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Durability of anode supported Solid Oxides Fuel Cells (SOFC) under direct dry-reforming of methane

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HIGHLIGHTS

► Durability of Ni-YSZ conventional anode supports under dry-reforming.

► Direct dry-reforming of methane in SOFCs.

► Carbon formation mechanics and morphology within Ni anodes fed by dry methane.

► CO₂ mitigation for carbon formation in SOFC anodes.

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ABSTRACT

The present work investigates the performance and degradation mechanisms of a Ni-based anode supported Solid Oxides Fuel Cells (SOFC) operating at ~800 °C on direct internal reforming of dry CH_4-CO_2 mixtures. The catalytic properties of the anode support were first studied in a micro-reactor configuration to determine safe conditions (i.e., without carbon formation) under which a dry conversion of the methane can occur directly *within* the fuel cell. A full electrochemical characterization of complete cells followed to preliminarily assess their resistance towards carbon formation when operating on direct dry-reforming. Ageing tests of ~300 h each have been performed in galvanostatic mode, with impedance spectra taken every 50 h of continuous operation to monitor the trend over the time of the different polarization contributions. *Post-mortem* microstructural analysis was carried out after each experiment to verify the morphology and nucleation of carbon deposited in the anode electrode.

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1. Introduction

The study of the catalytic properties of SOFC Ni-based anodes is relevant for the development of high temperature fuel cells that can sustain direct internal conversion of the feeding fuel. In this case, the anode electrode not only provides the active sites for the electro-catalytic oxidation of H₂ (and CO), but also those promoting a full conversion of the fuel (CH₄, in this study). Ni appears to be a suitable candidate as it is a good electro-catalyst at SOFC relevant temperatures, as well as an excellent catalyst for heterogeneous gas reactions [1]. For instance, pellets consisting of Ni supported on Al–Mg oxides have been extensively used over the last decades within commercial reactors for hydrocarbon steamreforming and CO methanation [1–3].

* Corresponding author. E-mail addresses: lanzini.andrea@gmail.com, andrea.lanzini@polito.it (A. Lanzini). Following the considerations reported above, conventional Ni– YSZ anode supports appears to be able to sustain direct internal reforming, showing a high (selective) catalytic activity to convert methane in H_2 and CO, respectively.¹ (Low methane conversion rates would reduce system efficiency – assuming unconverted fuel leaves the SOFC – while also increasing the risk of carbon deposition in the anode.)

In the literature, Ni-based anodes have been already reported to have the capability to operate in direct internal reforming [4-11]. Steam-reforming reactions are those generally investigated. CO₂-reforming (also known as dry-reforming) represents an interesting option under the following circumstances: (i) the anode





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¹ Note that often the issue with Ni anodes it is not the slow reforming kinetics, rather the kinetics can be too fast resulting in a sudden cooling of the anode inlet region due to the strong endothermicity of the reactions involved. A local cooling of the anode can increase the risk of cracking of the thin electrolyte layer – due to excessive thermal gradients established across the fuel cell [4] – while also lowering average cell performance.