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Thermoelectric characterization of an intermediate temperature solid oxide fuel cell system directly fed by dry biogas

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ABSTRACT

A properly manufactured intermediate temperature Solid Oxide Fuel Cell (SOFC) can be directly fed by dry biogas, considering also the electrochemical partial and total oxidation reactions of methane in the biogas at the anode. In this way the methane in the biogas is electrochemically consumed directly at the fuel cell without the need to mix the biogas with any reforming gas (steam, oxygen or carbon dioxide).

In this article, a numerical model of an SOFC system with Ni-Fe/CGO electrocatalyst anode protective layer directly fed by dry biogas, in cogenerative arrangement and with anode exhaust gas recirculation is formulated.

The influences of biogas composition, of fuel cell operating current density and of percentage of recirculated anode exhaust gas on the SOFC system performances were evaluated by calculation code.

An SOFC test bench was set up to validate the calculation code results experimentally.

Furthermore, the numerical model also considers the anode carbonation and evaluates the amount of carbon that can be formed in the anode at chemical equilibrium and quasi-equilibrium conditions associated with the specific anode protective layer used.

1. Introduction

Biogas is a gas mixture consisting mainly of methane produced by anaerobic bacterial fermentation of organic residues from plant or animal wastes. The residues can be useful agro-industrial waste (shredded corn, sorghum or other crops), industrial food waste (flour waste or expired products), industrial animal waste (animal waste or carcasses) or the Organic Fraction of Urban Solid Waste (OFUSW). The whole process sees the decomposition of the organic material by means of specific bacteria with the resulting production of biogas mainly made up of methane (CH_4) and carbon dioxide (CO_2).

The CO_2 produced by the oxidation of methane thus obtained allows the budget of the carbon dioxide emitted into the atmosphere to be balanced: in fact, the CO_2 emitted by the combustion of the biogas is the same CO_2 fixed by plants (or taken from animals indirectly through plants), contrary to what happens for the CO_2 emitted ex novo from the combustion of fossil fuels. A further ecological advantage in the use of biogas is to prevent the spread in the troposphere of the methane released naturally during the decomposition of the residues: in fact, methane is a greenhouse gas 25 times more potent than CO_2 [1] and its degradation into CO_2 and water for electrochemical oxidation is therefore desirable.

In view of both a better energy rationalization and eco-environmental sustainability, solid oxide fuel cells (SOFC) are able to convert the properly purified biogas directly into electric energy distributed where it can be used and with a higher energy conversion efficiency compared to energy systems fed by biogas, resorting to the traditional combustion process. Moreover, the same SOFC make also thermal energy available for cogenerative use in their immediate vicinity, since they operate at high temperature [2].

Among high temperature fuel cells, only SOFC can directly oxidize a good part of the CH_4 content in biogas to produce electric energy by two of its anode electrochemical reactions [3–6] and the materials and the catalysts used to make the anode strongly influence the chemical reactions that take place in the anode.

Although the high temperature operation of conventional SOFCs (i.e. Ni-YSZ/YSZ/YDC/LSFCO) can be useful for the internal reforming of organic fuels, the risk associated with the direct utilization of

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Nomenclature

Symbols

F	molar flow [mol s^{-1}]
K	equilibrium constant [-]
p	pressure [atm]
k, a, b	constants [-]
j	current density [A m^{-2}]
A	active surface [m^2]
Fa	Faraday constant [C mol^{-1}]
T	temperature [K]
v	stoichiometric coefficient [-]
f	factor [-]
V	voltage [V]
R	resistance [Ω m^2]
P	power [W]
η	efficiency [-]
G	mass flow [kg s^{-1}]
S	entropy [J mol^{-1} K^{-1}]
ΔV	voltage loss [V]
ΔH	enthalpy variation [J mol^{-1} or J kg^{-1}]
H	enthalpy [J kg^{-1}]
χ	mass fraction [-]
U	utilization factor [-]
x	molar fraction [-]
c	specific heat [J kg^{-1} K^{-1}]
LHV	low heating value [J kg^{-1}]

Subscripts

$CH_4, CO, H_2O, H_2, CO_2, N_2, O_2$	methane, carbon monoxide, water or steam, hydrogen, carbon dioxide, nitrogen, oxygen
wgs	water gas shift chemical reaction
sr	steam reforming chemical reaction
dr	dry reforming chemical reaction
in	at the inlet
a	anode
b	electrochemically consumed
po	partial oxidation
to	total oxidation
c	the fuel cell element
out	at the outlet
i	generic index
rec	anodic recirculation
mix	mixing point
hetox	hydrogen electrochemical total oxidation
mepox	methane electrochemical partial oxidation
cmetox	carbon monoxide electrochemical total oxidation
ca	cathode
N	Nernst
CH_4/O	CH_4 electrochemical partial oxidation reaction
$CH_4/2O_2$	CH_4 electrochemical total oxidation reaction
H_2/O	H_2 electrochemical total oxidation reaction
CO/O	CO electrochemical total oxidation reaction
act	activation
conc	concentration
0	anode and cathode exchange
lim	limit
el	electric
SS	SOFC system
bio	biogas
th	thermal
lost	lost for chemical irreversibilities, for joule and contact effects and for polarization phenomena
tot	total
ph	preheating
gas	gas mixture
air	air
nraeg	not-recirculated anodic exhaust gas
raeg	recirculated anodic exhaust gas
B	burner
HE	heat exchanger
net	net
ref	reference
spcr	steam production chemical reaction
Bcr	Boudouard chemical reaction
ccr	cracking chemical reaction
C	carbon
m	mean
ox	oxidant
max	maximum value
p	at constant pressure

Superscripts

~	molar
→	vector

biofuels (i.e. biogas, bioalcohol, biodiesel, etc.) that generally contain an important level of contaminants, is extremely high [7]. The state-of-the-art anode of commercial SOFCs (nickel-yttria stabilized zirconia, Ni-YSZ cermet) is particularly sensitive to such risks, which would increase in favor of an irreversible cell degradation due to carbon deposition [8,9] and sulfur poisoning. Typically, these drawbacks can be mitigated by adding a purification step for the biogas and a chemical processor to produce a clean syngas from biogas by conventional Steam Reforming (SR), Partial Oxidation Reforming (POX), Auto-thermal Reforming (ATR) or Dry Reforming [10,11].

Alternatively, the addition of a large amount of water steam to the fuel (steam to carbon ratio approx. 2.5) can mitigate the carbon deposition mechanisms by creating the condition for an internal reforming [12]. In both cases, the associated increase in complexity and costs as well as the risk of damage to the cells can be an obstacle for the wide diffusion of this technology. The chance to overcome this barrier is essentially addressed by the development of a new anodic formulation that, at the same time, should not cause modifications in the well-established SOFC manufacturing process [8,13–18]. It has been observed that the interruption of the Ni-Ni network, which promotes the cracking process and the consequent formation and deposition of carbon fibers and soot, by introduction of a different transition metal and the addition of Ceria and Gadolinium Oxide (CGO), can improve the ionic conduction, oxygen storage and stability of the catalyst [19].

There are some articles in the literature in the field of numerical modeling and experimental analysis of SOFC fed by biogas [20–25]. In all the simulation models [20,22–25] a conventional Ni-YSZ SOFC anode without protective layer is considered, in [20,25] only the anodic electrochemical reaction of hydrogen consumption is considered, in [22–24] also the anodic electrochemical reaction of carbon monoxide consumption is considered and only in [23] the anodic electrochemical reaction of methane total oxidation is taken in account. Simulation models in [20,22–25] consider only the chemical reactions of steam reforming and water gas shift in the anode.

In the literature, there are some articles in the field of numerical modeling of SOFC systems fed by biogas [26–33]. In them the performance of SOFC systems with anaerobic digester, SOFC and