



SOFC direct fuelling with high-methane gases: Optimal strategies for fuel dilution and upgrade to avoid quick degradation



A. Baldinelli ^{a,*}, L. Barelli ^a, G. Bidini ^a, A. Di Michele ^b, R. Vivani ^c

^a Università degli Studi di Perugia, Department of Engineering, Italy

^b Università degli Studi di Perugia, Department of Physics and Geology, Italy

^c Università degli Studi di Perugia, Department of Chemistry, Biology and Biotechnology, Italy

ARTICLE INFO

Article history:

Received 20 May 2016

Received in revised form 16 July 2016

Accepted 19 July 2016

Available online 26 July 2016

Keywords:

SOFC

NiYSZ

Internal partial oxidation

Internal reforming

Natural gas

Biogas

ABSTRACT

In the outlook of the transition to the *carbon-free society*, low-carbon gases, such as natural gas or biogas, are very promising. The first is commonly used for stationary applications based on Solid Oxide Fuel Cells (SOFCs) equipped with external reformers. Similar installations are required when the SOFC is run on biogas. Yet, high SOFC operative temperature enables internal decomposition of light hydrocarbons, therefore allowing the suppression of external reforming. Evidently, this brings about benefits in terms of system complexity and cost reduction. Nonetheless, unlike reformed fuels, direct exposure to large amount of methane favours SOFC anodes degradation. Implementing a systematic experimental approach, this paper aims at determining a simple operative strategy to carry out direct feeding without meeting with quick degradation issues, producing interesting outcomes with regards to the management of SOFC-based systems. Particularly, the regulation of the oxygen-to-carbon (O/C) relative fraction of the fuel through air addition to natural gas and partial CO₂ separation from biogas is helpful in the prevention of those mechanisms. In this study, NiYSZ anode SOFCs are exposed to air-diluted natural gas and upgraded biogas, featuring O/C between 0.2 and 1.2. Tracing these cases, at 800 °C and 500 mA/cm² constant load, cell performances are measured over a time interval of 100 h. Finally, post-mortem analysis is performed on the specimens to investigate material morphological changes after the exposure to high-methane fuels. Results showed that O/C = 0.8 (+63% air) is the best case to employ air-diluted natural gas with stable and acceptable performances (867 mV). Similarly, running the fuel cell on upgraded biogas, a partial CO₂ separation to get an O/C = 0.4 (–60% CO₂) enables better and stable performance (880 mV). In both cases, neither significant catalyst coarsening nor carbon deposition were detected on the specimens.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Fossil resources exploitation widely characterized energy production during the last two centuries, leading to several environmental issues. Nowadays, consumption rates are no more sustainable for the preservation of resources and fossils high carbon content determines a significant environmental impact. Therefore, it is mandatory to decrease resources consumption by adopting more efficient systems and to increase the share of carbon-free or, at least, low-carbon fuel.

In this frame, natural gas [1] and biogas [2] are good candidates, since they meet with already known safety standards and they help in reducing GHG emissions [3]. Moreover, synthetic natural

gas (SNG) has become a real alternative [4,5], which contributes to overcome the problem of finite availability of fossil gas reservoirs.

For Solid Oxide fuel Cells (SOFCs), grid natural gas is commonly used as a fuel [6,7] and few demo installations running on biogas are coming into view. Existing systems based both on natural gas and biogas are usually equipped with an external unit where fuel steam reforming takes place [8–10]. However, compared to other fuel cell technologies, thanks to their high fuel flexibility, SOFCs offer the possibility to operate direct feeding, avoiding external fuel processing [11]. In the outlook of designing small-size plant, this represents a good potential for system complexity and cost reduction [12]. Furthermore, fuel external processing has its own conversion efficiency and associated energy losses are in the order of 15–30% [13]. Nonetheless, as debated in the literature [6,14], direct fuelling of unreformed gases to the SOFC might speed up fuel cell degradation.

* Corresponding author.

E-mail address: arianna.baldinelli@gmail.com (A. Baldinelli).

Nomenclature

| | | | |
|-------|--------------------------------------|---------------------------------|--------------------------------|
| EDS | energy-dispersive X-ray spectroscopy | SNG | synthetic natural gas |
| j | current density | SOFC | Solid Oxide Fuel Cell |
| NiYSZ | Nickel Yttria Stabilized Zirconia | T | temperature |
| OCV | open circuit voltage | XRD | X-ray diffraction |
| O/C | oxygen to carbon ratio | m-ZrO ₂ | monoclinic Zirconia |
| S/C | steam to carbon ratio | t-ZrO ₂ | tetragonal Zirconia |
| SEM | scanning electron microscope | ΔH _{25°C} ⁰ | standard enthalpy of formation |

1.1. SOFC tolerance to high-methane gases

Nickel is extensively employed as a catalyst for SOFC anodes because of many reasons: it is relatively cheap, easily available, it is a good promoter of both of hydrogen/carbon monoxide electrochemical oxidation [15] and internal cracking [16] and reforming [6]. In order to overcome undesired degradation phenomena occurring in Nickel-based SOFC [17], the research in the material science field provides some alternatives (perovskite-based or non-nickel-based anodes [18,19], the modification of the anode surface with other active oxides [20]), but all of them are not yet ready for a market-scale production.

As classified in [21], SOFC NiYSZ-anodes degradation might appear according to three kinds of mechanisms: deactivation and passivation, material transport and thermomechanical mechanisms. Because of either impurities deposition on the cell active surface or issues related to the catalyst, a worsening of cell performances is directly detectable over the time.

With regard to the deposition of poisonous compounds on Nickel catalysts, two issues are widely debated: sulphur [22,23] and carbon deposition (also referred to as coking). Specifically, coking is introduced as one of the main danger arising when fuels containing light hydrocarbons (i.e. methane) are used [24].

The chemistry of this phenomenon is complex, but it could be simplified considering the reactions which are more likely to occur, according to kinetic aspects [25]: Boudouard reaction (I), methane cracking (II) and heterogeneous water gas shift reaction (III).



The mentioned reactions lead to the deposition of solid carbon in the forms of graphite, nanotubes, whiskers (etc.), which then lay down on the Nickel particles surface reducing the catalyst active area. Besides the inhibition of the catalytic activity, solid carbon may either nucleate inside the catalyst grain causing the so-called metal dusting corrosion [26] and/or determine electrode pores occlusion, with subsequent local increase in the oxygen partial pressure and nickel re-oxidation [27].

Concerning the evolution of the catalyst phase, Nickel particles are subject to diffusion and agglomeration in the anode structure. This process is called sintering and it is one of the most prominent problem leading to the anode degradation. Because of the agglomeration of Nickel grains, the active area available for the electrochemical reactions at the TPBs decreases. Due to the same reason, less Nickel particles are connected to create a path for the charge transfer, resulting in a decrease of the cell conductivity. Moreover, a change in the catalyst particle size and distribution has also a repercussion on the electrode porosity. NiYSZ anodes are well-known to be sensitive to this kind of degradation; [28]

claims that this is related to normal ageing of the material, but in some cases, reactions occurring at the anode could favour a faster sintering.

At last, another issue has to be considered: the ageing of the Zirconia frame. Concerning SOFCs, state-of-the-art cells implement YSZ electrolytes and YSZ anode supports. Introducing extrinsic defects in the material through Y₂O₃ doping, two effects are sorted:

- trivalent Y³⁺ cations replace tetravalent Zr⁴⁺ cations, determining an oxygen vacancy (which is a defect with a positive charge). Consequently, the ionic conductivity for oxygen anions, which is proportional to the defects concentration in the material, increases.
- Zirconia phase is fully stabilized in the tetragonal phase (t-ZrO₂), which normally does not exist at temperatures lower than 1000 °C, where the monoclinic form (m-ZrO₂) is the most stable polymorph. t-ZrO₂ has a more compact structure and, for this reason, the distance between two reticular sites is shorter if compared to m-ZrO₂. Thereby, the energy required to move an oxygen anion to one site to another is lower, enhancing the ionic conductivity.

YSZ is subject to ageing phenomena which appear as a loss of ionic conductivity during operation at high temperature. Usually, ionic conductivity worsens as the lattice structure is facing relaxation [29]. Moreover, thermal or mechanical stresses could be the cause of a martensitic transition from the tetragonal to the monoclinic phase, which is also accompanied by a significant increase in volume [30].

1.2. Enhance SOFC tolerance to high-methane gases: a thermodynamic approach

The employment of carbonaceous fuels on SOFCs mainly brings to coking. According to thermodynamic predictions, coking is contrasted as long as oxygen-to-carbon ratio (O/C – for the rigorous definition, see Eq. (1) in Section 2.2) is increased in the anode gas mixture [17]. Therefore, when natural gas and biogas are fed to a SOFC, the regulation of the oxygen-bearer species concentration adjusts the fuel O/C on a favourable value. On one hand, in the event of a lack of oxygen, O/C regulation is achieved through air, steam or CO₂ addition. On the other hand, when biogas is used, CO₂ partial separation might be required, for the same purpose.

Oxygen-bearer gases promote the decomposition of methane into hydrogen and carbon monoxide, which are easily converted in the fuel cell. The decomposition of methane can be described in terms of partial oxidation (IV), steam (V) and dry methane reforming (VI).



Download English Version:

<https://daneshyari.com/en/article/765011>

Download Persian Version:

<https://daneshyari.com/article/765011>

[Daneshyari.com](https://daneshyari.com)