way, the reduction of the weight and the size of the whole system can be pursued for the following reasons:

- The assessment of a pure H_2 stream not requiring further separation steps.
- The reduction of the reactor volume with respect to the one required using sweep gas.
- The fact that the feed stream, coming out, for example, from a reformer, is already compressed.

The advantages offered by the use of a Pd–Ag membrane were already evaluated in our previous work [11] where a Pd–Ag membrane module was connected with a PEMFC. In that case, the Pd–Ag unit was used only as the purification stage for mixtures containing H_2 in different compositions without carrying on any reaction. The main innovation in this work is the substitution of the Pd–Ag purification stage with a Pd–Ag MR which allows not only the H_2 contained in the feed mixture to be recovered, but also the CO present in that stream (ca. 45% on dry basis) to be converted producing further H_2 which can be fed to PEMFC.

In the past, the system integration of membrane-based processes with PEMFC, particularly for fuel processors, has been rarely addressed in the literature despite its importance from a Process Intensification Strategy point of view. A fundamental characteristic necessary for the application on board of fuel processors is compactness as well as limited weight. Many studies in the literature propose the integration of high temperature conversion reactors as core of the fuel processors. Recently, Aicher et al. [12] designed, manufactured, installed and operated a complete, fully automated reformer fuel cell system. However, the system comprised an autothermal reformer, two WGS reactors, a tail gas combustor and a commercial PEMFC. Lyubovsky and Walsh [13] described a fuel processor based on methanol autothermal reforming operating at a high pressure followed by membrane-based hydrogen separation.

For only a few years, researchers have been looking at the possibility of integrating membrane reactors in fuel processors, to improve the performance and, in the meantime, reduce the size and the weight of these devices. Salemme and co-workers [14] carried out a simulation study for the analysis of the energy efficiency of an innovative fuel processor – PEM fuel cell systems, based on methane autothermal reforming for hydrogen production and on membrane technology for hydrogen separation. From the simulations, they observed that higher global efficiency values can be reached if the membrane separation unit is integrated into the water gas shift reactor.

A PEMFC/fuel processor stationary system fed with ethanol has been simulated by Mendes et al. [15] using a hysys process simulator. The conventional configuration of a fuel processor was compared with a configuration using a Pd–Ag membrane reactor, in terms of hydrogen yield and energy efficiency. It was shown that the MR-based fuel cell system was more suitable than the traditional reactor one for producing hydrogen. The MR-based fuel cell system was simpler than the traditional one with such a configuration the reduction in system complexity (along with synergetic effects) was confirmed into the logic of the process intensification strategy.

Wilson [16] elaborated a new fuel processor, which, instead of reforming, used methanol decomposition to enable the by-product and carbon monoxide (CO), to be used as the heat source. Pd–Cu based membrane foils had the role of segregating the CO for combustion in an integrated burner, maximizing the decomposition conversion, and providing pure hydrogen for a fuel cell. High and stable hydrogen yields were attained with optimized catalysts and fuel compositions. A 20 W autonomous power source based on this novel fuel processor demonstrated a fuel energy density >1.5 Wh g^{-1} (electrical), nearly twice as high as micro-reformer power sources.

In this work, the performance of an integrated system representing a part of a fuel processor, where the WGS reactors are substituted by a Pd–Ag MR was experimentally evaluated, also connecting a PEMFC. In particular, the upgrading of a stream, with the typical composition of outlet reforming streams (Table 3), was carried out to achieve higher CO conversion with respect to a traditional operation and, contemporarily, a pure H_2 stream, directly usable in a PEMFC.

Special attention was focused on the effect of the changes of operating conditions of the MR on the whole system performance. The effect of a buffer placed between the MR and the PEMFC as stabilizer was evaluated in terms of stability of the power supplied by the PEMFC. Moreover, the effect of the operating conditions on the integrated system performance were quantified in terms of plant efficiency, power supplied and hydrogen totally loss.

2. Materials and methods

The experimental analysis of the integrated system was carried out in two phases.

- Study of the performance of MR in terms of CO conversion and H_2 recovery for different feed pressures and GHSVs, at a set temperature of 290 °C (chosen referring also to the results obtained in our previous work [5]).
- Integration of the MR with the PEMFC and analysis of the performance of the membrane integrated system in terms of power supplied and efficiency.

The MR used to carry out the upgrading of the syngas mixture consists of two concentric tubes (Fig. 1): the outer tube is the shell; the inner tube is the Pd-alloy self-supported membrane. This membrane was blind on one side since it was chosen not to use sweep gas to promote the hydrogen permeation. The catalyst is packed in the shell side, since this configuration is more efficient for the heat exchange between the reaction zone and the furnace [17], allowing better catalyst exploitation and, also, a good membrane area utilization.

The MR geometric characteristics are resumed in Table 1.

The experimental apparatus used in the reaction tests is shown in Fig. 2. MR was placed in a temperature controlled electric furnace (with PID control). A mass flow controller (Brooks Instrument 5850 S) was used for feeding the gaseous mixture, whereas an HPLC pump (Dionex P680A) was used to feed water. A heating coil was located into the furnace to vaporize the water. The flow rates of the outlet streams were measured by means of bubble soap flow-meters.

The retentate and permeate streams were analysed by means of a gas chromatograph (Agilent 6890 N) with two parallel analytical lines. Each line was equipped with two columns: an HP-Plot-5A (for separating permanent gases such as H_2, N_2 and CO) and a HP-Poraplot-Q (for other

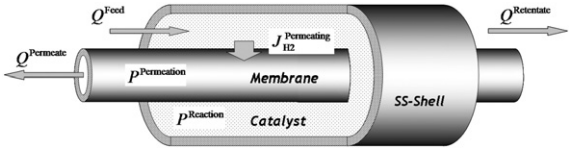

Fig. 1. MR configuration.