



Testing Novel Nickel and Cobalt Infiltrated STN Anodes for Carbon Tolerance using In Situ Raman Spectroscopy and Electrochemical Impedance Spectroscopy in Fuel Cells

Drasbæk, D. B.; Traulsen, M. L.; Walker, R. A.; Holtappels, P.

Published in:
Fuel Cells

Link to article, DOI:
[10.1002/fuce.201800193](https://doi.org/10.1002/fuce.201800193)

Publication date:
2019

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Drasbæk, D. B., Traulsen, M. L., Walker, R. A., & Holtappels, P. (2019). Testing Novel Nickel and Cobalt Infiltrated STN Anodes for Carbon Tolerance using In Situ Raman Spectroscopy and Electrochemical Impedance Spectroscopy in Fuel Cells. *Fuel Cells*, 19(4), 484-493. <https://doi.org/10.1002/fuce.201800193>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Testing Novel Nickel and Cobalt Infiltrated STN Anodes for Carbon Tolerance using *In Situ* Raman Spectroscopy and Electrochemical Impedance Spectroscopy

Daniel B. Drasbæk^{1*}, Marie L. Traulsen¹, Robert A. Walker², Peter Holtappels¹

¹Department of Energy Conversion and Storage, Technical University of Denmark, DTU Risø Campus, Frederiksborgvej 399, 4000 Roskilde, Denmark

²Department of Chemistry & Biochemistry and Montana Materials Science Program, Montana State University P.O. Box 173400 Bozeman, MT

[*]Corresponding author: dadr@dtu.dk

Abstract

Conventional SOFCs use Nickel Ytria-doped Zirconia cermet anodes, which are susceptible to degradation due to coking when operating with carbon containing fuels. Raman spectroscopy is a powerful tool for investigating surface chemistry and, when combined with electrochemical impedance spectroscopy under *in situ* conditions, the technique can report the real-time material composition of the electrode during the EIS measurements. Studies described in this work used *in situ* Raman spectroscopy and electrochemical impedance spectroscopy to examine the carbon tolerance of novel ceramic anode materials comprised of niobium doped strontium titanate infiltrated with nickel or cobalt nanoparticles. The susceptibility of these electrodes to coking were tested with CO/CO₂ mixtures and pure methane at 850°C. Data show that nickel-infiltrated STN electrodes are still prone to coking

This is the author manuscript accepted for publication and has undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the [Version of Record](#).

Please cite this article as [doi: 10.1002/fuce.201800193](https://doi.org/10.1002/fuce.201800193)

This article is protected by copyright. All rights reserved.

from methane. In contrast to STN electrodes infiltrated with nickel, cobalt-infiltrated STN electrodes showed no susceptibility to carbon deposition during methane exposure within the detection limit of the Raman measurements. Neither anode showed evidence of coking from the CO/CO₂ mixtures. Coking correlated closely with changes in EIS measurements, with the most noticeable effects appearing in the low frequency part of the spectrum. *Ex situ* SEM analysis of samples before and after operation illustrates the growth of the nanoparticles.

Keywords: Novel SOFC Anodes, *In situ* Raman spectroscopy, Hydrocarbon Fuel, Coke Formation, Nanocatalysts, Electrochemical Impedance Spectroscopy, Solid Oxide Fuel Cell.

1 Introduction

Solid oxide fuel cells (SOFCs) are able to electrochemically oxidize a large variety of fuels. The state of the art nickel yttria-doped zirconia cermet (Ni-YSZ) anodes are effective electrocatalysts for the oxidation of fuels such as H₂ and syn gas, but they are susceptible to degradation in performance due to redox cycling and poisoning by impurities such as sulphur [1]. Furthermore, conventional SOFC anodes will, when operated with carbon containing fuels, degrade due to the formation of carbon deposits on the electrode surface in a process often described as coking [2].

For several decades, research efforts have been directed towards the development of novel anode materials that are resistant to coking. One family of materials is based on donor-doped strontium titanate (SrTiO₃). These perovskite ceramics are expected to be resistant to conventional SOFC anode contaminants, since they are tolerant to both carbon and sulphur impurities in the ambient fuel atmosphere. Furthermore, they have a high electronic

conductivity and are redox stable [3-6]. Strontium titanate based anodes, however, have two major drawbacks: first, they have poor electrocatalytic activity towards fuel oxidation and second, they suffer from low ionic conductivity [4]. Current strategies for overcoming these drawbacks include designing infiltration procedures that introduce ionic conductivity and enhance the electrocatalytic activity for fuel oxidation. Recent work reported by T. Ramos et al. showed that materials such as B-site deficient $\text{Sr}_{0.94}\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_3$ (STN94) could compete with state of the art Ni-YSZ cermet electrodes, if an electrocatalyst like ruthenium or palladium and a mixed ionic electronic conductor such as gadolinium doped cerium oxide (CGO) were co-infiltrated into an STN scaffold [7-8]. Unfortunately, both ruthenium and palladium are precious metals and hence too costly to be used in any commercialization strategy. Instead, a low cost electrocatalyst would be better suited, hence the challenge to discover non-expensive, transition metals that can serve as effective electrocatalysts. Drasbæk et. al [to be published] have indicated that transition metals such as nickel and cobalt infiltrated into newly designed ceramic electrodes have similar electrocatalytic activity to state of the art Ni/YSZ cermet electrodes.

The studies of coke-induced degradation in SOFCs have mostly been based on a coupling between *in situ* electrochemical data and extensive *ex situ* measurements performed after the cell has cooled down and been disassembled. Even though these studies have provided useful information concerning the conditions responsible for sustained and stable SOFC operation, the studies themselves leave unanswered many questions regarding coking mechanisms and their direct impact on electrochemical performance. Specifically, most studies have not provided direct correlation between coking and the electrochemical performance motivating the need for direct or *in situ* studies that directly correlate material changes during operation with a device's electrochemical performance [9-13].

Vibrational Raman spectroscopy is a promising technique because of its ability to identify noninvasively chemical species present in SOFCs during operation. In addition, by measuring the Stokes-scattered light in the visible spectrum, vibrational Raman spectroscopy circumvents the challenges of having to identify small material specific signatures on top of the large blackbody emission emanating from the SOFC. This capability is particularly valuable if material changes occur only during operation and are not preserved when the device returns to room temperature [14]. Furthermore, in combination with microscope optics, Raman spectra with a spatial resolution as fine as $\sim 1 \mu\text{m}$ can be obtained and finally, Raman spectroscopy is able to identify molecular and material species and their rates of formation/disappearance with temporal resolution down to one second or even faster [15].

2 Experimental

2.1 Scientific Approach

The scope of the current study is to investigate the electrochemical performance and coking tolerance of novel STN based electrodes at open circuit potential (OCV) conditions.

Combined Raman and EIS measurements compare the spectroscopic and electrochemical behavior of SOFCs having STN electrodes infiltrated with nickel and cobalt nano-catalysts added to improve electrocatalytic activity. Notably, the nanosized electrocatalyst was, in this work, infiltrated without co-infiltrating CGO, since CGO itself increases an electrode's coking tolerance [7-8]. By infiltrating the transition metals without CGO, experiments are able to isolate the impact of the individual transition metals to the electrode's overall coking tolerance.

2.2 Experiment

For fabrication of the symmetrical cells the STN94 ink was spray deposited onto a pre-sintered 230-250 μm thick Sc_2O_3 , Y_2O_3 co-stabilized ZrO_2 (ScYSZ) electrolyte and sintered at 1200 $^\circ\text{C}$, for 8 hours in air. The sintered electrode thickness ranged between 20 and 40 μm . After sintering, the 5.3 cm \times 5.3 cm cells were laser cut into smaller pieces of 0.6 cm \times 0.6 cm. The symmetric cells were infiltrated with the electrocatalysts by a wet infiltration procedure, where a drop of the metal nitrate solution is placed upon the surface of the cell for approximately one minute and an absorbent laboratory tissue was then used to absorb excess liquids. Capillary forces drive a uniform distribution of the infiltration solution throughout the porous structure. Both sides of the symmetric cell were subjected to this procedure before the cell was heated to 350 $^\circ\text{C}$ for 30 minutes in order to decompose the nitrates and evaporate the impregnation solution. Afterwards, the cells were wiped off, using dry absorbent laboratory tissues, to remove residues from the surface, and then infiltrated again. This wet infiltration procedure was repeated three times in total, with the last heat-treatment step prolonged to two hours. The infiltration procedure resulted in an average weight gain of 0.86 wt% for the nickel oxide infiltrated cells and 0.71 wt% for the cobalt oxide infiltrated cells, relative to the total mass of the cells.

Before the *in situ* Raman experiment, a layer of platinum paste was painted onto each side of the cell, to act as current collecting layer and platinum wires were attached in order to connect to the external circuit. However, an electrode area of approximately five mm^2 was left unpainted, in order to ensure that the incident laser light used for Raman studies could probe the electrode surface. One important point to note is that the electrode does not contain either an ionic conductor or a mixed ionic electronic conductor. Consequently, the triple phase boundary of the electrodes is constrained to the interface between the electrolyte and the

electrode, and overall electrochemical performance is expected to be lower than state of the art SOC fuel electrodes and contribute to an increase of the observed polarization resistances throughout the experiment.

Characterization of sample microstructure and composition before and after testing was carried out using scanning electron microscopy (SEM) combined with energy dispersive spectroscopy (ZEISS Merlin, Carl Zeiss, Germany). The microstructure of the cells were investigated using a broken cross-section, without any pretreatment of the samples. The samples were examined prior to and after operation.

The *in situ* Raman data were obtained using a Renishaw InVia Raman spectrometer system coupled with a Linkam heat-stage that allowed for control of temperature, gas-composition and the electrochemical polarization. The Raman spectrometer was equipped with a 532 nm diode laser and laser power in the $\sim 1\mu\text{m}$ diameter beam spot was less than 8 mW. The Stokes scattered Raman light from the sample was collected and dispersed onto the CCD detector of the spectrometer.

Throughout the *in situ* Raman experiments, electrochemical measurements were performed using a Gamry Reference 600 potentiostat. Electrochemical impedance spectroscopy data were acquired under open circuit potential, with a 25 mV amplitude, between 0.1 Hz-1.0 MHz, with 10 points/decade for reference measurements repeated several times during the experimental procedure. When performing temporal investigations, the same settings as for the reference measurements were applied, however the frequency range was reduced to 0.5 Hz-1.0 MHz.

Through the experiments, the cells were exposed to synthetic air (20% O₂ and 80% N₂), humidified hydrogen (3% H₂O/H₂), 50% CO₂/CO and pure methane, all with a total gas flow

of 1.8 L hr^{-1} at ambient pressure. Before and after each experiment with carbon containing atmospheres, reference measurements were performed with humidified hydrogen in order to confirm continued cell performance and identify if any degradation had taken place.

The experimental procedure of the *in situ* Raman experiment consisted of heating the cells in synthetic air to $850 \text{ }^\circ\text{C}$. When the operational temperature was reached, the cells were reduced using humidified hydrogen and the reference cell performance was measured with electrochemical impedance spectroscopy. Following the reference measurements, the atmosphere was changed to 50% CO_2/CO in order to investigate the general performance using CO as fuel, under open circuit potential and to confirm that carbon was not forming via the Boudouard reaction [16]. The atmosphere was then changed back to humidified hydrogen for reference measurement of the performance and establish that exposure to CO_2/CO did not compromise cell performance. Finally, the atmosphere was changed to pure methane in order to characterize the cell's tolerance to coking. The duration of the methane exposure varied, depending on the cell's EIS diagnostics under conditions known to promote aggressive coking on traditional Ni-YSZ anodes. After the coking tolerance of the cells had been tested, the atmosphere was returned to humidified hydrogen for 20 minutes before a final reference measurement was performed. The cells were then re-oxidized for comparison with the original surface chemistry and afterwards cooled to room temperature for *ex situ* analysis.

During the different gas exposures, Raman spectra were acquired continuously with a 30 seconds exposure time per spectrum. Reference Raman measurements of cell surface composition were acquired with a 60 second exposure. Raman data were analyzed and plotted using Origin 2018. The background was subtracted from the data using a built-in background subtraction algorithm to more precisely identify peak positions and linewidths and to facilitate comparison between spectra. Furthermore, a MatLab script was developed for the analysis of

Raman peak intensities as a function of time. Impedance data were analyzed using impedance transforms in the Python based software RAVDAV developed by C. Graves [17]. All impedance spectra were corrected for stray inductance that was calculated using the Kramers-Kronig procedure and afterwards subtracted from the data.

One notable observation was that when carbon accumulated onto the anode surface, deposits took the form of well-known graphitic carbon structures [18]. These structures give rise to two specific Raman signals, commonly known as the G-band (at 1580 cm^{-1}) and the D-band (at 1350 cm^{-1}). The G-band is due to the E_{2g} mode associated with the ‘breathing’ of the carbon ring in graphitic carbon. The D-band originates from the sp^2 hybridized graphitic structures having numerous grain boundaries and/or site defects [18]. At the elevated operation temperatures, Raman features are expected to shift towards lower energies due to the thermally induced lattice expansion [19].

3 Results and Discussion

STN has several well-defined features in the room temperature Raman spectrum. However, at 850°C , these features lose resolution and devolve into three broad peaks (centered at 400 , 770 and 1020 cm^{-1}) but the consistent appearance of these features ensured that observations made during experiments were not instrumental artifacts. For the nickel infiltrated STN cells, nickel oxide was not observed directly in the Raman spectra, despite bulk NiO having a strong vibrational signature at 1060 cm^{-1} [20]. However, the presence of NiO was inferred from the coke that formed during exposure of the reduced anode to methane and from the *ex situ* EDS and SEM measurements performed after experimental operation. Notably, STN has no catalytic activity for fuel oxidation and is not expected to promote coking.

During exposure to 50% CO₂/CO, no coking was observed in the Raman spectra for the nickel nanoparticle infiltrated cells, as seen in figure 1a, an observation consistent with thermodynamic expectations [16]. Nevertheless, when exposed to 50% CO₂/CO a slow, steady increase in polarization resistance was observed in the impedance data, following a discontinuous fast rise in polarization resistance at the start of CO₂/CO exposure. The steady increase in polarization resistance, observed in figure 1b, is not related to a change in atmosphere as it occurs after the change from humidified hydrogen to 50% CO₂/CO. Instead, the slow, steady rise in polarization resistance is believed to result from one of three sources: a long period required for cell stabilization with changes in pO₂, irreversible agglomeration of the nickel nanoparticles, and/or coking is occurring at levels below the detection limit of the Raman microscope. The latter is improbable since the formation of CO is thermodynamically favored over carbon formation at 850 °C. However, it can be observed that the increase in polarization resistance almost behaves asymptotically, but towards a linear increase instead of a constant value (figure 1c). It is known from previous work by Drasbæk et. al [to be published] that the nanoparticle agglomeration stabilizes within the first 25 hours at 850°C. Hence, throughout the experiments a minor linear increase in polarization resistance could be observed, which is due to irreversible agglomeration of the nanoparticles. The increase in polarization resistance observed in figure 1b is therefore a result of both a minor irreversible agglomeration of the nanoparticles, but dominated by the stabilization in the CO₂/CO gas atmosphere. This is further indicated by the fact that the cell performance in humidified hydrogen seems stabilizes at $41 \pm 2 \text{ } \Omega \text{ cm}^2$ after two to three hours of operation at 850 °C, as seen in figure 1d. Hence, the irreversible degradation of the cell performance makes up $9.0 \text{ } \Omega \text{ cm}^2$ of the increase seen in figure 1b, which correlates to the linear increase observed in figure 1c. The remaining increase observed in figure 1b is due to the change in atmosphere.

When the atmosphere is changed from humidified hydrogen to methane, coking on the nickel nanoparticle infiltrated STN electrodes is readily observed in the Raman spectra. Spectra in figure 2a show that both the G- and the D-band are slowly increasing in intensity during exposure to methane. Notably the G-band intensity steadily increases for ~7 minutes before leveling out, as can be seen in figure 2b. The impedance spectra in figure 2c show that the polarization resistance increases dramatically when the atmosphere is changed from humidified hydrogen to methane. The initial increase, within the first four minutes, is due to an increase in reaction resistance for the methane fuel oxidation reaction. The time needed for exchanging the Linkam stage atmosphere is roughly estimated to be 1-2 min based on the flowrate and stage chamber volume. The slow, but steady, increase observed after approximately four minutes is no longer linear as seen in figure 2d. The increase is therefore attributed to carbon accumulation based on the correlation between the steady increase in polarization resistance and the appearance of the G-band, as can be seen in figure 2d, where the polarization resistance and the G-band intensity have been plotted as functions of time.

Efforts to remove deposited carbon with humidified hydrogen were unsuccessful despite reports that show steam by itself is a very effective reforming agent for removal of deposited carbon on Ni-YSZ cermet electrodes [21]. The peak intensities of the G- and the D-bands were measured over the 18 minutes of exposure to humidified hydrogen. Results in figure 3b show that these conditions (humidified hydrogen, 850°C, OCV) led to only partial carbon removal from the electrode surface. The Raman spectroscopic data agree with the electrochemical data, since the total polarization resistance observed in the EIS traces never returns to its original value of 40.1 $\Omega \text{ cm}^2$ observed prior to the methane exposure, see figure

3a. However, a correlation between the removal of deposited carbon with the decreasing polarization resistance is clearly visible in figure 3c.

In addition to the nickel infiltrated STN cells investigated in this work, cells infiltrated with cobalt oxide nanoparticles were also investigated. In contrast to the nickel oxide infiltrated cells, clear evidence of cobalt oxide was observed in room temperature *ex situ* Raman measurements, seen in figure 4a. Peaks originating from the Co_3O_4 are clearly observed at 193, 477, 518, 615, and 684 cm^{-1} [22]. However, only two features from the cobalt oxide nanoparticles persisted at operational temperatures, prior to the anode reduction as can be seen in figure 4b. This disappearance can be ascribed to an overshadowing effect by the broad peaks originating from the STN and centered around 415, 780 and 1021 cm^{-1} . However, the disappearance might also be a result of a decomposition of the Co_2O_3 since the 651 cm^{-1} band has elsewhere been ascribed to CoO [22].

During the 50% CO_2/CO exposure, no coking was observed on the cobalt oxide infiltrated cells, again, consistent with thermodynamic expectations. Similar to the nickel nanoparticle infiltrated STN electrodes, polarization resistances increased gradually during CO_2/CO exposure. This similarity in performance degradation between the nickel and cobalt infiltrated electrodes implies that the observed performance loss was due to changes in the STN and not due to changes induced by the infiltrate.

Unlike the nickel infiltrated cells, the cobalt infiltrated cells showed no evidence of coking when exposed to pure methane at open circuit voltage. Figure 5 shows the last obtained Raman spectrum acquired from the nickel and the cobalt infiltrated electrodes following 13 minutes of exposure to

methane. The nickel containing STN electrode shows clear evidence of carbon accumulation whereas the cobalt containing electrode appears free of any observable carbon.

The EIS data from the cobalt infiltrated cells is reported in figure 6, which show a similar abrupt increase in polarization resistance, as observed for the nickel infiltrated cells. Again, this increase is attributed to a changeover in fuel from humidified hydrogen to dry methane and the corresponding changes in electrochemical activation and fuel transport properties. However, unlike the nickel infiltrated cells, the data show no further slow and steady rise in polarization resistance at later times. Since no carbon deposition was observed in the Raman spectra and no continuous increase in polarization resistance took place with cobalt oxide infiltrated STN cells, we conclude that the cobalt electrocatalyst does not promote coking and may even inhibit carbon accumulation.

With regards to the reference performance of both the nickel and the cobalt infiltrated cells, EIS data showed that a general degradation in performance took place throughout the duration of each cycling experiment. This degradation is likely a consequence of nanoparticles agglomeration, a hypothesis that was tested by ex situ SEM investigations. Tests performed with as-prepared electrodes showed that the oxide nanoparticles were small, with diameters between 8-10 nm. Images acquired after thermal cycling and electrochemical measurements showed nanoparticles grew to 50-300 nm in diameter as seen in figure 7. Notably, no structural differences were found between the cobalt- and nickel nanoparticles after the cells had been tested at 850 °C.

For reference to the infiltrated STN cells, an equivalent experiment was performed using a Ni-YSZ cermet electrode. Ni-YSZ electrodes exposed to methane are highly susceptible to

coking [23]. Figure 8b shows both the G- and the D-band intensities as the electrode is exposed to methane. Intensity in both features is readily apparent after only four minutes, signifying rapid carbon accumulation. Signal intensities were also 5-10 times larger than those reported for the Ni-infiltrated STN electrodes (figure 2b). Impedance spectra shown in figure 8a describe behavior consistent with the Raman spectra, since an initial jump can be seen in the polarization resistance followed by a slower continuous increase. This initial jump in polarization resistance is again attributed to an increase in reaction resistance as the fuel changes from hydrogen to methane. The steady increase in polarization resistance continued until methane exposure was stopped. In addition to a change in reaction resistance, carbon deposition in the porous anode is also expected to increase the low frequency, mass transport contribution to the EIS trace. Unfortunately, there is here not a clear correlation between the G-band intensity and the increase in polarization resistance as seen in figure 8c. A more detailed analysis of this degradation mechanism, hence, remains to be tested explicitly.

After exposure to pure methane, the atmosphere over the Ni-YSZ cermet electrode was changed to humidified hydrogen for 25 minutes in an attempt to remove the deposited carbon. However, the intensity of both the G- and the D-band did not decrease significantly, as seen in figure 9b, although the total polarization resistance almost returned to its initial value of $1.93 \Omega \text{ cm}^2$ prior to the methane exposure (figure 9a). This behavior contrasts with the Ni-nanoparticle infiltrated STN electrodes where polarization resistance never recovered (figure 3c). Notably, the correlation between total polarization resistance and G-band intensity is for the removal of the deposited carbon, again clearly visible in figure 9c.

When performing an *in situ* Raman experiment, one has to be careful correlating electrochemical and spectroscopy data. Raman experiments need an optically accessible area on the electrode surface free of platinum paste and current collectors. On the other hand, the

current collectors have to coat the electrode surface to impose the symmetric electrical fields needed for exact electrochemical data. Hence, dual Raman-electrochemical studies will always include a level of uncertainty in both the series and polarization resistance in the impedance spectroscopy data and the Raman spectra that might not reflect the electrochemically active material [24]. Additionally, the most electrochemically active part of the electrode is closest to the electrolyte-electrode interface, rather than at the surface of the electrode which is monitored optically. To minimize this problem, electrolyte supported cells were investigated, instead of electrode supported cells meaning that the electrode thickness could be decreased down to 20-30 μm . The decrease in electrode thickness is nonetheless not enough to probe only the electrochemically active surface area and hence, one needs to assume that the Raman data truly represent the chemical composition of the electrochemically active boundary between the electrode and electrolyte. This assumption is supported first by the low overpotential applied during EIS at OCV and second by, the direct correlation observed between the total polarization resistance and the G-band intensity, when plotted as functions of time.

Using gaseous methane to investigate the coking tolerance of novel electrode materials is reasonable since it is a fuel commonly used in SOFC systems. Furthermore, previous reports have shown that exposing state of the art Ni-YSZ electrodes to pure methane under open circuit potential will result in the carbon deposition at 730 $^{\circ}\text{C}$ [21, 25]. Furthermore, polarizing the cell to overpotentials of 0.30 V and 0.60 V against OCV results in identical coking rates for state of the art Ni-YSZ cermet electrodes, when using methane as fuel [26]. Notably, when using alcohols instead of alkanes as fuel, the carbon deposition rate and the influence of polarization change. Eigenbrodt et. al have shown that the influence of polarizing

cells operating with methanol to an overpotential of 0.60 V decreases the carbon deposition rate by a factor 3, with respect to the carbon deposition rate at OCV [26].

Carbon deposition was found to occur on state of the art Ni-YSZ cermet electrode and on the nickel nanoparticle infiltrated cells. However, the amount and structure of deposited carbon differs. Figure 8a shows that on the Ni-YSZ electrodes, the D-band is the most dominating peak, corresponding to deposited carbon having many grain boundaries and/or site defects. In contrast, the G-band dominates the carbon signal from the nickel infiltrated STN electrodes. This dominant G-band contribution corresponds to a more highly ordered graphitic structure of the deposited carbon in accordance to Eigenbrodt et. al. [26].

The difference in the carbon deposit structure between the two kinds of cells, suggests why differences are observed in the attempts to remove carbon using humidified hydrogen. Raman data from the nickel nanoparticle infiltrated STN cells (figure 3b) suggest that almost all of the carbon could be removed during the 18 minutes exposure to humidified hydrogen. In contrast, significant carbon remains on the Ni-YSZ cermet electrode after 25 minutes of exposure to humidified hydrogen (figure 9b), even though the carbon responsible for the D-band intensity should be more easily removed according to Eigenbrodt et. al. [26], albeit under different oxidizing circumstances. In reference [26], the authors used air to remove accumulated carbon while in references [21, 27], the oxidizing agent (steam) was entrained in Ar. The remaining carbon on the Ni-YSZ cermet electrode could be explained simply by the amount of carbon that was formed and, correspondingly, by the amount of Ni in the anode. The nickel nanoparticle infiltrated STN cells contains around 10 wt% nickel oxide, prior to reduction, while the Ni-YSZ cermet electrode contains around 55 wt% nickel oxide, prior to reduction. As stated above, the deposited carbon is different in nature for the two types of

electrodes. This condition could explain the difference in carbon removal and indicate that the nature of the deposited carbon influences on the coking reversibility. Furthermore, since some carbon remains on both types of electrodes, one might question if the reducing capability of hydrogen interferes with the carbon oxidation, since hydrogen's ability to re-reduce any partially oxidized intermediates might offset the oxidizing powers of the steam. If hydrogen can limit carbon oxidation, then a different mechanism for carbon removal may be operative. This question is an interesting one that could generate new studies, beyond the scope of this work. In contrast to the Raman spectra, the electrochemical impedance data (figure 3a and figure 9a) suggest that the Ni-YSZ cermet electrode almost fully recovers from the exposure to methane, while irreversible degradation has happened on the nickel nanoparticle infiltrated STN cells.

A second question this study could not fully resolve is the origin of the polarization resistance's slow increase in cells fabricated with infiltrated STN electrodes. This effect might be due to a continuous agglomeration of the nanoparticles at 850 °C. This thermally induced agglomeration of the nanoparticles have a linear behavior. However, the thermally induced continuous agglomeration of the nanoparticles should also be visible with electrodes exposed to humidified hydrogen. As can be seen in figure 1c and figure 3a, however, the polarization resistance only decreases before eventually stabilizing with humidified hydrogen. In addition, the linear behavior in polarization resistance is not observed after the CO₂/CO exposure. This result suggests either that the agglomeration of the nanoparticles is completed after the CO₂/CO exposure or that it is an atmosphere-dependent degradation instead of thermally driven degradation, which implies a more complex, irreversible degradation mechanism. Hence, the full mechanism responsible for the irreversible degradation is not yet fully understood and motivates further investigation.

In brief, introducing methane as the working fuel to infiltrated STN anodes leads to an abrupt increase in polarization resistance due to the change in the fuel gas and thereby the fuel oxidation reaction resistance. This effect is fully reversible in Co-infiltrated anodes but only partially reversible in Ni-infiltrated anodes. The polarization resistance does not vary systematically so long as no observable coke forms. The appearance of carbon in the Raman spectra is always correlated with a continued slow and steady additional rise in polarization resistance. Similar effects are observed with conventional Ni-YSZ anodes. From this correlation, one can posit that coking of the anode diminishes electrochemical performance, likely due to blocking of anode sites, internal reforming activity, and/or mass transfer limitations that result from decreasing microstructure porosity [2]. These results are highly suggestive and will be pursued more thoroughly in future work.

4 Conclusions

In situ synchronous Raman spectroscopy and EIS were used to investigate the susceptibility of novel SOFC anode materials to coking at 850 °C. The STN based cells infiltrated with nickel oxide or cobalt oxide were, after reduction in hydrogen, first exposed to 50% CO₂/CO in order to investigate the general performance when using CO as fuel. Neither electrode showed evidence in the Raman spectrum of carbon formation during CO₂/CO exposure. The carbon tolerance of these novel electrodes in the CO₂/CO atmosphere thus makes them potential candidates for CO₂ electrolysis cells, yet the influence of current on the coking in these electrodes requires further investigation. Second, electrodes were exposed to pure methane to further investigate the coking tolerance. Raman data demonstrated that infiltrated nickel oxide particles promoted coking during pure methane exposure, even though nickel loadings were so low that the expected NiO vibrational feature could not be observed in the

pre-reduced anodes. Deposited carbon could be partially but not entirely removed, by the use of humidified steam. Similar cobalt loadings showed evidence of Co_3O_4 in Raman spectra recorded on the pre-reduced electrodes. The Co_3O_4 disappeared upon electrode reduction, presumably due to formation of metallic Co, and the cobalt containing electrodes showed no evidence of coking, within the resolution of the Raman spectroscopy, when exposed to methane.

The observations from the *in situ* Raman spectroscopy were supported by EIS results showing a gradual rise in the electrode's polarization resistance for nickel containing electrodes upon methane exposure. In contrast, the cobalt containing electrode did not show a similar, slow and steady increase in polarization resistance when exposed to methane. The findings were supported by a control experiment performed on a traditional Ni-YSZ SOFC cermet anode. Altogether, these results evidences a remarkable carbon tolerance of cobalt oxide infiltrated STN anodes.

Acknowledgements

The authors acknowledge colleagues at DTU Energy for technical assistance and fruitful discussions. Furthermore, the authors would like to acknowledge the financial support from the project "BALANCE" (European Union's Horizon 2020 research and innovation program under grant agreement number 731224).

RW gratefully acknowledges support from the Otto Mønsted Foundation's Visiting Professorship Program and from the United States Office of Naval Research (N00014-17-2315).

References

- [1] D. K. Niakolas, *Appl. Catal., A : General* **2014**, *486*, 123.
- [2] A. Lanzini, P. Leone, C. Guerra, F. Smeacetto, N.P. Brandon, M. Santarelli, *Chem. Eng. J.* **2013**, *220*, 254.
- [3] T. Ramos, C. Bernuy-Lopez, B. R. Sudireddy, J. J. Bentzen, W. Zhang, P. S. Jørgensen, L. T. Kuhn, *ECS Trans.* **2012**, *45*, 389.
- [4] P. Blennow, K. K. Hansen, L. R. Wallenberg, M. Mogensen, *Solid State Ionics* **2009**, *180*, 63.
- [5] M. C. Verbraeken, B. Iwanschitz, A. Mai, J. T. S. Irvine, *J. Electrochem. Soc.* **2012**, *159*, F757.
- [6] Q. Ma, F. Tietz, A. Leonide, E. Ivers-Tiffée, *J. Power Sources* **2011**, *196*, 7308.
- [7] T. Ramos, S. Veltzé, B. R. Sudireddy, P. Holtappels, *ECS Electrochem. Lett.* **2014**, *3*, F5.
- [8] T. Ramos, S. Veltzé, B. R. Sudireddy, P. S. Jørgensen, L. Theil Kuhn, P. Holtappels, *Fuel Cells* **2014** *14*, 1062.
- [9] X. Lu, P. W. Faguy, M. Liu, *J. Electrochem. Soc.* **2002**, *149*, A1293.
- [10] M. Liu, M. E. Lynch, K. Blinn, F. M. Alamgir, Y. M. Choi, *Mater. Today* **2011**, *14*, 534.
- [11] M. B. Pomfret, J. C. Owrutsky, R. A. Walker, *Anal. Chem.* **2007**, *79*, 2367.
- [12] D.J.L. Brett, P. Aguiar, R. Clague, A.J. Marquis, S.Schöttl, R. Simpson, N.P. Brandon, *J. Power Sources* **2007**, *166*, 112.
- [13] X. Li, J. Lee, K. S. Blinn, D. Chen, S. Yoo, B. Kang, L. A. Bottomley, M. A. El-Sayed, S. Park, M. Liu, *Energy Environ. Sci.* **2014**, *7*, 306.
- [14] M. L. Traulsen, M. D. McIntyre, K. Norrman, S. Sanna, M. Mogensen, R. A. Walker, *Adv. Mater. Interfaces* **2016**, *3*.

- [15] J. D. Kirtley, D. M. Halat, M. D. McIntyre, B. C. Eigenbrodt, R. A. Walker, *Anal. Chem.* **2012**, *84*, 2745.
- [16] T. L. Skafte, P. Blennow, J. Hjelm, C. Graves, *J. Power Sources* **2018**, *373*, 54.
- [17] C. Graves, Ravdav data analysis software, version 0.9.8. DTU. **2015**.
- [18] M. S. Dresselhaus, A. Jorio, M. Hofmann, G. Dresselhaus, R. Saito, *Nano Lett.* **2010**, *10*, 751.
- [19] N. R. Raravikar, P. Keblinski, A. M. Rao, M. S. Dresselhaus, L. S. Schadler, P. M. Ajayan, *Phys. Rev. B* **2002**, *66*.
- [20] N. Mironova-Ulmane, A. Kuzmin, I. Steins, J. Grabis, I. Sildos, M. Pärs, *J. Phys.: Conf. Ser.* **2007**, *93*.
- [21] J. Kirtley, A. Singh, D. Halat, T. Oswell, J. M. Hill, R. A. Walker, *J. Phys. Chem. C* **2013**, *117*, 25908.
- [22] B. Rivas-Murias, V. Salgueiriño, *J. Raman Spectrosc.* **2017**, *48*, 837.
- [23] J. D. Kirtley, M. B. Pomfret, D. A. Steinhurst, J. C. Owrutsky, R. A. Walker, *J. Phys. Chem. C* **2015**, *119*, 12781.
- [24] M. Mogensen, and P. Holtappels. *Solid Oxide Fuels Cells: Facts and Figures* (Eds. P. Conner, J. T. S. Irvine), Springer, London, **2013**, pp. 25-45.
- [25] K. S. Blinn, H. Abernathy, X. Li, M. Liu, L. A. Bottomley, M. Liu, *Energy Environ. Sci.* **2012**, *5*, 7913.
- [26] B. C. Eigenbrodt, M. B. Pomfret, D. A. Steinhurst, J. C. Owrutsky, R. A. Walker, *J. Phys. Chem. C* **2011**, *115*, 2895.
- [27] M. D. McIntyre, J. D. Kirtley, A. Singh, S. Islam, J. M. Hill, R. A. Walker, *J. Phys. Chem. C* **2015**, *119*, 7637.

Figure Captions

Figure 1: 50% CO₂/CO exposure of the nickel infiltrated STN cells. a) The Raman spectra obtained during the exposure. Notable, Spectra are vertically shifted for clarity and the broad peak observed around 765 cm⁻¹ originates from the STN electrode material. b) The electrochemical impedance spectra obtained from the nickel oxide infiltrated cells during the 50% CO₂/CO exposure. c) The total polarization resistance plotted as a function of time, combined with a linear fit on the linear part of the graph. d) The electrochemical impedance spectra obtained from the nickel oxide infiltrated cells when exposed to humidified hydrogen after the exposure to 50% CO₂/CO.

Figure 2: Methane exposure of the nickel infiltrated STN cells. a) The Raman spectra obtained during the methane exposure, notably, spectra are vertically shifted for clarity and the broad peak centered at around 775 cm⁻¹ originates from the STN electrode material. b) The peak intensity of the G- and the D-band as a function of time. c) The electrochemical impedance spectra obtained from the nickel oxide infiltrated cells during methane exposure. d) The peak intensity of the G-band plotted together with the total polarization resistance as a function of time.

Figure 3: Removal of deposited carbon from the nickel infiltrated STN electrodes using humidified hydrogen. a) The electrochemical impedance spectra obtained from the nickel oxide infiltrated cells during carbon removal procedure. b) The peak intensity of the G- and the D-band as a function of time. c) The peak intensity of the G-band plotted together with the total polarization resistance as a function of time.

Figure 4: a) The Raman spectrum obtained from the cobalt oxide infiltrated STN at room temperature. b) The Raman spectrum obtained from the same cell at 850 °C prior to reduction in

humidified hydrogen. Notable, the broad peaks centered around 415, 780 and 1021 cm^{-1} originate from the STN electrode material, while the sharp peaks originates from cobalt oxide species.

Figure 5: Comparison between the nickel and cobalt infiltrated STN cells. Seen in the figure is the last Raman spectrum obtained before ending the methane exposure. Notable, the broad peak centred around 775 cm^{-1} originates from the STN electrode material.

Figure 6: The electrochemical impedance spectra obtained, from a cobalt oxide infiltrated cells, during the methane exposure.

Figure 7: SEM investigation of the nanoparticle infiltrated STN electrodes: a) The nickel oxide nanoparticles as infiltrated b) The nickel oxide infiltrated cell after usage. c) The cobalt oxide nanoparticles as infiltrated. d) The cobalt oxide infiltrated cell after usage. Examples of nanoparticles are marked with red arrows. Notice that the scale bars differ.

Figure 8: Methane exposure of a state of the art Ni-YSZ cermet electrode. a) The electrochemical impedance spectra obtained, from the state of the art Ni-YSZ electrode, when exposed to pure methane. b) The peak intensity of the G- and the D-band from potential carbon deposition, as a function of exposure time. c) The peak intensity of the G-band plotted together with the total polarization resistance as a function of time. Notable, the steady increase in polarization resistance continued until methane exposure was stopped, not shown here.

Figure 9: Removal of deposited carbon from the Ni-YSZ cermet electrode using humidified hydrogen.

a) The electrochemical impedance spectra obtained from the Ni-YSZ cells during carbon removal procedure. b) The peak intensity of the G- and the D-band as a function of time. c) The peak intensity of the G-band plotted together with the total polarization resistance as a function of time.

Author Manuscript