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.

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 CH4–CO2 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.

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 steam-reforming and CO methanation [1–3].

Following the considerations reported above, conventional Ni–YSZ anode supports appear to be able to sustain direct internal reforming, showing a high (selective) catalytic activity to convert methane in H2 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

1 Note that often the issue with Ni anodes 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.
exhaust is partially recirculated to convert the inlet fuel – therefore both H₂O and CO₂ becomes available for methane reforming; (ii) biogas is used as a fuel, hence a significant amount of CO₂ (ranging between 30 and 50 vol.%) is already available in the inlet feed stream.

The main concern that arises when the Ni phase in an SOFC anode directly deals with a carbon fuel (e.g., CH₄ or CO) is the risk of carbon deposition. Ni is indeed active towards catalytic steam and dry-reforming, but also toward carbon forming reactions. The two main reactions generally involved with carbon build-up in the Ni anode support are the following:

- **methane cracking**: CH₄ → 2H₂ + C(s);
- **Boudouard reaction**: 2CO → CO₂ + C(s).

### 1.1. Carbon formation

It is well known from the literature [12] that carbon can form with different morphology according to thermodynamic conditions, substrate and precursor. A rough distinction can be drawn among amorphous, filamentous and graphitic carbon [13]. The latter is generally found at higher temperatures and on low surface area catalysts (e.g., those employed in steam reforming reactors), while amorphous carbon is more likely to be found at lower temperatures and with higher surface area catalysts (e.g., those used for methanation reactors). Surface nickel carbide could also form on Ni at temperatures lower than 325 °C, which is of no interest for SOFC applications.

Considering that Ni–YSZ anodes have a relatively high surface area [14–16] and a nominal operating temperature of 750–800 °C (that could be reduced locally to 600–650 °C because of the endothermic reforming reactions), temperature and substrate conditions are such that amorphous carbon is the most favoured type to form on Ni-based anode supports.

Amorphous carbon can grow in different forms; a general distinction can be drawn between films and filaments. Filamentous (or vermicular) growth is often observed in SOFC anodes, even if it is likely that more types of carbon simultaneously form on the same structure. Bartholomew emphasizes how, at high temperatures, amorphous carbon can convert to the more high density graphitic forms while retaining its overall film or vermicular form [12].

Filamentous carbon represents a well-known form of carbon, which is able to deactivate a Ni catalyst. Baker et al. [13] devoted several studies to the growth and formation of carbon filaments, and described them as having a duplex structure, consisting of an amorphous core surrounded by a graphitic skin; a metal component is also present either as a particle at the head of the filament or as dispersion along the body of the filament. The appearance can be slightly different depending on the catalyst morphology (particle size, surface area, etc.). A typical appearance of carbon filaments is the whisker-like mode, where the catalyst particle is located at the filament head and has been carried away from the support surface during the growth process. The catalyst particles are encapsulated with a layer of carbon, which results in catalyst deactivation. This morphology was proposed by Baker et al. according to controlled oxidation studies of filaments produced from the interaction of nickel with acetylene. This study revealed that the various constituents of the C-deposit exhibited different oxidation rates. At 600 °C the central core oxidized first, causing some catalyst particles to fall down into the filament tube. Amorphous carbon was observed to oxidize under the same conditions. At 725 °C the filament skin started to oxidize and this action coincided with the onset of un-catalyzed gasification of graphite. According to Baker et al. [13], filamentous carbon has a high surface area which promotes the deposition of amorphous carbon, which fills the gaps between the catalyst particles. Therefore, for SOFC applications it is highly relevant to study how to avoid the onset of carbon filaments in the anode structure.

Rostrup-Nielsen et al. [17,13] studied extensively the mechanics of carbon formation; they found deviations from graphite equilibrium for CO and CH₄ decomposition on a large number of nickel catalysts in the temperature range of 450–700 °C [18], and observed whisker-like carbon formation. Rostrup-Nielsen et al. suggested that these deviations could be explained by the extra energy required by the surface and defect structure of the filaments.

Alstrup et al. [19] suggested a model for carbon filament growth. According to this model, an unstable carbide causes reconstruction of the Ni particle; a phenomenon which takes during an induction period. Subsequently, the carbide is decomposed into amorphous carbon, while some surface carbide is still present after the decomposition. In the steady-state growth period, the carbon atoms produced by the surface reaction diffuse rapidly through the surface carbide, maintaining a constant carbon concentration just below the selvedge. A gradient is therefore maintained, causing migration of carbon atoms to the rear end of the particle where they segregate on the interface between filament and particle.

Specifically for SOFC anodes, where the temperature range can be very wide (roughly 500–850 °C for planar-type cells), and the catalyst microstructure is generally quite complex and variable, it is certainly not straightforward to predict which kind (or form) of carbon will be produced once favourable thermodynamic conditions are established. In [20,21], following an exposure to dry methane at 1000 °C, carbon nanotubes (OD less than 50 nm) were observed on supported ZrO₂ catalysts, while bulky carbon filaments or fibres (OD ~ 3 μm) plus spheres agglomerates were both observed in the Ni–YSZ cermet. The explanation proposed by Takeguchi et al. [20] is that the growth of a carbon nanotube, with a diameter close to that of the Ni particle, can originate from supported fine Ni particles. In contrast, since the Ni–YSZ cermet is prepared from a powder mixture of NiO and YSZ calcined at 1400 °C, the Ni particles are too large to produce carbon nanotubes, but carbon in a vermicular or whisker like form can still grow.

Takeguchi et al. [21] pointed out that the Ni–YSZ cermet structure looks favourable for the growth of carbon fibres (also known as vermicular or whisker carbon). These authors proposed a carbon growth and formation mechanism involving: (i) the dissolution of adsorbed carbon atoms in the metal crystallite, (ii) diffusion through the metal and (iii) precipitation of carbon atoms at the rear of the metal particle to form a polymeric carbon filament, a process similar to that proposed by Baker et al.

### 1.2. Temperature programmed experiments

Temperature-programmed techniques provide a fast, effective experimental method to study several catalytic reactions over a wide range of temperatures. Temperature-programmed desorption, oxidation, reduction, etc., can be all employed to characterize various properties of a catalyst [22].

Concerning SOFC anode materials, temperature programmed oxidation experiments are generally employed to determine whether carbon is deposited during reforming reactions and in which amount; they are also used to speculate about the type of carbon deposited under severe conditions (dry carbon fuel without H₂O or CO₂). Baker et al. [23–25] studied the activity and deactivation of different anode materials using temperature programmed techniques. The experimental setup used in their work is similar to the one used in this study. In [23], Ni–YSZ cerments were exposed to dry methane; both temperature-programmed and isothermal reactions (TPRₓ and IsoT, respectively) with dry methane diluted in He were performed to characterize the catalytic behaviour of
the anode cermets. Temperature-programmed oxidation (TPO) and hydrogenation (TPH) were performed to speculate on the nature carbon formation on the Ni after an exposure to a carbon fuel and to quantify the overall amount deposited. Results showed that dry methane mostly undertakes the cracking reaction (Eq. (1)), decomposing into gaseous H2 and surface carbon species. The methane-cracking reaction is indeed favoured by the high temperature, with the conversion of methane starting roughly 300°C. In the 300–900°C temperature range, TPO spectra were collected after exposing each sample to a dry methane at a fixed temperature thus showing indeed a maximum quantity of carbon deposited right at 900°C. For isotherm exposures with the carbon-forming fuel above 700°C, two distinct CO2 peaks could be subsequently observed during the TPO; according to the authors, two different carbon species were formed on the Ni samples that were oxidized to CO2 at different temperatures (thus producing two peaks in the TPO experiment).

In [26], Arepo et al. showed how an addiction of H2 in a dry CH4 feed mitigates carbon formation. The hydrogen in the inlet stream easily adsorbs on the Ni surface, and reduces the catalytic active area available for methane decomposition.

2. Experimental

2.1. Micro-reactor apparatus for temperature-programmed experiments

The micro-reactor apparatus (Fig. 1) used for this study consisted of a quartz tube (OD 6 mm) 40 mm long, with a central enlargement to fix the catalyst (i.e., the catalytic bed). The tube was vertically inserted in an electrically heated furnace, regulated by a PID controller (Eurotherm, UK). The catalyst was loaded in the reactor bed, packed with a small amount of quartz wool; it consisted of small pieces of a fractured Ni-YSZ anode support2 (H.C. Starck, DE), for a total weight of 50–100 mg. A K-type thermocouple was placed adjacent to the catalyst bed, into the annular space between the reactor and the furnace, to monitor and control the catalyst temperature. A temperature difference of less than 1–2°C was measured between this thermocouple placed in the way just described, and another placed inside the catalyst bed.

Mass-flow-controllers (Bronkhorst, NL) were connected upstream of the quartz tube to produce gas mixtures with various compositions. The outlet of the catalyst bed was then connected to a quadrupole mass spectrometer (MS), ThermoScientific, UK.

To prevent carbon removal (and Ni re-oxidation) after treating the catalyst with the dry CH4 mixture, the catalyst volume was purged with pure Ar (or N2) right after the carbon fuel exposure. Two valves placed at both ends of the quartz tube were used to isolate (in a stagnant flow condition with inert gas atmosphere) the catalyst’s volume. Furthermore, by letting the bypass valve open for few seconds when purging with Ar, while leaving the valve at the other end of the quartz tube closed, a slight overpressure was established in the catalyst volume, preventing inward air leakage. Preliminary experiments showed that, if the catalyst was cooled down with flowing Ar (or N2), carbon was removed to some extent due to trace levels of O2. By isolating the catalyst volume according to the procedure just described, undesired carbon removal prior to TPO was minimized.

A nominal gas flow rate of 50 N ml min⁻¹ was used for all experiments within the micro-reactor apparatus, except for TPO experiments where a flow rate of 80 N ml min⁻¹ was used, yielding a space velocity through the catalyst bed of around 6.6 cm s⁻¹. Since the catalyst weight ranged between 50 and 100 mg, a gas residence time in the range of 1–2 × 10⁻³ g min cm⁻³ was fixed. Comparable values were used by Laosiripojana et al. [27,28] when studying the catalytic properties of SOFC anode materials in a similar experimental set-up.

The typology of experiments carried out in this study can be classified as follows:

- **Temperature-programmed reaction (TPRx)**: the catalyst temperature was steadily increased from room temperature up to 800–900°C at a rate of 10°C min⁻¹.
- **Isotherm reaction (IsoT)**: the catalyst was heated to the target temperature in either flowing H2–Ar or H2–N2. The carbon fuel mixture was then directly fed to the catalyst at this temperature, which was kept constant. This technique was specifically used to study the stability of the dry-reforming reaction (CH4 + CO2 → 2H2 + 2CO) over short periods of time.
- **Temperature-programmed oxidation (TPO)**: the temperature within the catalyst bed was increased from room temperature to 900°C at 10°C/min. The gas flowing in the catalyst bed was a mixture of 2 vol.% O2, balance Ar. The nominal gas flow rate was 80 N ml min⁻¹. The formation of carbon species on the catalyst surface was quantified by measuring the CO and CO2 production rates, originating through carbon removal via gasification (2C + O2 → 2CO) and oxidation (C + O2 → CO2), respectively.

Prior to both the TPRx and IsoT experiments, the catalyst was reduced through a temperature-programmed reduction (TPRd) in a 10 vol.% H2 mixture (balance Ar), with a stabilization period of 2–3 h at 800°C. The measured level of NiO reduction was around 95%, meaning that NiO was almost fully converted to Ni.3

Quantitative measurements of gas conversion within the catalyst bed were determined using the MS. Calibration curves for each gas were obtained prior to, and after, each experiment by separately feeding the MS with known concentrations of every gas. When the label ‘a.u.’ (meaning auxiliary unit) is shown in the vertical axis of graphs present in this work, raw intensity values

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2 The anode support is fabricated by tape-casting.

3 Ni reducibility was evaluated by calculating the ratio between the total H2 consumed during the temperature-programmed reduction (TPRd) of the NiO–YSZ sample and the stoichiometric amount required for a full reduction of the NiO to Ni.
acquired from the MS were used. When gas flow rates were shown instead, these were derived thanks to a calibration of the instrument toward known gas mixtures and thus the conversion of acquired MS intensity values in actual volumetric flow rates.

2.2. Test apparatus for electrochemical tests on single cells

A test rig consisting of two ceramic housings placed into an electrically heated furnace was used to characterize full (i.e., anode + electrolyte + cathode) planar-type anode-supported cells. Gas reactants were distributed through channels machined directly on one side of the housings, delivering the gas in radial direction from the centre to the outer zone (i.e., the border) of the cell. Electrons were collected through a Ni mesh on the anode side, and a Pt mesh at cathode. The present housings do not require sealing of the anode and cathode compartments; therefore, exhaust gases are allowed to burn at the outer border of the fuel cell. Various mixtures of H2, N2, CH4, CO2 and CO, were fed to the anode, and are allowed to burn at the outer border of the fuel cell. Various mixtures of H2, N2, CH4, CO2 and CO, were fed to the anode, and to the cathode, regulated by mass flow controllers (Bronkhorst, The Netherlands). Electrochemical characterization was carried out with an electronic load (Kikusui Electronics Corp., Japan), in conjunction with an additional power supply in current-following mode (Delta Elektronica, The Netherlands). Electrochemical impedance spectroscopy was measured with a Gamry FC 350 instrument (US) in a frequency range between 1 mHz and 300 kHz. More detail on this experimental apparatus can be found in [29,30].

The experiments were performed on circular seal-less anode supported planar cells of 80 mm diameter, with a screen printed cathode active area of ~47 cm². Every single cell consisted of the following layers: a 490–530 µm thick Ni–YSZ cermets porous anode support; a ~5 µm anode functional layer of the same material; a ~5 µm dense 8YSZ electrolyte; a 2–3 µm thick barrier layer of Yttria Doped-Ceria (YDC); a 33–35 µm cathode perovskite made of porous Lanthanum Strontium Cobalt Ferrite oxide (LSF).

In particular, the experimental analysis was performed in order to assess the long-term durability under direct dry-reforming of methane. Ageing tests in galvanostatic mode lasting ~300 h each were carried out by feeding the cell with mixtures having different CH4/CO2 ratios. The time-evolution of electrochemical processes was monitored, taking impedance spectra after every 50 h of operation to identify the different polarization contributions over time.

In particular, Fig. 2 shows how the higher the temperature in micro-reactor bed containing the catalyst (the SOFC anode support), the higher is the catalytic cracking of methane with production of H2 (yellow line) and carbon build-up on the Ni–YSZ microstructure. When cooling down the reactor, the reaction is no gradually suppressed: the CH4 (violet line) increases up to its reference value, i.e. with no methane conversion at all, whereas H2 goes to zero. Hence, it is important to avoid pure dry methane feeds (thus containing neither steam nor CO2) for Ni-based anode supports operating at 750–800°C.

After exposing a previously reduce anode sample at 800°C for 2 h, with the same dry feed as Fig. 2, a TPO experiment was conducted (Fig. 3) to study the formation of carbon over the anode surface. Three well-defined peaks were visible (CO2 peaks at ~555 and ~710°C, respectively; CO peaks at ~625°C). Each peak is related to either oxidation or gasification of previously deposited carbon onto the Ni–YSZ anode support. Interestingly, a similar C-removal pattern (i.e., same number of peaks at roughly same temperatures) was observed in an experiment (not shown) carried out on calcined Ni–YSZ powder (sieved at 250 µm) that had been exposed to the same experimental conditions (carbon-deposition during the IsoT experiment and subsequent removal with TPO) under the same experimental apparatus used for all experiments discussed present study. Owing to the observed carbon oxidation patter in TPO experiments, different carbon is deposited on the Ni–YSZ catalyst regardless its microstructure (Ni–YSZ tape-casted anode support vs. calcined 250 µm sieved Ni–YSZ powder). In it was found that carbon is removed from Ni-catalyst in a temperature range of 450 – 650°C, which is quite similar to what observed in this study.

According to quantitative measurements, the total carbon deposited in Fig. 3 was ~19 mg with an initial catalyst weight (before reduction and carbon exposure) of ~70 mg.

In Fig. 4a, a TPRx at 800°C for a CH4:CO2 1:2 vol. fuel mixture is given. CO2 in excess is provided to produce a ‘safe’ dry-reforming condition, i.e. not prone to form carbon onto the anode support.

3. Results

3.1. Experiments in the micro-reactor apparatus

Experiments in micro-reactor on samples were conducted prior to the electrochemical tests on full cell in order to preliminarily investigate the catalytic properties of the Ni-based anodes towards dry-reforming and carbon forming reactions.

In Fig. 2, Isotherm experiments with a pure dry methane mixture (10% CH4, balance Ar) are shown. Trends clearly indicates how the methane cracking reaction (CH4 → 2H2 + C(s)) is favoured by the high temperature as predicted by thermodynamic equilibrium considerations. In particular, Fig. 2 shows how the higher the temperature in micro-reactor bed containing the catalyst (the SOFC anode support), the higher is the catalytic cracking of methane with production of H2 (yellow line) and carbon build-up on the Ni–YSZ microstructure. When cooling down the reactor, the reaction is no gradually suppressed: the CH4 (violet line) increases up to its reference value, i.e. with no methane conversion at all, whereas H2 goes to zero. Hence, it is important to avoid pure dry methane feeds (thus containing neither steam nor CO2) for Ni-based anode supports operating at 750–800°C.
based on thermodynamic equilibrium calculations. As shown in the graph, no conversion of methane with CO$_2$ is observed below 500 °C ca.; the almost horizontal lines of CH$_4$ and CO$_2$ on the left side of the graph show this. When the temperature in the micro-reactor fixed-bed rises above 500 °C, methane conversion with CO$_2$ starts according to the dry-reforming reaction (CH$_4$ + CO$_2$ → 2H$_2$ + 2CO). Thus methane and carbon dioxide are gradually consumed while H$_2$ and CO are produced (see the right side of the graph in Fig. 3a).

An almost full conversion of methane is observed at a temperature above ~700 °C. The conversion of methane essentially follows the stoichiometry of the dry-reforming reaction, with only negligible reverse water gas shift reaction occurring (RWGS: H$_2$O + CO → H$_2$ + CO$_2$); this can be observed in Fig. 4b where the CH$_4$ feed is fully converted consuming an almost equal amount of CO$_2$, while the excess CO$_2$ remains unconverted.

Similar results (not shown) were obtained with CH$_4$:CO$_2$ mixtures 1:1 and 1:1.4 vol., respectively. The methane feed always resulted fully converted with excess CO$_2$ (in case of the 1:1.4 vol. mixture) unconverted.

In Fig. 4b, an IsoT at 800 °C is given for a sample exposed to a CH$_4$:CO$_2$ 1:1.4 vol. feed gas composition. The conversion of CH$_4$ with CO$_2$ is stable, with an almost equi-molar production of H$_2$ and CO.

TPO experiments (Fig. 5a–c) were conducted on anode samples previously exposed for ~2 h to a pure dry methane feed; total flow rate is 80 Nml min$^{-1}$, with a gas composition of 2 vol.% O$_2$, balance Ar.

200–300 nm. The filaments clearly originate from Ni particles within the anode support structure.

3.2. Full electrochemical characterizations

The galvanostatic cell behaviour for the equi-molar CH$_4$–CO$_2$ feed (test #1) is shown in Fig. 7. After a relatively short period of initial stable performance, the cell voltage (dark blue line) steadily decays over the time; after ~250 h of test a non-linear and even steeper degradation of the cell voltage occurs. Carbon formation in the anode electrode of the fuel cell is clearly observed in the post-mortem analysis, whose results will be provided in detail in what following in this work. The formation of whiskers in the anode electrode is clearly detrimental to the fuel cell performance; carbon plugs the pores of the anode electrode	extsuperscript{4} thus enhancing mass transport limitation (in fact, the gas reactant has to flow through the 500 μm thick anode support before reaching the active sites of the electrode, the so-called three-phase-boundary region located in proximity of the electrolyte). Also, the Ni active sites for the direct reforming of CH$_4$ in H$_2$ and CO are gradually deactivated as a consequence of carbon formation/deposition; the catalytic active area is indeed reduced by encapsulation and/or coverage of Ni particles by carbon ones. The lower CH$_4$ conversion into H$_2$ and CO has a negative effect on the fuel cell performance due to the reduced ability of Ni to toward direct CH$_4$ electro-oxidation.

(The initial and final voltage trend observed in Fig. 7 is related to the start-up and shut-down of the fuel cell, respectively; during the start-up phase, the OCV exceeds that measured at 800 °C because of the peculiar temperature-dependency of the Nernst voltage, which is higher at lower temperatures considering for

\textsuperscript{4} A mean pore size of ~1 μm with an overall porosity of ~30% is given in [15] for the same anode support used in this study. More details about the morphology of the full anode-supported cells studied in this work can be also found in [15]. The thick anode support is covered by a 10 μm active layer with a similar Ni granulometric distribution, but definitely less porous.
example the hydrogen oxidation equilibrium electrochemical potential.)

Fig. 8 shows the evolution of impedance spectra measured during the experiment shown in Fig. 7 (EIS data are measured at regular intervals of 50 h each, with the ‘0 h’ curve showing the cell performance at beginning of the dry-reforming experiment, after the initial stabilization phase in H₂ fuel).

In a commercial size anode-supported fuel cell, as the one here investigated, three main potential losses are recognized [32,33], which are related to (i) materials and interfaces ohmic resistances due to the transport of ions and electrons through them; (ii) concentration polarizations that are caused by the resistance to fuel and oxidant mass transport through the electrodes; (iii) activation polarizations related to the electrolyte/electrodes electrochemical reactions. Impedance diagrams (such as the one in Fig. 8) can provide a breakdown of the total loss (polarization) into an ohmic resistance, \( R_s \), measured at high frequency, and a polarization resistance, \( R_p \), measured at medium and low frequency, reflecting losses due to chemical, electrochemical, and transport processes. In particular, the first intercept of the EIS curve on the real-axis gives the overall ohmic resistance of the cell; the first (and smaller) circle found in the medium-to-high frequency range can be attributed to activation losses, while the second (and bigger) circle found at
lower frequencies is connected to mass transport limitations in the fuel cell electrodes, especially in the thick anode support for the cells investigated in this study.

Looking at Fig. 8, cell degradation appears to be connected with an increase of all of three polarization contributions just mentioned. During the first 200 h of operation, the overall degradation rate is rather constant and certainly caused also by physical processes having a response in the medium to high frequency range, related to charge transfer. Severe mass transport limitations occur after 250 h of operation (red curve in Fig. 8), when the anode support is plugged with carbon and the reactant flow is somehow limited/prevented to reaching the electrochemical active sites found in proximity of the electrolyte interface. Notably, also the ohmic resistance of the cell is steadily increasing over the time (look at the gradual shift over the time and toward the right of the first intercept on the real-axis of the measured spectra). Being the Ni anode relatively thick, a gradual coarsening of the Ni phase of the electrode – accelerated by dry-reforming [34,35] – may be easily responsible of such increased ohmic resistance of the fuel electrode.

The steady accumulation of carbon deposition over the Ni catalyst is therefore responsible for an enhanced mass transport limitation in the anode support, but also for deactivation of the catalyst in term of electrical, catalytic and electrocatalytic activity.

Post-mortem SEM observations of the anode electrode (top view) tested with an equi-molar CH4–CO2 mixture confirmed that a copious amount of carbon whiskers formed inside the anode structure (Fig. 9). By visual inspection of the cell after the test, a circular black area of ~2 cm in diameter appeared in the fuel inlet region, confirming that a conspicuous amount of carbon was formed. Most probably, the fast catalytic dry conversion of methane lowers the gas and fuel cell temperature at cell inlet region, where carbon is then formed due to the favourable thermodynamic conditions.

Not surprisingly, carbon deposits were especially found on the outer layer of the anode substrate, in the proximity of the fuel distribution channels. Otherwise, the anode/electrolyte interface was ‘clean’ (SEM micro-graphs for this region are not given here) and no carbon was found by microstructural analysis.

FE-SEM observations (Fig. 10) revealed that the carbon filament diameter ranged between 30 and 40 nm; in agreement with studies previously reported in the literature [13].

FE-SEM observations also contributed to both clarify the morphology of carbon filaments as well as the whisker nucleation from the Ni structure (Fig. 11). Fig. 11a shows a carbon filament with a catalyst particle at its head (conventional or whisker-like growth), whereas Fig. 11b shows nucleation from a catalyst particle (extrusion filaments).

In Fig. 12, the galvanostatic behaviour of a cell operated with a CO2-rich (CH4:CO2 1:2 vol.) dry methane mixture (test #2) is given. Cell degradation takes place with a slope only slightly less pronounced than the CO2-lean mixture of test #1 (Fig. 8), followed however by sudden voltage decay after 200 h of operation.

In Fig. 13, EIS spectra acquired during the galvanostatic experiment of Fig. 12 are also given. As for the previous test (#1), a gradual increase of ohmic and the activation losses is observed, suggesting an on-going deactivation of the Ni (electro-)catalyst. Concentration losses remain almost unchanged in the first 150 h of test, suggesting that carbon build-up is almost not occurring. This is consistent with the post-mortem analysis. Carbon deposition was indeed not observed in the anode support of Figs. 12 and 13 (neither by visually inspecting the cell right after the test, nor through a detailed post-mortem microstructural analysis carried out on the same). Hence, even though CO2 addition effectively prevented carbon deposition (also in agreement with test results from the micro-reactor configuration), long stable cell operation was not achieved due to catalyst deactivation by direct-reforming reactions.

In a previous work [7], with identical cell and testing apparatus, a stable performance for ~100 h (with basically no degradation) was observed with a CH4:CO2 1:1.5 vol. mixture and operation at
a current density of 0.5 A cm$^{-2}$ and 33% FU. Even though the period investigated was too short to observe severe degradation effects caused by prolonged exposure to a carbon-rich fuel, the operation at reduced FU was enhancing the life-time of the fuel cell. The seal-less experimental set-up used for the characterization of planar anode-supported cells studied in this work, and also in [7], clearly suffers at high FU operation; in fact, the outer border of the anode supports corresponds also to the outlet channel of the anode feed, which is exposed to the oxidant atmosphere of the oven and some cathode air back-flow toward the anode chamber (note the due to $N_2$ dilution of the oxygen feed, the cathode volumetric flow rate is always higher than the anode one, for all experiments). The above-mentioned aspects are all co-responsible for an high p(O$_2$) that causes re-oxidation of the Ni found on the edge of anode. During long-term tests at high FU (Figs. 7 and 12), the observed severe degradation of the cell performance – roughly after 200 h of continuous test – might be well related to a mechanical failure of the cell, with cracks originating from the border of the cell, where Ni re-oxidation produces a local change in the volume of the anode support.

In Fig. 14 an ageing test investigating a variable CH$_4$:CO$_2$ volumetric ratio during the same experiment is shown. The direct-reforming test started with the CO$_2$-rich mixture (CH$_4$:CO$_2$ 1:2 vol.) – not prone to carbon deposition – followed by the CH$_4$:CO$_2$ 1:1.5 vol. mixture and eventually the equi-molar CO$_2$-lean feed. Each fuel composition was tested for almost 100 h, with on overall experiment lasting more than 350 h. Degradation occurs with the CO$_2$-rich mixtures, but is almost stopped when feeding the anode with an equi-molar composition. Results of Fig. 14 clearly indicate that an excess of CO$_2$ does not help in reducing degradation of the fuel cell. Anode re-oxidation at the edge of the fuel cell is promoted by the excess of CO$_2$ since the latter contributes to producing an even more oxidizing atmosphere. Carbon formation, which should be relevant for the equi-molar feed according to previous catalytic tests, could be observed on the anode outer surface only in a very limited amount, mostly concentrated at the centre of the cell and thus corresponding to the fuel inlet region. The steam and CO$_2$ produced by the electrochemical reactions along the fuel electrode indeed gradually shifts the inlet feed mixture to a composition safer in term of carbon formation.

4. Discussion

The properties of a commercial Ni–YSZ SOFC anode electrode were studied first in term of its catalytic activity toward selected dry reactions and subsequently in term of its combined catalytic and electrocatalytic behaviour during fuel cell relevant operating conditions.

Ni-based SOFC anodes, operating at 750–800 °C, are active towards the catalytic conversion of dry methane mixtures either via carbon-forming reactions (mostly methane cracking,) or via dry-reforming – provided that CO$_2$ is also available with the fuel, as for biogas coming from anaerobic digestion processes. Catalytic experiments carried out on Ni–YSZ anode supports (i.e., temperature programmed reactions in a micro-reactor configuration) as well as full electrochemical characterization of complete cells
consisting of the same anode supports, showed that CO₂ addition mitigates against carbon deposition, potentially obviating the risk of carbon build-up in the Ni-based anode supports. Therefore, ensuring that a proper amount of an oxygen carrier (CO₂, in this case) is present within the methane feed is crucial to avoid carbon formation during direct reforming operation. However, gradual catalyst deactivation occurs regardless the amount of CO₂ available. Actually, an higher amount of CO₂ is not beneficial.

The full direct dry-reforming option thus remains a challenge for Ni-based SOFC anode-supported cells. Regarding the role of CO₂, even if it effectively help in mitigating carbon deposition, the Ni catalyst results gradually deactivated by direct dry-reforming reactions. In addition, an excess of CO₂ might increase the risk of Ni re-oxidation in portions of the anode H₂-lean.

Developing more robust anode electrodes, or understanding the degree of direct internal reforming that is sustainable for stable operation are of interest for further studies around the topic of direct dry-reforming in SOFC. This topic has a practical relevance especially for biogas fed fuel cell systems [36–39]: for instance, a biogas rich in CO₂ could feed the SOFC directly without the need of an external reformer section or in case of a methane-rich biogas, the dry-reforming reaction could be promoted by the recirculation of a fraction of the anode exhaust (that is rich in H₂O, but also CO₂). Also, using the CO₂ for reforming in a SOFC might become a good alternative to steam, whose management is generally more complex in term of BOP, especially if an external water source has to be used.

5. Conclusions

The influence (and role) of CO₂ in dry CH₄/CO₂ anode feeds with regard to degradation issues of Ni-based anode-supported SOFC was investigated in the present work. The mitigation effect of CO₂ toward carbon deposition in Ni anodes exposed to dry CH₄-CO₂ feeds, was studied in detail thanks to catalytic and electrochemical experiments. According to thermodynamic equilibrium calculations, at 800 °C a CH₄:CO₂ 1:2 vol. ratio in the anode feed should be sufficient to avoid solid carbon formation. Experiments indeed showed the higher the amount of CO₂ in the anode gas composition, the less carbon was formed. Still, a gradual deactivation of the Ni catalyst was observed during electrochemical experiments. Therefore, assuring a carbon-free operation is not the only issue to be solved during direct dry-reforming. The observed increase of ohmic and activation polarizations in EIS experiments suggests that a gradual deactivation of the Ni (due to accelerated coarsening) is also playing an important role as major source of electrode degradation. Future work will aim to understand (i) the degree of direct dry-reforming that may be tolerated by a Ni anode-supported SOFC; (ii) the optimal amount of oxygen carrier (CO₂, H₂O or O₂) to feed to a biogas stream in order to promote a durable direct fuel conversion.

Part of this work has been also devoted to the study of carbon formation in the Ni–YSZ anode under dry feeds of methane. TPO experiments revealed a peculiar oxidation (and gasification) pattern for the C removed, which is consistent with the morphology observed in SEM and FESEM micro-graphs, and with relevant literature describing carbon whiskers as filaments with a dual structure, converted (during a TPO) to either CO or CO₂ at different temperatures (CO peaks at ~625 °C, while CO₂ peaks at ~555 and ~710 °C, respectively). Post-mortem analysis of the tested Ni–YSZ samples and anode-supported cells also well elucidated the morphology of the carbon filaments formed, as well as the mechanisms of carbon interaction with the Ni metal catalyst particles.

References