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Evaluating the drop of electrochemical performance of Ni/YSZ and Ni/ScSZ solid oxide fuel cells operated with dry biogas

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Summarv

This work is aimed at evaluating the influence of carbon deposition on the power density drop of in-house fabricated Ni/YSZ and Ni/ScSZ solid oxide fuel cells (SOFCs) operating in dry internal reforming of simulated biogas (CH₄/ $CO_2 = 2$). An immediate drop of open-circuit voltage (OCV) and maximum power densities is observed when the fuel changes from hydrogen to biogas, 86.5% and 33.3% for the Ni/YSZ and Ni/ScSZ cells, respectively with mass transfer polarisation dominates Ni/YSZ polarisation. Carbon deposition is investigated as the cause of the reduction in performance by quantification of deposited carbon by temperature programmed oxidation (TPO) and catalytic activity test. Results from TPO analysis show unexpectedly higher amount of carbon on the Ni/ScSZ cells $(2.35 \times 10^{-3} \text{ mgC/mg}_{cat})$ as compared to Ni/YSZ $(5.68 \times 10^{-4} \text{ mgC/mg}_{cat})$ despite higher performance of the former. Catalytic activity tests reveal a low carbon oxidation rate compared to an initially higher methane decomposition reaction, leading to carbon deposition in both cells, in which the methane decomposition reaction of Ni/ScSZ is higher. Different effects are observed on the pellets, where the carbon deposited on Ni/YSZ deactivates the reforming reaction sites as quick as 20 minutes into the operation, whereas carbon deposited on the Ni/ScSZ pellet did not show the same blocking effect on the catalyst due to the different carbon morphology formed. A graphitic whisker-like rod structure is observed on Ni/ScSZ while amorphous non-crystalline carbon covers the Ni/YSZ pellets with 3 hours exposure to high methane content dry biogas ($CH_4/CO_2 = 2$). The difference of carbon structure affects the amount of carbon quantified in the TPO analysis where most of the amorphous carbon oxidises while some of the graphitic carbon deposits remain.

KEYWORDS

biogas, carbon, degradation, solid oxide fuel cell

1 | INTRODUCTION

In line with the increasing greenhouse gas (GHG) emissions from human activity, the EU has set an ambitious goal of cutting emissions by 80% to 95% by 2050, compared to 1990, which has accelerated research into cleaner and renewable energy production.¹ Solid oxide fuel cells (SOFCs) technology with over 90% combined heat and power (CHP) efficiency and significantly less carbon footprint offers a solution to meet the increasing energy demand without sacrificing the environment.² The high temperature requirement in SOFCs enables operation with a variety of fuels, such as bio-hythane,^{3,4} propane,^{5,6} methane,⁷⁻⁹ syngas,^{6,10} biogas,¹¹⁻¹³ ethanol^{14,15} and ammonia,^{16,17} accompanied with insignificant emissions of SO₂, NO_x and particulate matter.^{18,19} Among the alternative fuels, biogas is widely available across the globe from anaerobic digestion in wastewater treatment facilities²⁰ and does not contribute to fossil CO₂ emissions. Countries such as China, India, and emerging economies countries including Malaysia, Vietnam, Nepal and Pakistan offer various biogas support programmes for domestic biogas utilisation and feed in tariffs (FiT).^{1,21} Based on estimates from the World Biogas Association 2019s report, the current potential of electricity generation from biogas is 87 TWh globally with current technology's maximum efficiency of 40%.²¹ With SOFC possessing a higher electrical efficiency (60% electrical efficiency),²² a greater amount of energy can be harnessed from this currently under-utilised source.

Wastewater biogas consists of 60% to 80% methane (CH₄), 30% to 50% CO₂ and traces of impurities (H₂S, siloxanes and ammonia), varied based on the sources.²³ The main difference of biogas compared to natural gasbased fuels is the natural existence of CO₂, which is beneficial as an oxidising agent and aids suppressing the effect of H₂S¹³. Several studies have also investigated CO₂ as an alternative to steam addition in hydrocarbon fuelled SOFCs.^{12,24} Saadabadi et al²² recently reviewed the potential and constraint of using biogas with special focus on using dry biogas in internal reforming. Hagen et al^{13,16} and Johnson et al²⁵ focus on the implementation of biogas as fuel with H₂S, which was reported to be successful with an excess of CO_2 . Lanzini et al^{26,27} tested SOFC with biogas with traces of typical contaminants such as C₂Cl₄, D4 and HCl in biogas obtained from municipal sewage water treatment. Santarelli et al²⁸ studied different compositions of dry biogas on Ni/YSZ SOFC anode cermets, both using modelling and experiment validation with result suggesting a range of $0.5 < CH_4/CO_2 < 0.75$ to avoid carbon deposition. SOFC modelling experiments with biogas on SOFC single cells and stacks have been carried out to critically evaluate the influence of operation parameters and efficiency of the system.^{24,28,29} Recent techno-economic studies and demonstration of industrial scale SOFC with wastewater biogas showed that the system is feasible technically and in terms of cost, especially when coupled with a gas turbine^{18,30,31} in a hybrid system.

Although biogas has a high methane content, direct electrochemical reaction of CH_4 (Equation (1)) is much slower than that of hydrogen (Equation (2)) and CO (Equation (3)).^{22,32} Prior to the electrochemical reaction of hydrogen and carbon monoxide, the reforming reaction takes place either in an external chamber or internally on the SOFC anode. In internal reforming systems, the reforming reaction is assumed to take place on the entire available surface of Ni particles; that is, both in the anode substrate (AS) and anode functional layer (AFL) regions, while the electrochemical reaction only occurs at the triple phase boundary (TPB) which is the interface between AFL and electrolyte.^{33,34} The main reforming reaction with dry biogas will be dominated by the carbon dioxide dry reforming reaction (Equation (4))^{35,36} and accompanied by a small extent of steam reforming (Equation (5)) due to the increasing existence of steam on the anode along the fuel flow path from the ongoing hydrogen electrochemical reaction (Equation (2)). The reverse water gas shift reaction (Equation (6)) may also occur at SOFC operating temperature.

Electrochemical reactions:

$$CH_4 + 2O_2 \rightarrow 2H_2O + CO. \tag{1}$$

$$\mathrm{H}_2 + \frac{1}{2}\mathrm{O}_2 \to \mathrm{H}_2\mathrm{O}. \tag{2}$$

$$\mathrm{CO} + \frac{1}{2}\mathrm{O}_2 \to \mathrm{CO}_2. \tag{3}$$

Carbon dioxide (dry) reforming:

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO. \tag{4}$$

Steam reforming reaction:

$$CH_4 + H_2O \rightarrow 3H_2 + CO. \tag{5}$$

Reverse water-gas shift reaction (RWGS):

$$\mathrm{CO}_2 + \mathrm{H}_2 \to \mathrm{H}_2\mathrm{O} + \mathrm{CO}. \tag{6}$$

The carbon dioxide dry reforming reaction (Equation (4)) is an overall reaction of high temperature methane decomposition (also known as methane cracking reaction) (Equation (7)) and carbon oxidation by carbon dioxide (Equation (8)).^{33,36} If the rate of reaction of

methane decomposition (Equation (7)) is faster than the rate of carbon oxidation (Equation (8)), solid carbon will be produced and deposited on the anode catalyst. Another two possible routes for carbon deposition in SOFCs are through the Boudouard reaction (Equation (9)) (below 650° C) and the reverse syn-gas reaction (Equation (10)) (850° C-1000°C).

Methane high temperature decomposition:

$$CH_4 \rightleftharpoons C(s) + 2H_2. \tag{7}$$

Carbon oxidation by CO₂:

$$C(s) + CO_2 \rightleftharpoons 2CO. \tag{8}$$

Boudouard reaction:

$$2CO \rightleftharpoons C(s) + CO_2. \tag{9}$$

Reverse syn-gas reaction:

$$H_2 + CO \rightleftharpoons C(s) + H_2O. \tag{10}$$

Carbon deposition is unfavourable to SOFC operation as it reduces the available triple phase boundary (TPBs), which will lead to Ni catalyst deactivation by carbon chemisorption or physical adsorption on the metal surface, catalyst (Ni) encapsulation by carbon particles, growth of carbon filaments, pore blockage and dissolution of carbon atoms.^{37,38} Carbon removal may be possible through oxidation by CO_2 (Equation (8)) or by H_2O in a steam reforming system^{12,39} and also by oxidation by the oxygen ions diffusing through the electrolyte from the current producing electrochemical reactions at the TPB.^{33,40,41} The use of excess CO₂ or steam is reported to be necessary to reduce the carbon deposition in dry biogas application, but also accompanied by lower electrochemical performance due to fuel dilution.^{22,24,36} To avoid fuel dilution, various attempts have focused on enhancing the reforming ability of the anode materials as the rate of carbon deposition and carbon removal is also affected by the catalytic activity of the anode.^{22,36}

Several anode modification strategies have been tested with methane as representative of hydrocarbon fuel such as using Ni-free copper-ceria–based anodes,^{5,15,42-44} perovskites-based anodes,⁴⁵⁻⁴⁷ substitution of the ceramic oxides,^{48,49} and anode surface modification.^{38,50-53} In spite of the carbon affinity to Ni, Ni is still preferred due to its higher electrical conductivity, superior catalytic activity and compatibility with other SOFC layers.²² As Ni/ScSZ cells have the similar properties to Ni/YSZ cells, whilst ScSZ has higher ionic conductivity, research work comparing these two anode

materials has been widely reported, including the imple-

mentation of biogas as fuel. With Ni/ScSZ cells, the carbon affinity on the Ni is reduced by the stronger interaction of Ni with ScSZ than with YSZ.41,54 Previous work on Ni/ScSZ reported by Sumi et al^{55,56} compared the cell performance and carbon structure on Ni/YSZ and Ni/ScSZ in dry and humidified methane with hightemperature SOFC (1000°C). They^{55,56} reported faster degradation of Ni/YSZ in both dry and humidified methane while Takahashi et al⁵⁷ reported otherwise on the cell performance in dry biogas and humidified methane with an SOFC test at 800°C. Tested with humidified methane. Ke et al⁵⁴ reported different temperaturedependent carbon deposition behaviour, where carbon deposition decreased with elevated temperature for Ni/ScSZ and vice versa for Ni/YSZ. Ni/ScSZ cells were also observed to have better steam enrichment on the Ni which aids carbon oxidation.⁵⁴ The contradictive performance result of Ni/YSZ and Ni/ScSZ⁵⁵⁻⁵⁷ as anode catalysts may have been influenced by different responses to carbon deposition with a different nature of fuel feed, either solely methane, humidified methane, dry biogas or dry biogas with an excess of oxidants. As real biogas has a high CH_4/CO_2 ratio which lies in the carbon deposition region,⁵⁸ most of the work reported is done in excess of oxidant, either steam, CO₂ or air.^{12,57,59} Limited work has been carried out with a high CH₄/CO₂ ratios. Our previous work has shown the electrochemical performance difference with Ni/YSZ and Ni/ScSZ investigated at 750°C with a high ratio of $CH_4/CO_2 = 2$ to imitate real biogas composition, in which a significant performance drop (80%) was observed in Ni/YSZ cells when the fuel was switched from hydrogen to dry biogas while Ni/ScSZ cells showed better adaptability (40% drop).⁶⁰ In-depth carbon evaluation was not evaluated, with the assumption that the higher amount of carbon deposited on Ni/YSZ cell, based on the extent of drop of performance. Sumi et al⁵⁵ observed a similar cell performance drop and detected different carbon structures on Ni/YSZ and Ni/ScSZ cells in humidified methane, but did not report on carbon quantification comparisons of the tested cell. Although many papers have presented the thermodynamic equilibrium plots with carbon-containing fuel compositions, Kim et al⁶¹ and Ke et al⁵⁴ had previously shown deviations of carbon deposition behaviour in the observed SOFC cells, especially when working with different anode catalysts. Carbon quantification on SOFC tested cells would validate the different responses of the catalysts (or anode materials) to carbon-containing fuels, whilst most of the work investigated and quantified carbon deposition with a quartz chamber^{62,63} where only chemical reactions took place but no influence of electrochemical reaction was recorded. This present study

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investigates carbon deposition as the underlying reason for the performance drop in SOFC fuelled by dry biogas with high CH₄/CO₂ ratio. The different influence of carbon on the Ni/YSZ and Ni/ScSZ cells investigated by quantification of carbon on the SOFC tested cells with temperature-programmed oxidation (TPO) analysis accompanied by catalytic performance activity test and SEM microstructural analysis of the pellets.

EXPERIMENTAL 2

2.1 **Materials**

The starting particle size (d_{50}) of NiO used in the anode substrate (AS) was $8.101 \pm 0.085 \,\mu m$ (Type A, Hart Materials Ltd, UK) while the electrolyte size were 0.855 \pm 0.103 µm for YSZ (TZ-8YS, TOSOH, Japan) and 0.514 \pm 0.053 µm for ScSZ (10Sc1CeSZ, DKKK, Japan). Finer NiO starting particle size of $0.637 \pm 0.145 \,\mu m$ (Type F, Pi-Kem, UK) was used for the anode functional layer (AFL).

2.2 Methodology

2.2.1 | Fuel cell setup and cell performance

The Ni/YSZ and Ni/ScSZ in-house cells were fabricated by aqueous tape casting described in previous work.⁶⁰ Individual cells were mounted using excess of silver paste (DAD-87, Shanghai Research Institute) on a 3 cm diameter × 50 cm length double-layer alumina cylinder with fuel fed to the anode while the cathode was exposed to ambient air with no artificial air movement, as depicted in Figure 1. Silver paste and silver wires were used to connect the cells to a Solartron Analytical No 1470 E and 1455 FRA analyser for electrochemical performance and impedance measurements. Prior to all SOFC electrochemical tests, flow rate test was performed using He to ensure there was no leakage on the silver paste sealing after heating up.

The electrochemical performance tests with hydrogen fuel were carried out at a flow rate of 21 mL/min of H₂ and He at 7 mL/min in reduction setting for 24 hours before switching the feed to biogas. In the biogas setup, CH₄ and CO₂ in a ratio of 2:1 (14 mL/min CH₄, 7 mL/min CO₂) were used in place of H₂. This ratio was selected according to the typical methane-to-carbon dioxide ratio from biogas sourced from anaerobic digestion⁶⁴ and based on the C-H-O ternary diagram⁶⁵ which indicates the possibility of carbon build-up with this composition at SOFC operating temperature (700°C-900°C). Helium (He) was used as a fuel diluent and inert gas carrier. To identify any lasting effect of running an SOFC in biogas on the cell performance, a post-biogas test with hydrogen was performed. The H₂ flow rate was maintained at 5 mL/min during furnace cooling down after the test to avoid oxidation of carbon and nickel. As the focus of this paper is on the post-test analysis, only *i*-V curves and EIS analysis at 0.7 V are elaborated here.

2.2.2 **Carbon deposition post-test** analysis

Temperature programmed oxidation

TPO experiments were performed to quantify the carbon amount on the actual SOFC tested. Due to the destructive de-mounting technique, the SOFC cells break into fragments. The sample fragments were positioned in the middle of a quartz tube chamber and blown with compressed air at 50 mL/min for carbon oxidation. The furnace



FIGURE 1 Schematic of SOFC cell mounting and test rig setup [Colour figure can be viewed at wileyonlinelibrary.com]

ramped at 5°C/min and annealed for 1 hour for complete carbon burn-off. The gas outlet was connected to a mass spectrometer (MKS-Cirrus). Before the actual sample, calibration with a known amount of carbon graphite powder was performed to construct a calibration curve using the resulting CO_2 peak area.

Catalytic activity test

Catalytic activity tests were performed to establish the discrepancy between Ni/YSZ and Ni/ScSZ in terms of the catalytic reaction with simulated biogas. Anode pellets with a cermet ratio of 65:35 were mixed with 3 wt% of PVA, cold-pressed and sintered at 1400°C for 4 hours. The 1 cm diameter pellets were positioned in a quartz tube chamber and purged with the same biogas flow rate used for the electrochemical reaction at 750°C for 3 hours. The exhaust gasses were directed to the mass spectrometer for analysis.

Microstructure analysis with scanning electron microscopy

The scanning electron microscopy (SEM) images were taken across the unpolished cross-section of the anode pellets with Philips XL30 ESEM-FEG Environmental-SEM at 20 000 magnification and 10 kV acceleration in secondary electron (SE) mode. The samples were coated with Pd/Pt to aid carbon detection by SEM.

3 **RESULTS AND DISCUSSION**

3.1 **Electrochemical performance**

The theoretical EMF (E_0) value of an SOFC with pure H₂ and O_2 at atmospheric pressure and 750°C is 0.99 V.^{32,66} From the Nernst equation (Equation (11)), the operating open circuit voltage (OCV) value can be increased (or decreased) by varying the fuel composition, the gas pressure and the fuel flow rate.⁶⁶

$$E = E_0 + \frac{RT}{2F} \ln\left(\frac{pH_{2(anode)} \times pO_{2(cathode)}}{pH_2O_{(anode)}}\right), \qquad (11)$$

where E_0 is the theoretical EMF for the respective temperature (0.99 V at 750°C), R is the gas constant (8.314 J/ K/mol), F is the Faraday constant (96 484 C/mol), 2 is the number of electrons in the reaction and pH_2 , pO_2 and pH₂O represent the partial pressure of the respective gases.

Assuming maximum hydration of 6%⁶⁶ and helium dilution of 25% on the anode (He/Biogas = 0.25), and 21% of O_2 (air assumed to be at 1 atm) on the cathode side, the operational OCV calculation with Nernst Equation is 1.076 V, as calculated below:

$$E = 0.99 + 0.4410 \ln\left(\frac{(0.75 \times 0.94) \times (0.21)^{1/2}}{0.06}\right) = 1.076 \,\mathrm{V}.$$

In the present work, the OCV value of Ni/YSZ in hydrogen was observed to be 0.99 V, while Ni/ScSZ had higher OCV (1.03 V). With the experimental setup with no air-flow on the cathode side, the OCV was lower than the calculated values on both cells. This is supported by the observation on the influence of fuel flow rate and operated partial pressure to OCV as investigated by Chiodelli and Malavasi.⁶⁶ When the SOFC operation switched from H₂ to biogas, the OCVs in both cells decreased to 0.89 V and 1.00 V for Ni/YSZ cell and Ni/ScSZ cells, respectively. The maximum power density of the Ni/YSZ cells dropped by 86.5% from 0.37 W/cm² to 0.05 W/cm^2 with the fuel switch as displayed in Figure 2A. In contrast, the drop in power density for the



FIGURE 2 Performance in H₂ and biogas at 750°C with (A) Ni/YSZ cell and (B) Ni/ScSZ cell [Colour figure can be viewed at wileyonlinelibrary.com]

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In the evaluation with electrochemical impedance spectra (EIS), the shape of the Nyquist plot of Ni/YSZ cells changed and quadrupled with an increase of the area-specific resistance (ASR) value from 0.62 Ω cm² to 2.52 Ω cm² (Figure 3) when the fuel switched from hydrogen to dry biogas. The less significant change in power densities was reflected by the smaller ASR shift from originally 0.46 Ω cm² to 0.62 Ω cm² with the fuel switch for the Ni/ScSZ cells (Figure 4). The impacts of the fuel change on the mass transfer resistance are reflected at the lower frequency region in EIS analysis, while charge transfer resistance is reflected at higher frequency region.^{34,58} In present work, Ni/YSZ cell shows large differences in the low-frequency region which indicates domination by the mass diffusion resistance in Ni/YSZ cell. The Nyquist and Bode plot of Ni/ScSZ in Figure 4 depicted an increase in the low and medium frequency region, but with significantly less than that of Ni/YSZ.

Previously, Troskialina et al³⁶ and Jiang et al³⁸ also observed the same pattern of decrease in the performance and impedance of Ni/YSZ cells in dry biogas with the same CH₄/CO₂ ratio and temperature. The same pattern arc increment with Ni/YSZ tested with H₂ and dry CH₄ was reported by Koh et al.⁵⁸ Koh et al⁵⁸ also reported significant performance differences with humidified and dry

In post biogas iV-PV measurements after 1.5 hours of OCV with the fuel switched back to hydrogen, the performance on both cells recovered instantly as portrayed in Figure 2. The OCVs restored to their original values whilst the maximum power density showed the performance recovered by 86.5% (0.32 W/cm) for Ni/YSZ and by 78.6% (0.33 W/cm) for Ni/ScSZ. The post-biogas test with Ni/ScSZ showed a lower restoration value of maximum power density compared to the initial performance in hydrogen due to Ni coarsening affected by incompatibility of starting materials sizes which will be discussed in a later paper. The performance recovery on Ni/YSZ cells in hydrocarbon fuelled SOFC with hydrogen was also reported by Troskialina et al.⁵¹ and on Cu-ceria-YSZ anodes by Kim et al.⁶¹

Carbon deposition quantification 3.2 with TPO

From the TPO calibration, the oxidation of carbon graphite started at 520°C and completed combustion at 600°C during the 1-hour dwelling stage. TPO results on the tested cells (Figure 5A) showed CO₂ peaks from Ni/YSZ



FIGURE 3 Comparison of impedance spectra of Ni/YSZ cells in 21 mL/min in hydrogen or in dry simulated biogas (CH₄/ $CO_2 = 2$) at 0.7 V in (A) Nyquist plot and (B) corresponding Bode plot [Colour figure can be viewed at wileyonlinelibrary.com]



FIGURE 4 Comparison of impedance spectra of Ni/ScSZ cells in 21 mL/min hydrogen or in dry simulated biogas ($CH_4/CO_2 = 2$) at 0.7 V in (A) Nyquist plot and (B) corresponding Bode plot [Colour figure can be viewed at wileyonlinelibrary.com]

samples at 400°C to 500°C, while the CO_2 peaks from Ni/ScSZ samples (Figure 5B) appeared at 600°C, close to the carbon graphite burn-off temperature. Hence, this adds evidence that different types of carbon existed on Ni/YSZ and Ni/ScSZ samples in the IT-SOFC operating regime; easily combusted carbon deduced to be amorphous carbon existed in Ni/YSZ cells, whereas graphitic carbon in Ni/ScSZ cells. The two peaks detected in this work were in agreement with the work carried out by Kim et al⁶¹ with n-butane tested with YSZ and ceriabased YSZ cells. However, in their work, due to different fuel and oxidising environment, with H₂O as the oxidant, higher oxidising temperatures were observed.



FIGURE 5 CO₂ peaks from carbon burn-off from SOFC tested cells: (A) Ni/YSZ and (B) Ni/ScSZ [Colour figure can be viewed at wileyonlinelibrary.com]

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Table 1 shows the average calculated amount of carbon based on the CO₂ peaks from Figure 5 and TPO calibration from the known amount of carbon graphite compared to literature. In the present work, a higher amount of carbon was detected on the Ni/ScSZ samples, compared to Ni/YSZ cells despite a larger performance drop in the Ni/YSZ cells. After 24 hours of testing in dry biogas, the average amounts of carbon deposited on Ni/ScSZ and Ni/YSZ samples were 2.35×10^{-3} mgC/mg_{cat} and 5.68×10^{-4} mgC/mg_{cat}, respectively. The amount of carbon deposition was the amount of carbon deposited less the amount of carbon that had been oxidised to CO₂ or CO during the post biogas SOFC electrochemical reaction with hydrogen.

Comparing the carbon amount to the literature, ^{54,62,67} the amounts of carbon found on the Ni/YSZ anode in this study were remarkably low. In work by Somalu et al,⁶² the average carbon deposited on Ni/YSZ cells after 1 hour test at 700°C was 3.2×10^{-3} mgC/mg_{cat}, whereas in the present study, the average carbon accumulation on a Ni/YSZ cell after 24 hours test was 5.68×10^{-4} mgC/ mg_{cat} . Somalu et al⁶² and Eguchi et al⁶³ evaluated the amount of carbon deposited from methane on the SOFC cermet at 700°C in a quartz tube chamber and not in SOFC mode; that is, with no influence of the electrochemical reaction. This indicates the expected high contribution to carbon oxidation and removal from the electrochemical reaction, and also indicates that OCV operation of an SOFC in carbonaceous fuels will always lead to carbon deposition, no matter what the anode composition, simply due to thermodynamic equilibrium conditions for the fuel composition present. On the other hand, Gunji et al⁶⁷ and Ke et al⁵⁴ found a dependency on the amount of carbon deposited on difference oxides depending on temperature. At high temperature (900°C and above) carbon deposition was lower than that at 800°C in Ni/ScSZ, which contradicts Ni/YSZ behaviour.⁵⁴

TABLE 1	Carbon deposition com	parison of Ni/YSZ and Ni/	ScSZ cells with differer	nt anode ratios and	operating parameters
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Parameter	40% Ni (S/C = 0.8 for 1 h) 700°C	20% Ni (S/C = 0.6 for 5 h) 700°C	10% Ni (S/C = 0.6 for 5 h) 700°C	61% Ni (S/C = 0.03 for 10 h), 800°C	61% Ni (S/C = 0.03 for 10 h), 900°C	61% Ni (S/C = 0.03 for 10 h), 1000°C	65% Ni (BG 2:1 CH₄: CO₂ for 24 h), 750°C
Ni/ScSZ	0.28 mgC/mg _{cat}	11.7 mgC/mg _{cat}	15.8 mgC/mg _{cat}	4.75 mgC	0.1 mgC	0.05 mgC	2.35×10^{-3} mgC/mg _{cat}
Ni/YSZ	0.35 mgC/mg _{cat}	33.4 mgC/mg _{cat}	39.6 mgC/mg _{cat}	0.5 mgC	2.0 mgC	Not evaluated	$5.68 \times 10^{-4} \text{ mgC/}$ mg _{cat}
Quartz or post SOFC?	Quartz	Quartz	Quartz	Post-SOFC	Post-SOFC	Post-SOFC	Post-SOFC
Current density	N/A	N/A	N/A	0.5 mA/cm^2	0.5 mA/cm ²	0.5 mA/cm ²	0.4 mA/cm ²
Reference (et al)	Somalu ⁶²	Eguchi ⁶³	Eguchi ⁶³	Ke, ⁵⁴ Gunji ^{54,67}	Ke, ⁵⁴ Gunji ^{54,67}	Ke, ⁵⁴ Gunji ^{54,67}	Present study

Abbreviations: mgC/mg_{cat}, weight of carbon in mg per weight of catalyst; N/A, not applicable; SOFC, solid oxide fuel cell; S/C: steam to carbon ratio.

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Besides the present work and Ke et al,⁵⁴ no other work quantified the deposited amount of carbon on tested cells with respect to differences between Ni/YSZ and Ni/ScSZ cells. Comparison to the work by Ke et al⁵⁴ with electrolyte supported cells (ECS) is difficult as the authors did not report the amount of carbon with respect to the catalyst amount. Therefore, the comparison amount per SOFC cell will be inaccurate due to differences in surface area between anode and electrolyte supported cells. As shown in Table 1, the amount of carbon reported hugely varied between present work and the literature as the amount of carbon deposited not only influenced by the catalytic activity, but also by the cermet ratio, electrode microstructure, and operating conditions. Hence, comparison across different reports, even with slight differences in details, will be inaccurate. Regardless of the high amount of carbon observed in graphitic carbon morphology, the electrochemical performance of the Ni/ScSZ cells was higher.

3.3 Catalytic activity test

A catalytic reaction test with the same CH_4/CO_2 ratio was carried out to understand the response of the different cermet anode catalyst by assessing the amount of hydrogen and carbon monoxide produced in the outlet stream. Figure 6 shows similar initial amounts of hydrogen and carbon monoxide produced by the samples which reflected the methane decomposition reaction (Equation (7)) and carbon oxidation by carbon dioxide (Equation (8)). However, the amount of hydrogen

plummeted after 20 minutes in the Ni/YSZ cell, whereas a less severe effect was observed in Ni/ScSZ cells. The hydrogen amount produced by the Ni/ScSZ material fluctuated. The rate of hydrogen produced in Ni/ScSZ cells slightly reduced after 20 minutes of exposure but then increased with a peak at 63 minutes, where the hydrogen amount started to decline and remained steady until the end of 90 minutes catalytic activity test.

The partial pressure or the amount of carbon monoxide presents the degree of carbon oxidation reaction by carbon dioxide (Equation (8)). After 90 minutes, the amount of carbon monoxide produced in the Ni/ScSZ chamber was higher than with Ni/YSZ (13% difference), but the gap of carbon monoxide produced between Ni/ScSZ and Ni/YSZ cell was not as significant as with hydrogen (67% difference). It was also observed that the amount of carbon dioxide on Ni/ScSZ decreased more while the amount of methane remained more or less constant. The difference in carbon dioxide amounts between the two cell materials reflected differences in carbon oxidation by carbon dioxide catalytic activity on different anode materials. This observation was supported by Eguchi et al's work⁶³ with methane, where initially a higher reforming rate was observed in the Ni/YSZ cell, but rapidly dropped after 600 minutes, leading to speculation that the anode was deactivated by carbon deposition. On the other hand, steady operation was observed on Ni/ScSZ cell until the end of the 900 minutes test.⁶³

Figures 7 and 8 show the actual cermet pellets and the microstructural analysis with SEM after the catalytic activity test. Ni/YSZ pellets (Figure 7) remained intact, but the microstructural analysis showed coral-like





FIGURE 7 Ni/YSZ anode pellet surface; (A) actual pellet, (B) at the centre of pellet with larger overview and (C) focused on the coral-like Ni surface structure [Colour figure can be viewed at wileyonlinelibrary.com]

FIGURE 8 Ni/ScSZ anode pellet surface; (A) actual pellet, (B) near the edge with two different structure observed and (C) at the edge focusing on graphitic carbon filament [Colour figure can be viewed at wileyonlinelibrary.com]



structures on the Ni surface with exposure to biogas. The rough structure can be caused by either encapsulation, chemisorption or physical absorption of amorphous carbon on the Ni surface.^{37,68} The dissolution of carbon in the bulk Ni (metal) led to a deactivation of the catalytic reforming area, reflected by the drop of hydrogen and carbon monoxide production in Figure 6. Carbon growth in Ni/ScSZ cells (Figure 8) showed rod-like filamentous growth, deduced to be graphitic carbon. Although the amount of hydrogen and carbon monoxide produced seemed to be less affected by the graphitic carbon deposition in Ni/ScSZ, undesired stress and fracture in the pellet was observed on the Ni/ScSZ pellets (Figure 8A).

Different carbon structures were reported on Ni/YSZ and Ni/ScSZ in previous work with high temperature SOFC,^{41,55} showing the evidence of filamentous carbon. However, none reported on the coral-like structure observed on Ni/YSZ pellets. Filamentous carbon growth was found at the edge and cracks while no coral-like structure was observed on the Ni/ScSZ pellets. Although a severe carbon deposition was observed on the pellets in this section, all these were not observed on the tested cells after 24 hours operation in SOFC electrochemical test with dry biogas (supplied in Figure A1). In SOFC operation, the electrochemical reaction continuously occurred, constantly oxidising carbon near the TPB area while carbon accumulated on the anode in the quartz chamber.

The first part of this work showed a drastic drop of performance with the fuel switch from hydrogen to biogas and better performance restoration when tested in hydrogen after biogas operation on Ni/YSZ cell. A less severe effect was observed with Ni/ScSZ in biogas operation. However, the amounts of carbon quantified on Ni/ScSZ cells were higher than on Ni/YSZ cells, despite the better performance in dry biogas. The catalytic activity test verified the carbon deposition impact on the carbon dioxide dry reforming reaction (Equation (4)), where the rate of methane decomposition (Equation (7)), reflected by the amount of hydrogen produced on Ni/YSZ and Ni/ScSZ, were similar initially. Due to a slower rate of the carbon oxidation reaction by CO_2 (Equation (8)), solid carbon started to deposit on both cells. On Ni/YSZ cells, the carbon deposited inhibited the catalytic surface area and resulted in limited methane decomposition activity. Whilst the behaviour of the reforming activity on Ni/ScSZ anodes after carbon deposition was altered, it did not completely deactivate the reforming catalytic ability of the material. This observation reflects the situation during OCV that was sustained in dry biogas operation for 90 minutes before SOFC operation began with varied current density to obtain the iV-PV curves. The rate of carbon deposition and the rate of carbon oxidation were closely related to the anode materials, where in this case, from the catalytic activity test, Ni/ScSZ was a better catalyst for both the methane decomposition reaction and carbon oxidation.

The hindered methane decomposition reaction which led to low amount of H_2 caused high mass-transfer polarisation on Ni/YSZ, hence the significant performance drop. From Figure 6, the partial pressure of H_2 with Ni/YSZ was significantly low, while unreacted CH₄ WILEY-ENERGY RESEARCH

and CO accumulated on the anode surface Although direct oxidation of CH_4 and CO is theoretically possible with SOFC, CH_4 and CO can be 10 times slower to diffuse through the triple phase boundary than that of H_2 due to their size and molecular weight.³² Hence, led to substantially high mass-transfer polarisation³² (or mass diffusion resistance) as displayed by the Nyquist and Bode plot in Figure 3. This was not observed on Ni/ScSZ (Figure 4) as high amount of H_2 present as depicted by the catalytic activity test in Figure 6.

The higher amount of carbon found in Ni/ScSZ in post-operational analysis can be explained by the significantly higher rate of methane decomposition and the type of carbon formed on both cells. Ni/ScSZ cells showed a consistently higher rate of methane decomposition, while the rate of carbon oxidation was only slightly higher than for Ni/YSZ. The continuous methane decomposition released higher amounts of hydrogen, inevitably accompanied by more carbon on the Ni/ScSZ anodes. This led to a higher amount of carbon deposited on Ni/ScSZ while the amount of carbon on Ni/YSZ was lower due to less methane decomposition. Noncrystallised amorphous carbon was observed on Ni/YSZ pellet (Figure 7), while whisker and rod-like structures were observed on Ni/ScSZ (Figure 8). Amorphous carbon is thermodynamically metastable,⁶⁹ hence easier to oxidise while whisker or rod-like graphitic carbon is more stable, supported by the difference in the carbon burn-off temperature in the TPO analysis. Graphitic carbon that was more difficult to oxidise remained, while almost all the amorphous carbon was oxidised. This observation also meant that carbon deposition with amorphous carbon is reversible, however with very limited power produced during SOFC operation due to limited amount of available reactant. This also explains the better recovery in Ni/YSZ cells, since it shows that the cell performance in hydrogen after biogas was almost unaffected as almost all amorphous carbon had been oxidised. Although scarce, the reversibility of the carbon deposition with a small extent of degradation was also previously reported by Kim et al⁶¹ with Cu-based anodes. In a work by Shiratori et al⁷⁰ with high temperature SOFC (1000° C), no carbon was detected on Ni/ScSZ cells, analysed with the FESEM microstructural analysis which may reflect all carbon including graphitic carbon has been oxidised at this temperature. Although small amounts of graphitic carbon were reported to have a positive influence on the electrochemical performance by enhancing the anode conductive network as reported by Mallon and Kendal⁷¹ and Dhir et al,⁷² excessive carbon build-up must be avoided as it will lead to stress, fracture the support or push the metal particles off the support as described by

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Boldrin et al^{37} and as observed in the present work (Figure 8).

4 | CONCLUSIONS

This study inspected the cause of electrochemical performance drop observed with Ni/YSZ cells and Ni/ScSZ in dry biogas with high CH₄/CO₂ ratio operated in IT-SOFC regime. From the results, the significant (80%) performance drop in Ni/YSZ cell was confirmed to be due to the deposited carbon which blocked the reaction sites and led to limited hydrogen availability on the anode. The slow diffusion of CH₄ and CO to the triple phase boundary region led to significantly high mass transfer polarisation in Ni/YSZ, hence the large drop of performance. On the other hand, the impact of mass-transfer polarisation was negligible on Ni/ScSZ due to higher hydrogen availability from the continuous methane reforming reaction which also concludes that Ni/ScSZ was a better catalyst for methane decomposition. The difference of the impact of carbon deposition and methane reforming activity on the cell performance deduced to be from the different influence of type of carbon formed on the anode catalyst: amorphous carbon with noncrystalline structure deposited on Ni/YSZ and whiskerlike graphitic carbon on Ni/ScSZ cells. Excessive amorphous carbon deposition without immediate oxidation led to carbon adsorbed onto the Ni surface and deactivated the catalyst, while excessive graphitic carbon caused problems in mechanical stability of the support catalyst. In addition, carbon quantification also affected by the oxidising nature of the carbon, in which graphitic carbon, which is more difficult to oxidise remains, resulting in 69.9% more carbon, whilst almost all the amorphous carbon oxidised.

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DATA ACCESSIBILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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FIGURE A1 Anode substrate of (A) Ni/YSZ and (B) Ni/ScSZ with 25k magnification after cell test. Coarse particles represent Ni $(d_{50} = 8.101 \pm 0.085 \mu m)$, while small circular particles represent electrolyte material: YSZ (0.855 $\pm 0.103 \mu m$) or ScSZ (0.514 $\pm 0.053 \mu m$)

