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Trace compounds impact on SOFC performance: Experimental and modelling approach

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HIGHLIGHTS

- VOCs contained in biogas from anaerobic digestion were tested on SOFC performance.
- Sulfur, Siloxane and Tars were chosen as biogas model compounds for SOFC experimental testing.
- The multiphysic model was validated in hydrogen and with sulfur using experimental data.

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ABSTRACT

Issues related to SOFCs performance and durability are strictly dependent on the feeding fuel quality. SOFC capability to be fed with fuels different from hydrogen opens to scenarios in which a big variety of fuels can be used at the aim. Unfortunately, problems related to anode deactivation due to the contaminants presence can arise. The present work investigates the performance of anode supported solid oxide fuel cells in case of co-feeding of different trace compounds. Electrochemical impedance spectroscopy is the investigation technique used to analyze the impedance spectra. Typical biogas from OFMSW trace contaminants that follow an initial failure in the cleaning system, such as sulphur, aromatic compounds and siloxanes, have been simultaneously tested. Tests showed that the most deleterious impact for the SOFC was due to the H_2S action. This influences mostly the electrochemical losses respect to diffusion losses, even if this last are not null and can be accounted as a secondary effect. On the contrary, the co-presence of D4 and H_2S mitigates in the short-term the effect that the only D4 produces when fed with biogas. The most relevant consequence produced by C_7H_8 was recorded in the low frequency of Nyquist plot, affecting mainly the mass transport phenomena. Experimental tests are accompanied by the implementation of the fuel cell model through COMSOL Multiphysics software to study the effect of pollutants on fuel cell performance.

1. Introduction

Issues related to climate change increase in fuel costs and continued increase in energy demand, they can be faced with more efficient energy systems based on renewable sources. Fuel cells are promising energy generators that exploit the direct conversion of chemical content into electricity using a wide variety of fuels. In fact, they can accomplish high conversion efficiency coupled to economic and environmental advantages. Fuel cells are electrochemical devices able to directly transform free energy of a chemical reaction into useful electrical and thermal energy. These devices are able to avoid the limitations related to the Carnot cycle [1]. One of the main advantages of SOFC is their fuel flexibility, low noise, and pollutant emissions limitation. A SOFC system can be fed with natural gas, biogas from anaerobic digestion process, landfill gas, etc. [2–7]. This fuel mixture can directly feed the anode of the cell, prior a gas cleaning section in a direct internal reforming condition. This condition offers a significant cost reduction, higher efficiencies and faster load response of a solid oxide fuel cell (SOFC) power plant. On the contrary, a complete internal reforming may lead to several problems related to the high content of carbon compounds able to promote the carbon deposition phenomena. The problem can be avoided with partial pre-reforming of natural gas or biogas. Moreover, fuel mixtures can contain several trace compounds that can decrease the SOFC performance and act as contaminants for the SOFC anode electrode. These compounds can deactivate nickel active sites at the three-phase boundary, they can promote the carbon deposition and obstruct the anode pores. The nature and pollutant concentrations are strictly related to the adopted process and to the

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Nomenclature

ASR	area specific resistance
CH_4	methane
CO	carbon monoxide
CO_2	carbon dioxide
CPE	constant phase element
D4	octamethylcyclotetrasiloxane
DIR	direct internal reforming
ECM	equivalent circuit model
EIS	electrochemical impedance spectroscopy
FM	Fick Model
FU	fuel utilization
H_2	hydrogen
H_2S	hydrogen sulphide
HTFC	high temperature fuel cell
ITFC	intermediate temperature fuel cell
MIEC	mixed ionic electronic conduction
MSM	Maxwell Stephan Model
MUMPS	multi-frontal massively parallel sparse direct solver
Ni-YSZ	nickel mixed with ceramic material YSZ
OCV	open circuit voltage
OFMSW	organic fraction municipal solid waste
$ppm_{(v)}$	parts per million by volume
R_{high}	high frequency arch resistance, electrochemical resistance
R_{ion}	pure resistive element
R_{low}	low frequency arch resistance, mass transport resistance
R_p	total resistance
S/C	steam to carbon
SMR	steam methane reforming
SOFC	solid oxide fuel cell
SSA	specific surface area
TAR	Tar is a complex mixture of condensable hydrocarbons, which includes single ring to 5-ring aromatic compounds along with other oxygen-containing hydrocarbons and complex PAH
TPB	three phase boundary
WGS	water gas shift
YDC + LSCF	yttria doped ceria/lanthanum strontium cobalt ferrite oxide
YSZ	yttria-stabilized zirconia
Θs	surface coverage

treated substrates [8–9]. Previous studies have been focused on the consequences of a single trace contaminant, highlighting that sulphur, chlorine, silicon and aromatic compounds can degrade irreversibly cell performances above fixed values [10–14].

Kazunari et al. [15] studied a SOFC that operates at a temperature of 800 °C fed with methane, 50% externally reformate adding 5 $ppm_{(v)}$ of H_2S under galvanostatic conditions. An initial voltage drop followed by a nearly-stationary phase was showed. The drop is mostly due to an anodic over-voltage compared to an increase in ohmic losses. The voltage decrease is strictly related to the number of clogged active sites. For small concentration of sulphur, reversible phenomenon associated to adsorption/desorption were observed [2,7,16–18].

Although many modified Ni-based cermet anodes have been declared to have improved sulfur tolerance and coking resistance, they still show insufficient performance. Except for a few cases, a rapid degradation in electrode performance is observed at the initial stage. More research is needed to further improve the sulfur tolerance of Ni-based anode to allow practical application on carbonaceous fuels [19,20].

- Ways to improve sulfur tolerance of Ni-based SOFC anodes are based on:
- changing the ionic conducting phase in Ni-based anodes,
- tailoring the electronic conducting phase through alloying,
- modifying the surface or bulk of Ni-based anode.

Based on calculations, Sasaki et al. [21] demonstrated that some metal oxides, such as Ce, Y, La, etc. and metals like Ru or Co were tolerant in a sulfur-containing reducing atmosphere at 800 °C. Among the alternative ionic conductor phases, the overwhelming majority were of the doped or undoped ceria oxides such as GDC [22,23] due to their good performance and more importantly, low cost. Ceria was found to be a good sulfur sorbent in reducing atmosphere at high temperature because it reacted with H_2S to form Ce_2O_2S [24].

An et al. demonstrated that alloying of Ni with other metals could restrain the sulfur- and carbon- binding. Therefore the catalytic activity of Ni cermet anode was maintained [25].

Bulk incorporation of oxides into Ni-based SOFC anode also showed an improved sulfur tolerance. Using a comprehensive thermodynamic study, Silva et al. showed that the bulk nickel sulfide activity depended on sulfur chemical potential, which in turn controlled the sulfur chemisorption on Ni surface. Oxide, especially BaO, incorporation into anode could lower the sulfur chemical potential and further reduce the sulfur coverage on Ni surface [26].

Literature studies revealed that high attention has been reserved to the effects of sulphur compounds at the anode of the cell. On the contrary, silicon compounds impact on SOFC systems have not been analysed exhaustively. However, the effects of these substances require a specific attention. The research of Madi et al. [27] is conducted on a single cell investigating the effects of different siloxanes concentrations. In that specific case, the octamethylcyclotetrasiloxane (D4) was identified as model compound for siloxanes. The experiment concerns the investigation of cell performance when it is fed with a $50\%_{(v)}$ DIR condition of reformed biogas. After reaching the stable operating condition, it was added 1 $ppm_{(v)}$ of D4 for 495 h. The cell voltage showed a gradual decrease at 0.25 mV/h. This decreasing ratio become bigger increasing the D4 concentration up to 2 and 3 $ppm_{(v)}$. It was reached values of 0.34 and 0.39 mV/h, respectively.

Lorente et al. [28] investigated the effect of TARs quantity equal to 15 g/Nm^3, i.e. typically produced by a fluidised bed reactor. The power line has been heated to an adequate temperature to avoid TAR condensation. The greater effect observed is represented by carbon deposition, as reported also by Papurello et al. [11]. It was observed that anodes made of cerium have better characteristics than those in YSZ because the former has high reducing ability.

All these impurities were investigated separately at the anode, however, they are simultaneously contained in biogenous fuels. For this reason, the fuel cell analysis can not appear from the operation under biogenous fuel feeding. The contemporary presence of multiple compounds at the anode can represents severe issues when the cleaning system is under initial failure. This paper wants to fill the gap between modeling results and experimental tests on the SOFC versatile fuel feeding with renewable fuels. This fuel can come from dry anaerobic digestion of organic waste and the contemporary impact of more than one trace compounds is investigated, also using a multiphysics model.

2. Methods and materials: experimental tests

A Solidpower planar ASC cell was used for the experimental tests. The experimental set-up used was described elsewhere [13,17,29].

Different feeding conditions were tested on the cell, starting from the direct internal reforming condition up to consider the contemporary presence of trace compounds, typical from biogenous fuels. It was focused the investigation on the low and ultra-low concentrations on fuel cell performance. This concentration level is representative of the initial