IOP Conference Series: Materials Science and Engineering

PAPER • **OPEN ACCESS**

The effects of Sn infiltration on dry reforming of biogas at solid oxide fuel cell operating conditions over Ni-YSZ catalysts

To cite this article: Lina Troskialina and Robert Steinberger-Wilckens 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **509** 012064

View the article online for updates and enhancements.

This content was downloaded from IP address 223.215.101.36 on 13/10/2019 at 23:27

IOP Conf. Series: Materials Science and Engineering **509** (2019) 012064 doi:10.1088/1757-899X/509/1/012064

The effects of Sn infiltration on dry reforming of biogas at solid oxide fuel cell operating conditions over Ni-YSZ catalysts

Lina Troskialina[1], Robert Steinberger-Wilckens[2]

[1] Jurusan Teknik Kimia, Politeknik Negeri Bandung, Bandung, 40012, Jawa Barat, Indonesia
[2] Center for Fuel Cell and Hydrogen Research, School of Chemical Engineering, University of Birmingham, Birmingham, B15 2TT, United Kingdom here
Email: lina.troskialina@polban.ac.id; r.steinberger-wilckens@bham.ac.uk

Abstract. This work presents successful infiltration of Ni-YSZ-based catalysts for dry reforming of biogas over a temperature range of 600–800°C. Ni catalysts over YSZ support are commonly used as solid oxide fuel cell (SOFC) anode material to catalyse the fuel, normally hydrogen, in electrochemical oxidation reaction to generate electricity. The objective of this work is to find suitable SOFC anode catalyst materials to enable the SOFCs to operate on biogas as a renewable and low cost fuel. There are challenges when biogas is used as fuel; biogas dry reforming is slow and deleterious carbon deposition is unavoidable. The slow electrochemical reaction leads to low SOFC performance. While accumulation of carbon deposits may reduce the catalytic activity, decrease the SOFC performance and can lead to a complete failure of the SOFC operation. In this work, tin salt was used as a dopant in careful infiltration of Ni-YSZ catalysts. Characterisations of the catalysts were performed using SEM, XRF and XPS. Dry reforming reactions were carried out in a quartz tube reactor attached to a quadrupole mass spectrometer to monitor the product gases. Various compositions of CO_2:CH_4 mixtures were used to simulate biogas. It was observed that at small quantities of less than 1 weight % Sn/Ni loadings, dry reforming of biogas produced much higher level of the desired CO and H_2 gas products compared to that obtained over non-infiltrated NiYSZ catalyst. The developed Sn-Ni-YSZ catalysts were able to operate continuously for more than 48 hours without noticeable performance degradation. More work is still in progress; however, this work so far concludes that Sn-doped Ni-YSZ catalysts have improved dry reforming of biogas at SOFC operating temperatures and so promised successful operations of SOFCs using biogas, a renewable fuel source, to produce sustainable electricity with high efficiency.
Keywords: dry reforming; biogas; SOFC anode infiltration; carbon deposition; NiYSZ

1. Introduction

The Fuel cell technology is an attractive alternative to conventional methods of energy generation. Several of the attractive points of fuel cell technology are the very low or almost ‘zero’ level of pollutants such as NO_x, SO_x, and particle emissions, potential high efficiency operation, and the highly modular nature, which allows for distributed power generation. The solid oxide fuel cell (SOFC), which operates at 600-800°C, is one of several types of fuel cell which offers promising clean and efficient energy production with added benefit of being fuel flexible. The high operating temperature of SOFC allows for direct use of methane and hydrocarbons through internal reforming and is beneficial for recovering heat as a by-product for operating as a combined heat and power (CHP) generator [1-4]. The benefit of SOFC in being capable of utilising hydrocarbons as fuel is added especially when the hydrocarbons

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd

come from renewable sources such as biogas. Modelling and evaluation of the economic value of operating an SOFC system in biogas fuel has shown promising results [5, 6]. Biogas is a methane rich gas phase product of anaerobic digestion of hydrocarbons and protein containing wastes. Biogas contains mainly CH_4 and CO_2 in various compositions plus other impurities depending on the source of the biomass.

The challenge for SOFC operation with direct biogas fuel is the low power produced originating from the lower heating value of the biogas compared to that of natural gas and the high possibility of carbon deposition on the anode catalyst surface which always accompanies hydrocarbon reforming and can lead to rapid SOFC performance degradation. Generally, carbon deposition is avoided by adding steam to the fuel feed with a ratio of 2 mole water to 1 mole carbon [7, 8]. However, this provision of steam in the feed supply adds complexity to the SOFC system and reduces overall efficiency.

Dry reforming is an endothermic catalytic reaction of methane and carbon dioxide, which produces CO and H_2. The reaction takes place above 400°C and can be represented by the overall reaction (1):

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H2 \qquad Kp_{800°C}=300 \qquad (1)$$

Two major steps are involved in reaction 1, methane decomposition (reaction 2) which produces carbon and hydrogen, followed by carbon oxidation by CO_2 (reaction 3) to form CO. Therefore, unreacted CH_4 and CO_2 plus CO, C, H_2 and H_2O as products are present in the system. In a reactor with the presence of CH_4, CO_2, CO, C, H_2 and H_2O, carbon accumulation is possible especially when carbon-forming reactions occur faster than carbon removal (or oxidation) reactions. Other possible reactions in the system are CO disproportionation and CO reduction by hydrogen as outlined in reactions 4 and 5 below. According to their low values of Kp, these two reactions are less likely to take place under normal SOFC operating conditions compared to the first three reactions. Another reaction, which may take place in an SOFC anode with hydrocarbon fuel, is water gas shift (WGS) reaction (reaction 6). This reaction produces H_2 from CO interaction with steam at high temperature.

$$CH_4 \rightleftharpoons C_{(adsorbed)} + 4H_{(adsorbed)} \qquad Kp_{800°C}=21.20 \qquad (2)$$

$$C_{(adsorbed)} + CO2_{(absorbed)} \rightleftharpoons 2CO_{(adsorbed)} \qquad Kp_{800°C}=7.90 \qquad (3)$$

$$2CO_{(adsorbed)} \rightleftharpoons C_{(adsorbed)} + CO2_{(adsorbed)} \qquad Kp_{800°C}=0.13 \qquad (4)$$

$$CO + H_2 \rightleftharpoons C_{(adsorbed)} + H_2O_{(adsorbed)} \qquad Kp_{800°C}=0.13 \qquad (5)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad Kp_{800°C}=1.0 \qquad (6)$$

Since all of the above reactions are reversible, it is possible to remove carbon in this system by promoting the reverse of carbon deposition reactions. Hence, provision of excess steam to the gas feed stream is needed during steam reforming to facilitate carbon removal through the reverse of reaction 5. Similarly, excess CO_2 is needed in dry reforming to facilitate reaction 3, which is the reverse of reaction 4. However, in practice, provision of excess H_2O or CO_2 complicates the SOFC system by adding a component to the fuel supply sub-system and leads to a consequence of lower electrical and overall power output due to dilution of the fuel gas stream.

The quantity of accumulated carbon is affected not only by the gas composition in the system, which is defined by the equilibrium constants, but also by the rate of carbon deposition and carbon removal, which are affected by the catalytic activity of the anode surface of the given system. Therefore, it is of paramount importance that the anode in an SOFC is designed to facilitate the desired reactions and to suppress or inhibit the undesired reactions. It follows that carbon accumulation can be reduced by not only adding excess H_2O or CO_2, but also by modifying anode catalytic properties. Various attempts have been made and successes have been achieved in modifying SOFC anode materials to enhance hydrocarbon reforming and electrochemical oxidations of the reforming products, and to improve the resistance to carbon deposition [9-12]. Hence, formulating and modifying the composition of anode material in SOFC can play an important role in minimising carbon deposition.

Despite the high activity of nickel towards carbon formation, to date NiYSZ cermets are still the most commonly used SOFC anodes. Other anode types, such as Cu-based anodes or mixed ionic-electronic conductive oxides, have shown better performance towards minimising carbon formation; however, they still suffer from several drawbacks such as low catalytic activity towards electrochemical oxidation and hydrocarbon reforming, low mechanical strength, or incompatible thermal coefficient of expansion with other SOFC components.

Infiltrating NiYSZ anodes with metals such as Ce, Mg, Mo, Sn and Rh have been reported as one of the methods attempted. Especially with Sn infiltration, work based on experiments and density functional theory (DFT) calculations have shown that the presence of approximately 1.0 wt% or less Sn/Ni in the form of Sn/Ni alloys showed significant effects on reducing carbon deposition during steam reforming [9-11]. Further investigations suggested that compared to NiYSZ, Sn/NiYSZ was reported to have a lower tendency to form C-C bonding [12-14] which led to Sn/NiYSZ catalysts demonstrating lower carbon deposition. The success of using Sn as a dopant for Ni-based catalysts in reducing carbon deposition during steam reforming operations such as reported by Trimm [9], Kan *et al.* [11], Kan and Lee [15], Nikolla *et al.* [10], Nikolla *et al.* [12], Nikolla *et al.* [13], Nikolla *et al.* [14] and Nikolla *et al.* [16] led to this investigation of using Sn as a dopant for direct-biogas SOFC operations in dry reforming mode as presented in this paper. Recent reports show that SnNi alloys demonstrated excellent performance on SOFC operating in biogas. Sn-infiltration on NiO powders for NiGDC anode and on NiYSZ nanoparticles for SOFC anode have been used by Myung *et al.* [17] and Hua *et al.* [18] respectively. These investigations support the proposition that high efficiency SOFC operation in pure biogas is promising.

As can be predicted from the C-H-O ternary diagram in Fig. 1 [19, 20], to prevent carbon deposition an SOFC operating with dry reforming thermodynamically needs a higher excess CO_2 or higher molar ratio of CO_2:CH_4 in the system compared to the need for excess H_2O in steam reforming operation. This paper presents results of investigating the ability of SOFC anode operating in biogas under dry reforming mode (without the addition of steam) with a low carbon dioxide to methane ratio of 1:2 CO_2:CH_4. This ratio represents a common biogas composition. This ratio also represents a biogas composition with high risk of carbon deposition.

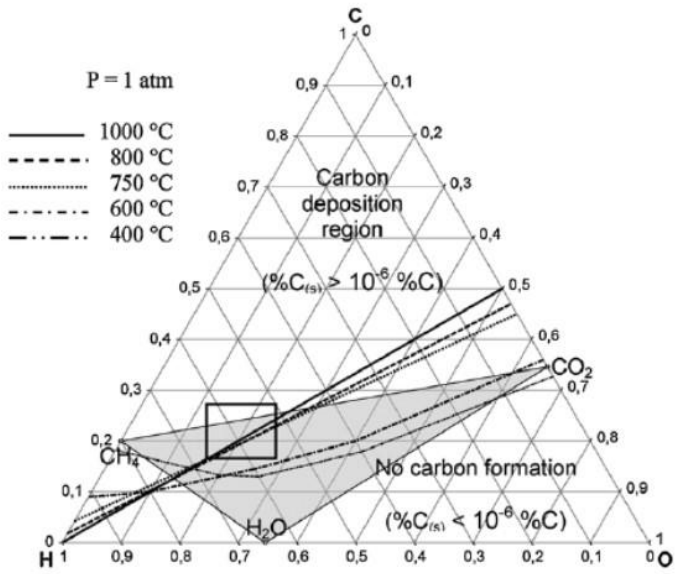


Figure 1. C-H-O ternary diagram at different operating temperature.

2. Materials and Methods

Commercially available Nickel Yttria Stabilized Zirconia (NiYSZ)-based pieces of planar SOFC anodes (NIMTE–Ningbo Institute of Materials and Energy Technology-China) with YSZ electrolyte layer (TOSOH TZ-8YSZ) were used as the catalyst material. The catalyst, weighing 500–785 mg for each charge, were placed in a quartz tube reactor. The reactor inlet is fed with simulated biogas at a certain ratio of CO_2:CH_4 with helium gas added as inert and partial pressure reference to enable calculation of other gases partial pressures. The SOFC anode outlet gas was fed to a Cirrus quadrupole mass spectrometer to allow for continuous monitoring of the anode gas composition.

Performance of the non-infiltrated and infiltrated catalysts in dry reforming reaction was observed. To prepare the Sn-dopant solution, $SnCl_2$ $2H_2O$ (Fisher Scientific, UK) was used as the Sn precursor and was dissolved in 95% ethanol. Sn-anode infiltration was carried out on sintered anode surface using a simple pipette drop method. Each drops of dopant solution contains 1 mg of Sn. The infiltrated anode discs were then dried and calcined. Before being used as the dry reforming catalyst, the discs were crushed into small pieces of 2-4 mm diameter. Gravimetric analysis and SOFC anode surface characterisations using XRF, SEM/EDX, XRD and XPS were used to confirm the presence of Sn in the Sn-infiltrated SOFC anodes.

3. Results and Discussion

This section presents results of physical properties characterisations of the catalysts using SEM/EDX, XRF and XPS analysis and of observing the activity of NiYSZ-based SOFC anode pieces to catalyse dry reforming of biogas. The catalytic activity of NiYSZ was measured in terms of the amount of H_2 and CO gases produced and percentage conversion of CH_4 and CO_2. The effects of operating temperature and CO_2:CH_4 ratio in the feed composition on the H_2 and CO gases produced were observed.

3.1. Gravimetric analyses, SEM/EDX, XRF and XPS

3.1.1. Gravimetric analysis. As represented in Fig. 2 gravimetric analysis showed that a linier relationship is obtained between the number of drops of Sn-salt solution and the anode weight gain. For each number of Sn-salt solution 6 sample repeats were used.

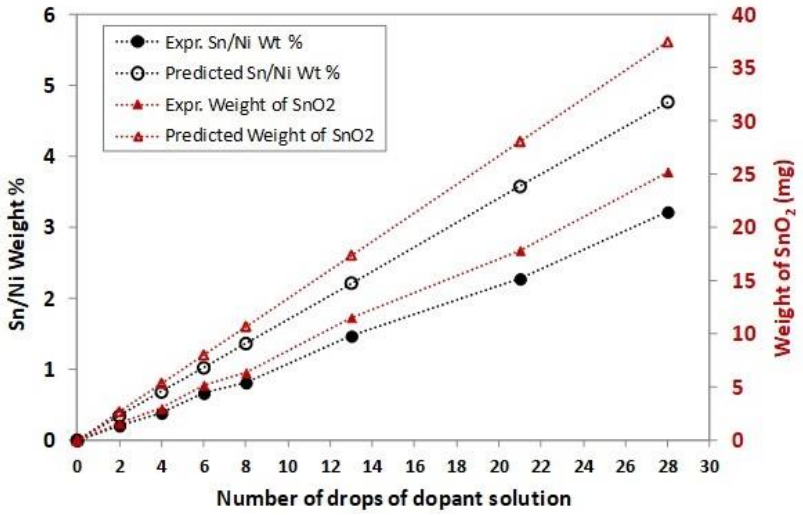


Figure 2. Results of gravimetric analyses of SOFC anode weight gain at different Sn loads.

3.1.2. SEM and EDX. SEM/EDX were used to characterise the cell microstructure. Detailed micrographs of the porous anode, dense electrolyte and porous cathode are described in [21]. The micrographs show that on the anode surface Zr-rich part forms more continuous part compared to Ni-rich part. They also

showed that anode pores are of less than 1µm diameter. The EDX map confirms that Sn is present and well distributed over the Ni particle sites, and much less on Zr-rich sites.

3.1.3. XPS and XRF. An SOFC anode disk which had been infiltrated with 28 drops of Sn-salt was used as the sample for XRF analysis. The results are presented in table 1 and Fig. 3. The spectra in Fig. 3 show Ni, Zr, Y and Sn peaks of principal line KA1 accompanied by KB1. Although rhodium is not on the list of the SOFC anode component, it appears in these spectra since the XRF detector we used contained Rh.

Table 1. Chemical composition of 28D-Sn-infiltrated SOFC anode obtained from XRF.

Atomic symbol	Atomic Number	Weight %	Atomic
Ni	28	48.07	
Zr	40	46.48	
Sn	50	4.80	
Y	39	0.65	
Atomic ratio Ni:Sn			20.3 : 1
Atomic % Sn			4.71
Weight % of Sn/Ni		9.99	

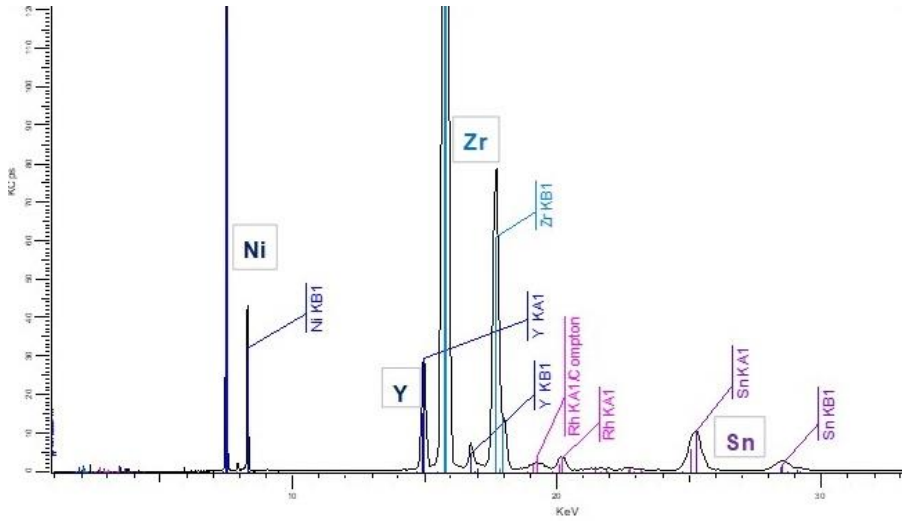


Figure 3. X-ray fluorescence spectra of 28D-Sn-infiltrated anode.

Table 2 shows the chemical composition obtained from XPS of the 28-drops 28D-Sn-infiltrated SOFC anode. It is shown that as high as 59.72 weight % Sn/Ni is identified by XPS. Since XPS analysis measures only a sample surface layer down to 20 nanometres deep, this high value of 59.72 weight % Sn/Ni indicates that the Sn content is highest on the anode surface. This is made clear when the value is compared to 9.99 weight % obtained from XRF and 4.77% obtained from gravimetric analysis which represent the Sn content in the bulk anode. The finding is in accordance with the observation presented by Nikolla *et al.* [13], Nikolla *et al.* [14].

Table 2. Chemical composition of 28D-Sn-infiltrated NiYSZ anode surface obtained from XPS.

Ni 2p %	O 1s %	Sn 3d %	Zr 3d %	At Ni:Sn	At % Sn	Wt % Sn/Ni
15.34	38.38	5.13	5.02	2.99 : 1	25	67.61

3.2. The effects of operating temperature

Fig. 4a and 4b show mass spectra of methane dry reforming product gases at different operating temperatures for non-infiltrated and Sn-infiltrated catalysts respectively. The biogas feed composition was 1:2:2 volume ratio of CO_2: CH_4: He which was the composition intended to be used for the SOFC operation. The spectra in Fig. 4a show almost equimolar H_2 and CO produced at 800°C but slightly higher CO produced at 750°C and 700°C. A similar trend is observed in Fig. 4a and 4b; that is the unreacted CO_2 and CH_4 are lowest at 800°C, and that the unreacted gas feed gradually increased and showed the highest values at 650°C. Both Fig. 4a and 4b also show that a decrease of 50°C resulted in the decrease of H_2 and CO produced by approximately 50%. The lower the temperature the less CO and H_2 were produced. At 650°C very little (less than 3%) CO and H_2 were produced which means that the activity of this NiYSZ catalyst at 650°C is very low hence this may not provide sufficient CO and H_2 for SOFC operation. At 750°C, the planned temperature to operate the fuel cell, approximately 5 vol.% H_2 and 7 vol.% CO are produced. These results show that at 750°C H_2 and CO are present as the dry reforming products and thus available for electrochemical reactions under fuel cell operation. It is interesting to compare the level of H_2 and CO partial pressures represented by the blue and yellow coloured curves in Fig. 4a and 4b. The results of dry reforming over Sn-infiltrated NiYSZ shows twice or higher H_2 and CO produced than that of non-infiltrated NiYSZ. This shows that Sn-infiltration improves dry reforming of CH_4 and increases the H_2 and CO production. Even at 650°C more CO and H_2 (between 5-7%) were produced over Sn-infiltrated catalyst than that over non-infiltrated catalyst.

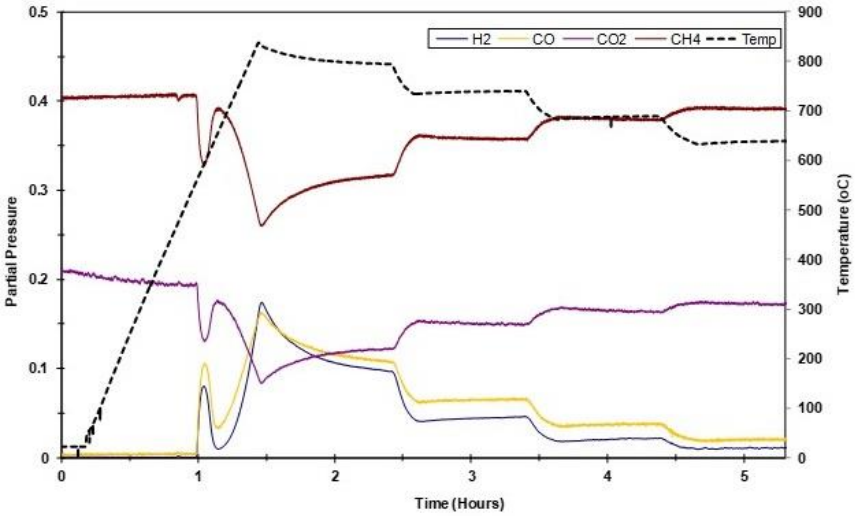


Figure 4a. Mass spectra of outlet gases from dry reforming over non-infiltrated NiYSZ anode at 650-800°C.

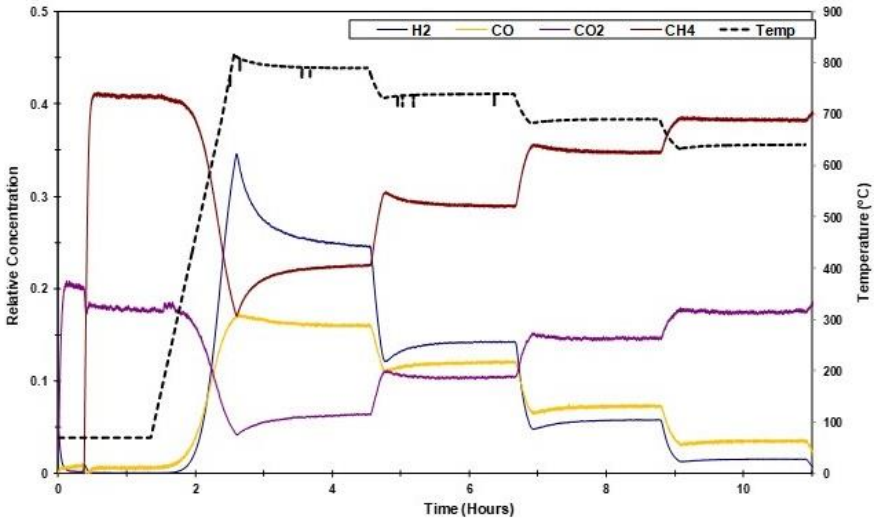


Figure 4b. Mass spectra of outlet gases during dry reforming over (6-drops) Sn-infiltrated NiYSZ anode at 650-800°C.

Fig. 5 shows % conversion of CO_2 and CH_4over non-infiltrated catalyst at different temperatures while Fig. 6 shows partial pressures of CO and H_2 produced. Fig. 5 and 6 clearly show that dry reforming of CH_4 is significantly affected by temperature; increasing temperature from 750°C to 800°C resulted in two folds of increase of CO_2 and CH_4 conversion and twice the amount of CO and H_2 produced. The very low CO and H_2 produced at 700°C and especially at 650°C indicate dry reforming on this NiYSZ anode at 700°C and 650°C are not efficient. This finding is an important input in selecting suitable SOFC operating temperature for direct biogas reforming. In Fig. 5 it is shown that CO_2 conversion was higher than CH_4 conversion. At 800°C, CO_2 conversion was 40% while CH_4 conversion was only 20%. This phenomenon is in agreement with that observed by Stagg *et al.* [22]. Stagg and co-workers reported that ZrO_2 as a Pt catalyst support for dry reforming of CH_4 plays a good role in promoting CO_2 dissociation, compared to SiO_2. In this work the ZrO_2 in NiYSZ may have acted as a promoter for CO_2 dissociation.

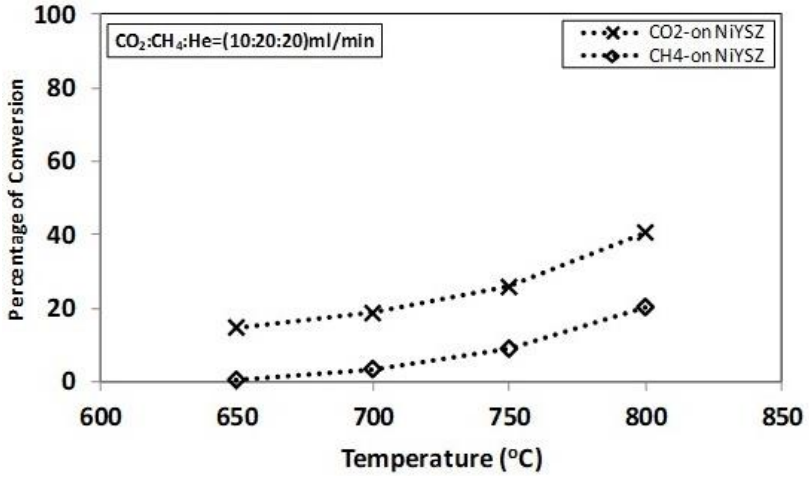


Figure 5. Percent conversion of CO_2 and CH_4 over non-infiltrated NiYSZ anode at 650-800°C.

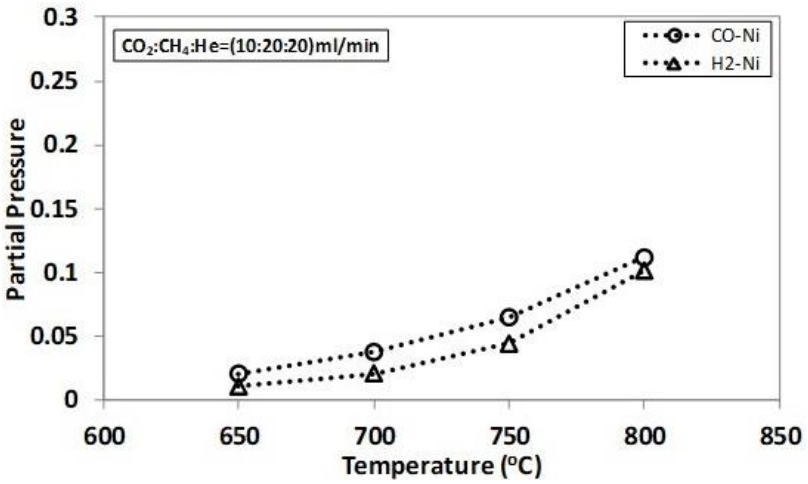


Figure 6. Partial pressure of CO and H_2 produced over non-infiltrated NiYSZ anode at 650-800°C.

3.3. The effects of different feed composition

Fig. 7 shows effect of different feed compositions on the outlet gas composition. The spectra were obtained from 500 mg Sn-infiltrated anode. The total volume of gas feed was kept at 50 ml min^{-1} with constant 5 ml min^{-1} helium flow and varied flow rates of CO_2 and CH_4. Fig. 7 shows that the highest level of H_2 and CO produced is at 1:1 ratio of CO_2:CH_4 feed which is expected from stoichiometry, but this is also in agreement with literature [22]. Fig. 7 also shows that at CO_2:CH_4 =1:2 H_2 produced is slightly higher than that from CO_2:CH_4=1:1, and CO produced is only slightly lower. This is a good indication for the planned SOFC operation; in that the SOFC is feasible to operate at 750°C and with CO_2:CH_4=1:2 to produce sufficient amount of CO and H_2 for electrochemical oxidation.

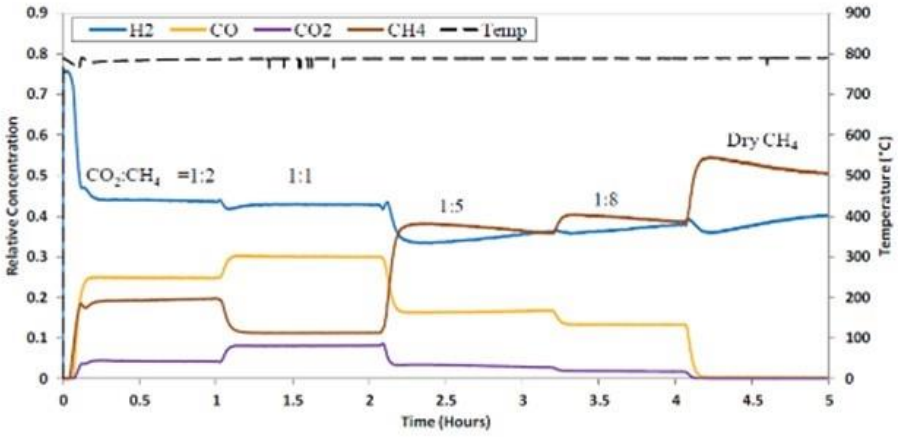


Figure 7. Mass spectra of outlet gases during dry reforming over (4-drops) Sn-infiltrated NiYSZ anode at 800°C and varied CO_2:CH_4 ratio.

Fig. 8 and 9 are the same experimental results with those in Fig. 7 but presented in bar charts to make comparisons of all gas partial pressures easier. Fig. 8 and 9 also show that it is the amount of CO produced which linearly corresponds to the different CO_2:CH_4 ratio in the feed; while H_2 produced was not linearly affected by CO_2:CH_4 ratio. The amount of CO produced decreases as the CO_2 concentration in the feed was decreased. This can be explained by the general understanding that dry reforming reaction, represented by equation 1, occurs via at least two reactions namely methane cracking, equation

2 which produces C and H_2, and oxidation of C by CO_2 to form CO which is also known as reverse Boudouard reaction (equation 3). Considering these three reactions it is clear that in a closed system, the amount of CO produced is directly affected by the available CO_2.

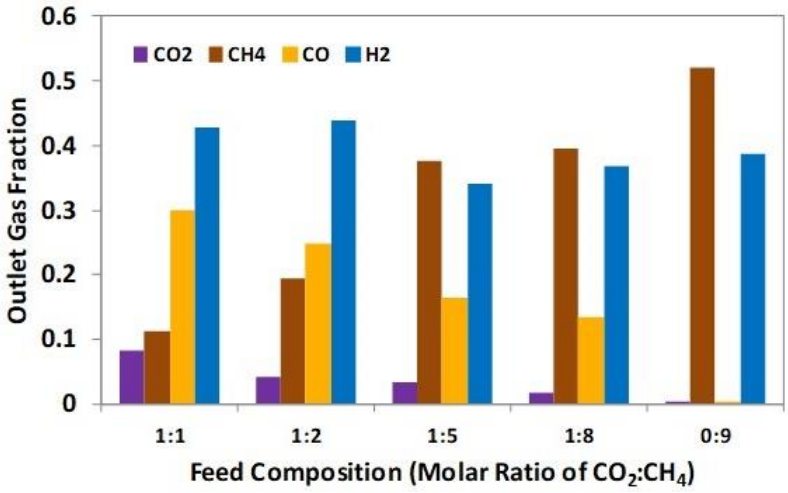


Figure 8. Dry reforming product gas fraction over 4-drops Sn-infiltrated NiYSZ anode at 800°C at varied CO_2:CH_4 ratio.

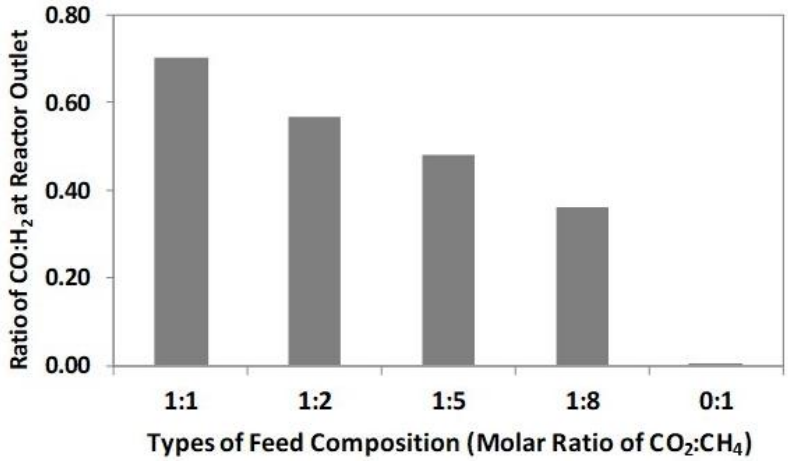


Figure 9. Ratio of CO:H_2 over 4-drops Sn-infiltrated NiYSZ anode at 800°C and varied CO_2:CH_4 ratio.

For an equilibrium dry reforming reaction without steam, the ratio of CO to H_2 present in the product stream is expected to be 1. Fig. 8 and 9 show that the ratio of CO:H_2 produced being less than 1 and the less CO_2 in the feed results in the less CO produced; this may indicate that carbon is formed during the dry reforming reaction and that the presence of CO_2 is essential to reduce carbon accumulation. The most important and promising result is that the Sn-infiltrated catalyst is able to catalyse methane dry reforming at 650–800°C with conversion at 750°C producing sufficient amount of CO and H_2 for electrochemical oxidation.

3.4. Overall discussion

Pieces of non-infiltrated SOFC and Sn-infiltrated SOFC anodes were tested as catalysts for dry reforming reactions. It was shown that at the observed temperature range (650°C to 800°C) Sn-infiltrated SOFC anodes converted more CO_2 and CH_4 and produced more H_2 and CO compared to non-infiltrated

ones. On both non-infiltrated and Sn-infiltrated anodes, more H_2 is produced at higher temperature (800°C) than at the lower temperatures of 650–750°C. It was observed that at 750°C and 1:2:2 ratio of CO_2: CH_4: He approximately 5 vol.% H_2 and 7 vol.% CO were produced on non-infiltrated NiYSZ SOFC anode while 15 vol.% H_2 and 13 vol.% CO were produced on Sn-infiltrated NiYSZ SOFC anode. These differences on the level of H_2 and CO produced from the dry reforming reaction and the fact that Sn-infiltrated anodes produced 2 to 3 times CO and H_2 compared to uninfiltrated anodes are considered sufficient for further investigation of the non-infiltrated and Sn-infiltrated SOFC anode electrochemical performance in the SOFC operation.

As expected from stoichiometry, observation of dry reforming at different CO_2:CH_4 ratios shows that equimolar feed of CO_2:CH_4 produced the highest amount of CO and H_2 compared to other feed compositions. The amount of CO produced is much affected by the composition of CO_2 in the feed. Rough comparison of dry reforming on 6-drops and 4-drops Sn-infiltrated SOFC anodes (Fig.s 4b and 7 respectively) shows that the Sn loading is another determining factors (other than temperature and gas composition) for the amount of H_2 and CO produced with 4-drops Sn-infiltrated anode showing better CO_2 conversion. This means that a very small quantity of Sn in NiYSZ anode makes a significant difference in the catalytic performance.

4. Conclusion

It was shown that Sn infiltration on anode surface significantly improved dry reforming of CH_4 over 650–800°C and methane to carbon dioxide ratio of 1:1 to all methane (90% CH_4 and 10% Helium) conditions. As a base for evaluation of SOFC operation with direct biogas feed, these results of dry reforming on SOFC anode pieces have shown that infiltration of SOFC anode with Sn dopant increased the yield of dry reforming products, namely CO and H_2, therefore Sn-infiltration is very promising to be used in improving electrochemical performance of SOFC operating on biogas. The Sn-infiltrated NiYSZ catalysts are expected to give higher electrochemical performance and less carbon accumulation when employed as SOFC anode.

References

[1] Laramie J and Dicks A 2003 *Fuel cell systems explained* (New York: John Wiley and Sons)
[2] Singhal S C and Kendall K 2003 *High-temperature solid oxide fuel cells: fundamentals, design and applications*: Elsevier)
[3] Fergus J, Hui R, Li X, Wilkinson D P and Zhang J 2016 *Solid oxide fuel cells: materials properties and performance*: CRC press)
[4] Taufiq B N, Kikuchi Y, Ishimoto T, Honda K and Koyama M 2015 Sensitivity Analysis for the Efficiency Improvement of a Light Integrated Gasification Fuel Cell Power Plant *ECS Trans.* **68** 1 333-42
[5] Siefert N S and Litster S 2014 Exergy & economic analysis of biogas fueled solid oxide fuel cell systems *J. Power Sources* **272** 386-97
[6] Lanzini A, Leone P, Guerra C, Smeacetto F, Brandon N and Santarelli M 2013 Durability of anode supported Solid Oxides Fuel Cells (SOFC) under direct dry-reforming of methane *Chem. Eng. J.* **220** 254-63
[7] Assabumrungrat S, Laosiripojana N and Piroonlerkgul P 2006 Determination of the boundary of carbon formation for dry reforming of methane in a solid oxide fuel cell *J. Power Sources* **159** 2 1274-82
[8] Sangtongkitcharoen W, Assabumrungrat S, Pavarajarn V, Laosiripojana N and Praserthdam P 2005 Comparison of carbon formation boundary in different modes of solid oxide fuel cells fueled by methane *J. Power Sources* **142** 1-2 75-80
[9] Trimm D L 1999 Catalysts for the control of coking during steam reforming *Catal. Today* **49** 1-3 3-10
[10] Nikolla E, Schwank J and Linic S 2007 Promotion of the long-term stability of reforming Ni catalysts by surface alloying *J. Catal.* **250** 1 85-93

[11] Kan H, Hyun S H, Shul Y-G and Lee H 2009 Improved solid oxide fuel cell anodes for the direct utilization of methane using Sn-doped Ni/YSZ catalysts *Catal. Commun.* **11** 3 180-3
[12] Nikolla E, Schwank J and Linic S 2009 Measuring and relating the electronic structures of nonmodel supported catalytic materials to their performance *J. Am. Chem. Soc.* **131** 7 2747-54
[13] Nikolla E, Schwank J and Linic S 2009 Comparative study of the kinetics of methane steam reforming on supported Ni and Sn/Ni alloy catalysts: the impact of the formation of Ni alloy on chemistry *J. Catal.* **263** 2 220-7
[14] Nikolla E, Schwank J W and Linic S 2008 Hydrocarbon steam reforming on Ni alloys at solid oxide fuel cell operating conditions *Catal. Today* **136** 3-4 243-8
[15] Kan H and Lee H 2010 Sn-doped Ni/YSZ anode catalysts with enhanced carbon deposition resistance for an intermediate temperature SOFC *Appl. Catal. B* **97** 1-2 108-14
[16] Nikolla E, Schwank J and Linic S 2009 Direct electrochemical oxidation of hydrocarbon fuels on SOFCs: improved carbon tolerance of Ni alloy anodes *J. Electrochem. Soc.* **156** 11 B1312-B6
[17] Myung J-h, Kim S-D, Shin T H, Lee D, Irvine J T, Moon J and Hyun S-H 2015 Nano-composite structural Ni–Sn alloy anodes for high performance and durability of direct methane-fueled SOFCs *J. Mater. Chem. A* **3** 26 13801-6
[18] Hua B, Li M, Sun Y-F, Zhang Y-Q, Yan N, Chen J, Li J, Etsell T, Sarkar P and Luo J-L 2016 Biogas to syngas: flexible on-cell micro-reformer and NiSn bimetallic nanoparticle implanted solid oxide fuel cells for efficient energy conversion *J. Mater. Chem. A* **4** 12 4603-9
[19] Kee R J, Zhu H and Goodwin D G 2005 Solid-oxide fuel cells with hydrocarbon fuels *Proc. Combust. Inst.* **30** 2 2379-404
[20] Girona K, Laurencin J, Fouletier J and Lefebvre-Joud F 2012 Carbon deposition in CH4/CO2 operated SOFC: Simulation and experimentation studies *J. Power Sources* **210** 381-91
[21] Troskialina L, Dhir A and Steinberger-Wilckens R 2015 Improved Performance and Durability of Anode Supported SOFC Operating on Biogas *ECS Trans.* **68** 1 2503-13
[22] Stagg S, Romeo E, Padro C and Resasco D 1998 Effect of Promotion with Sn on Supported Pt catalysts for CO_2 Reforming of CH_4 *J. Catal.* **178** 1 137-45