ELSEVIER

Theoretical analysis of a pure hydrogen production separation plant for fuel cells dynamical applications

L. Capobianco[a],*, Z. Del Prete[a], P. Schiavetti[a], V. Violante[b]

[a]*Department of Mechanics and Aeronautics, University of Rome "La Sapienza", Via Eudossiana 18, 00184 Rome, Italy*
[b]*ENEA, Frascati Research Centre, Via Enrico Fermi 45, 00044 Frascati, Rome, Italy*

Abstract

This article proposes a mathematical model and develops the numerical simulation of a single stage hydrogen production–separation process during transient behaviour, suited for proton exchange membrane (PEM) fuel cell (FC) applications. Methanol reforming process is performed in a commercial catalytic membrane reactor (CMR), filled with a commercial ZnO–CuO, alumina supported catalyst. The permeate hydrogen is accumulated in a reservoir volume (buffer) connected to the permeate side. This configuration was studied in order to avoid the feed back control of the reactor feeding, even when transient power loads to the cell are applied. By numerical simulation, we verified that the system comprised by the CMR and the PEM, with an appropriate constant reactor feeding flow, is always self-sustaining so that the hydrogen demand by the FC can be satisfied at all power regimes. The achievement of this goal was obtained by redistribution of the hydrogen produced in the reactor between the buffer and the exhaust tail gases. Only the control of two independent variables of the system, such as reactor temperature and pressure, are needed, therefore, the configuration proposed here results in a simplified approach to the control strategy for the entire system. We apply the theoretical analysis to a pilot plant designed and assembled at the University of Rome "La Sapienza", in order to verify its functional parameters and the theoretical performance of the system before its real operation.
© 2006 International Association for Hydrogen Energy. Published by Elsevier Ltd. All rights reserved.

Keywords: Fuel cells; Catalytic membrane reactor; Buffer; Methanol steam reforming

0. Introduction

In the recent years, an extensive work has been done concerning the use of proton exchange membrane (PEM) fuel cells (FCs) to clean energy and automotive applications. For the latter one, the main problem is still the safe and inexpensive storage of hydrogen on board. Therefore, many authors [1–7], instead of storage, focused on efficient "on board" production methods, by means of liquid and gaseous fuels reactions as: water gas shift of carbon monoxide, steam reforming of methane, steam reforming coupled by partial oxidation of a liquid fuel, thermal cracking of hydrocarbons. Moreover, the use of PEM FCs implies a number of problems, like purification and humidification of hydrogen feeding and control of gases pressure [8–12]. In this study, we examine by numerical simulations, the performance of an H_2 feeding system constituted by a catalytic membrane reactor (CMR) [10,13–15,33,35], by which the production and purification steps are integrated. CMRs are high efficiency devices

* Corresponding author. Tel.: +39 06 44585585;
fax: +39 06 4881759.
E-mail address: luigi.capobianco@uniroma1.it (L. Capobianco).

Nomenclature

A_m	total permeating membrane area, m^2
c	concentration in gas phase, mol/m^3
c_0	reference concentration, $(=P_0/(RT_0))$
C_{SI}^T, C_{SIa}^T	catalyst surface concentration of site types I or Ia $(I = 1, 2)$, mol/m^2
D	reactor diameter, m
D_m	membrane diameter, m
E	activation energy, $kJ/(mol\,K)$
F	molar flow rate, mol/s
F_0	reference molar flow rate, $(=(v_0 c_0 V_b)/L)$
$\widetilde{F}$	dimensionless molar flow rate, $(=F/F_0)$
J	molar flux, $mol/m^2\,s$
J_0	reference molar flux, $(=F_0/A_m)$
$\widetilde{J}$	dimensionless molar flux, $(=J/J_0)$
k_D	rate constant for methanol decomposition, $m^2/s\,mol$
k_R	rate constant for methanol reforming, $m^2/s\,mol$
k_W	rate constant for water gas shift reaction, $m^2/s\,mol$
K_D	equilibrium constant for methanol decomposition, $1/bar^2$
K_R	equilibrium constant for methanol reforming, $1/bar^2$
K_W	equilibrium constant for water gas shift
K^*	adsorption constant, $1/bar^{0.5}$
L	reactor total length, m
L_m	membranes total length, m
N_m	number of membranes
p_i	partial pressure of species i, bar
$p_{H_2}^{(rs)}$	retentate side partial pressure of hydrogen, Pa
$p_{H_2}^{(ps)}$	permeate side partial pressure of hydrogen, Pa
P	total pressure, bar
P_0	reference pressure, bar
P_c	cell power load, W
Q/δ	permeability, $mol/m\,s\,Pa^{0.5}$
r_i	overall rate of consumption of species i, $mol/m_{cat}^3\,s$
r_M	rate of reaction M, $bar/m_{cat}^3\,s$
R	gas constant, $bar\,m^3/mol\,K$
R'	gas constant in permeability expression, $J/mol\,K$
R_j	rate of reaction j, $mol/m_{cat}^3\,s$
S	surface area, m^2/gr
T	temperature, K
T_0	reference temperature, K
v	molar mean velocity, m/s
v_0	reference velocity, m/s
V	dimensionless velocity, $(=v/v_0)$
V_r	reactor volume, m^3
V_b	buffer volume, m^3
X	dimensionless length, (z/L)
y_i	molar fraction of species i
Y	dimensionless molar fraction, $(=y_i/y_{i0})$
z	reactor's axial coordinate, m

Greek letters

α	membrane to reactor length ratio $(=L_m/L)$
β	permeating zone surface to volume ratio $(=(4N_m\pi D_m)/(D^2 - N_m D_m^2))$
γ	hydrogen utilization factor $(=F_{H_2}^{(perm)}/(F_{H_2}^{(prem)} + F_{H_2}^{(out)}))$
δ	membrane thickness, m
ΔH_R	heat of reaction, kJ/mol
ΔH_c	high heating value of hydrogen, kJ/mol
ε	bed void fraction, $m_{void}^3/m_{reactor}^3$
η_c	cell efficiency
ν	stoichiometric coefficient
Π	dimensionless buffer pressure $(=P_b/P_0)$
φ_i	$(=((1-\varepsilon)/\varepsilon)r_i - U(z-L_1)(\beta/\varepsilon)J_{H_2})$
φ_t	$(=L\sum_i^{N_c}\varphi_i)$
Φ_i	$(=L\varphi_i/(c_0 v_0 y_{i0}))$
Φ_t	$(=L\varphi_t/(c_0 v_0))$
ρ_{cat}	catalyst density, kg/m_{cat}^3
τ	dimensionless time $(=v_0 t/L)$
ω	frequency, Hz

Superscripts

c	cell
in	reactor inlet conditions
out	reactor outlet conditions
perm	permeating

Subscripts

a	CH_3OH
b	buffer
d	decomposition
m	membrane
cat	catalyst
0	reference value
r	CO_2, reforming
s	H_2
w	CO, water gas shift