

The effect of H₂S on internal dry reforming in biogas fuelled solid oxide fuel cells

Wasajja, Henry; Saadabadi, S. Ali; Illathukandy, Biju; Lindeboom, Ralph E.F.; van Lier, Jules B.; Vellayani Aravind, Purushothaman

DOI

[10.1002/ese3.1021](https://doi.org/10.1002/ese3.1021)

Publication date

2021

Document Version

Final published version

Published in

Energy Science and Engineering

Citation (APA)

Wasajja, H., Saadabadi, S. A., Illathukandy, B., Lindeboom, R. E. F., van Lier, J. B., & Vellayani Aravind, P. (2021). The effect of H₂S on internal dry reforming in biogas fuelled solid oxide fuel cells. *Energy Science and Engineering*, 10(2), 374-383. <https://doi.org/10.1002/ese3.1021>

Important note

To cite this publication, please use the final published version (if applicable).
Please check the document version above.

Copyright

Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

Takedown policy

Please contact us and provide details if you believe this document breaches copyrights.
We will remove access to the work immediately and investigate your claim.

ORIGINAL ARTICLE

The effect of H₂S on internal dry reforming in biogas fuelled solid oxide fuel cells

Henry Wasajja^{1,2}  | S. Ali Saadabadi³ | Biju Illathukandy^{4,5} |
Ralph E. F. Lindeboom¹ | Jules. B. van Lier¹ | Purushothaman Vellayani Aravind^{3,6}

¹Water Management Department, Sanitary Engineering Section, Faculty of Civil Engineering and Geosciences, Delft University of Technology, Delft, The Netherlands

²Department of Electrical Engineering, Faculty of Engineering, Ndejje University, Kampala, Uganda

³Process and Energy Department, Faculty of 3mE, Delft University of Technology, Delft, the Netherlands

⁴Centre for Rural Development & Technology, Indian Institute of Technology Delhi, New Delhi, India

⁵Department of Mechanical Engineering, Government Engineering College, Kozhikode, India

⁶Energy and Sustainability Research Institute Groningen, Faculty of Science and Engineering, University of Groningen, Groningen, the Netherlands

Correspondence

Henry Wasajja, Water Management Department, Sanitary Engineering Section, Faculty of Civil Engineering and Geosciences, Delft University of Technology, Delft, The Netherlands.
Email: h.wasajja-1@tudelft.nl

Funding information

This work was supported by TU Delft Global initiative (fellowship number 15DGF214)

Abstract

Internal dry reforming of methane is envisaged as a possibility to reduce on capital and operation costs of biogas fuelled solid oxide fuel cells (SOFCs) system by using the CO₂ present in the biogas. Due to envisaged internal dry reforming, the requirement for biogas upgrading becomes obsolete, thereby simplifying the system complexity and increasing its technology readiness level. However, impurities prevailing in biogas such as H₂S have been reported in literature as one of the parameters which affect the internal reforming process in SOFCs. This research has been carried out to investigate the effects of H₂S on internal dry reforming of methane on nickel-scandia-stabilised zirconia (Ni-ScSZ) electrolyte supported SOFCs. Results showed that at 800°C and a CH₄:CO₂ ratio of 2:3, H₂S at concentrations as low as 0.125 ppm affects both the catalytic and electric performance of a SOFC. At 0.125 ppm H₂S concentration, the CH₄ reforming process is affected and it is reduced from over 95% to below 10% in 10 h. Therefore, future biogas SOFC cost reduction seems to become a trade-off between biogas upgrading for CO₂ removal and biogas cleaning of impurities to facilitate efficient internal dry reforming.

KEYWORDS

H₂S, Internal dry reforming, Ni-based catalyst, SOFC poisoning

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

© 2021 The Authors. *Energy Science & Engineering* published by Society of Chemical Industry and John Wiley & Sons Ltd.

1 | INTRODUCTION

Biogas is one of the most common energy carriers recovered from waste. It is mainly composed of CH_4 and CO_2 . In the presence of heat and a catalyst, CH_4 reacts with CO_2 to form H_2 and CO which are potential SOFC fuels. SOFCs operate often with Ni-based anodes at temperatures between 600 and 1000°C.¹ Ni can catalyse CH_4 and CO_2 reforming reaction at temperatures as low as 400°C.² SOFCs are reported to be tolerant to CO-containing fuels.³ This provides an opportunity for internal reforming in SOFCs, since Ni is also a catalyst for CH_4 reforming.⁴ Hence, there is a possibility to use biogas as a fuel for SOFCs.⁵ However, there are still technical challenges such as carbon deposition, thermal stress and gas contaminant poisoning for direct biogas-fuelled SOFCs.⁶ Therefore, currently research is being directed to develop more efficient Ni-based catalysts for electro-catalytic reforming.⁷

Possibilities of methane internal dry reforming in SOFCs were investigated by Goula et al.⁸ Authors observed that internal dry reforming is indeed feasible in SOFCs. However, full dry reforming is still a challenge especially if Ni-based SOFC anodes are used due to the risk of carbon deposition and nickel re-oxidation in the H_2 -lean portions of the anode.⁹ The possibility for internal dry reforming can greatly reduce the overall system costs by 6% if external reformers can be eliminated from the system.¹⁰ Also, Schubert and Kusnezoff¹¹ reported that direct internal reforming of SOFCs fuelled with biogas is preferred due to its foreseeable cost reduction in the overall plant investment. It is important to note that currently the major drawback of SOFC application in the energy sector is high upfront capital expenditures.¹² Therefore, for small-scale systems, internal dry reforming could also reduce the overall system costs, which is critical especially for systems less than 10 kW capacity.

However, gas impurities are generally considered to be detrimental to the reforming process and general operation of the SOFC system.¹³ Among the impurities in the biogas, H_2S is considered as the most detrimental and thermodynamically stable gas at the common operating conditions of SOFCs.¹⁴ It is generally agreed that H_2S may have an influence on both the chemical and electro-chemical reaction on the Ni anodes.^{15,16} These effects can be potentially influenced by a number of parameters ranging from fuel composition to materials from which SOFC anodes are developed.¹⁷ In SOFCs, biogas dry reforming would be preferred to steam reforming since it is seen as a possible mechanism of cost and system complexity reduction.¹⁸ Moreover, small-scale SOFCs are being promoted by a number of companies¹⁹⁻²¹ and such system would be suitable for internal dry reforming if they are to be fuelled by biogas.

Highlights

- Impact of H_2S on the reforming process depends on the catalyst, operating conditions and the gas composition.
- Experimental investigation of the effect of H_2S on internal dry reforming in the presence of a catalyst.
- Experimental investigation of effect of H_2S on dry reforming without the catalyst.
- H_2S concentration as low as 0.125 ppm in biogas is found to affect the internal dry reforming.
- Stringent gas cleaning is needed for biogas SOFC systems undergoing internal dry reforming

It has been reported that H_2S content in the gas as low as 2 ppm already has an effect on the internal SOFC steam reforming process.^{15,16} However, this effect could be different during dry reforming process in the presence of CO_2 .²² Moreover, even with reformed gas, H_2S as low as 0.5 ppm has been reported to affect the electro-chemical performance of SOFCs at 750°C.²³

Under syngas operation, nickel-gadolinium-doped ceria (Ni-GDC) anode material showed good performance as compared to other materials like nickel-yttria-stabilised zirconia (Ni-YSZ).²⁴ Ni-GDC has been reported to have an enhanced tolerance of H_2S in the presence of hydrocarbon (H/C) fuels, and this is attributed to CeO_2 which enhances reforming and as well as H_2S tolerance.¹⁷ Also, addition of Cu to Ni anodes could stabilise the active surface of the anode by limiting the rate of carbon deposition.²⁵ Therefore, the effect of H_2S on dry reforming could also be influenced by material composition of the anode.⁹

Under steam reforming conditions, H_2S has been reported to have a larger effect on reforming activity than on the electro-chemical activity even at H_2S concentration of 2–4 ppm levels.¹⁶ This is also in agreement with Aravind et al.²⁶ This could be due to the different reforming and electro-chemical sites within the cell. H_2S has been reported to decrease the rate of the water gas shift reaction.²³ Therefore, the effect of H_2S on the performance of SOFCs generally depends on material composition of the anode and operating parameters such as temperature.²⁷⁻²⁹ H_2S effect on the catalytic performance of a catalyst varies depending on the material composition.³⁰ Hence, in the presence of reforming gases, H_2S could have an effect on both chemical and electro-chemical process and this effect would vary depending on the specific operational conditions of the SOFC, its material composition and fuel gas composition.³¹

The effect of H_2S on dry reforming was investigated by Shiratori et al.³² In their experiment, they used an electrolyte supported Ni-ScSZ cermet SOFC of $8 \times 8 \text{ mm}^2$. A simulated biogas of $CH_4/CO_2 = 1.5$ at SOFC operating temperature of 1000°C was used at a current density of 200 mA cm^{-2} . Under these conditions, a 9% drop in voltage and 40% drop in reforming reaction rate was observed during poisoning of the cell by 1 ppm of H_2S . They observed that under these conditions, a concentration of 1 ppm H_2S is feasible during internal dry reforming. With real biogas, a constant voltage above 0.9 V was attained during the 50 h of operation with no observation of carbon deposition. Attempts to study the effect of H_2S on dry reforming by Xu et al.³³ were hindered by carbon deposition; therefore, no results were yielded from the experiment. Johnson et al.²² studied the effect of H_2S on dry reforming under catalytic conditions. They found out that the effect of H_2S was more severe under steam reforming as compared to dry reforming. This is also re-affirmed by Lakshminarayanan et al.³⁴ Also, it was reported that H_2S appears to increase the chances of carbon deposition.³⁵ Table 1 represents H_2S tolerance for different anode materials with varying gas composition and experimental conditions from selected literature.

It is generally agreed that H_2S may have an effect on the dry reforming process depending on the type of catalysts and operating conditions.^{36,37} But detailed analysis is still required to investigate the H_2S concentration limit for SOFCs and the performance of the cell close to real operating conditions of normal-sized SOFCs. Therefore, this research has given focus on investigating the effects of H_2S on dry reforming under both current load and open-circuit voltage (OCV) operating conditions of SOFCs. To the authors knowledge, no attempt has been done to investigate the effects of H_2S on dry reforming under typical SOFC operating conditions ($800\text{--}850^\circ\text{C}$) of relatively large surface area SOFC (close to real operating conditions of normal-sized SOFC) under current and OCV. Moreover, the boundary limit of H_2S concentration in fuel gas at a typical SOFC operational condition of $800\text{--}850^\circ\text{C}$ with internal dry reforming has not been investigated.

2 | MATERIALS AND METHOD

It is hypothesised that the effect of H_2S on dry reforming will vary depending on operating conditions. Hence, experiments were conducted under different operating conditions.

2.1 | Experimental setup

Experiments have been conducted to evaluate the performance of a SOFC under dry reforming in the presence of

H_2S at 800°C . The setup used is shown in Figure 1. In this experiment, commercial Ni-ScSZ electrolyte-supported cells with an active area of 81 cm^2 were used.

The gases were supplied from gas bottles. Composition and flow rate were varied using mass flow controllers (MFC) (Bronkhorst High-Tech BV). The inlet gas to the anode was trace heated to 130°C . Temperature of the oven was maintained by 4 electrical heaters controlled by the furnace control unit. The performance of the cell was analysed by Gammry FC-350. Outlet gas composition was analysed by micro gas chromatograph device. The anode outlet gas was dried using silica gel for analysis in Agilent 490 micro-GC columns (Molsieve 5A and PoraPLOT U). The cell temperature was measured by the k-type thermocouple (RS PRO, $-50^\circ\text{C}/+1200^\circ\text{C}$) closely placed at the anode side. The cells were placed between two ceramic blocks. To ensure gas tightness, mica (thermiculite) sheets were placed in the anode side and in the cathode side. To enhance gas sealing, extra weights were added on the top of the block as represented in Figure 1. For further details of the set-up, the reader is referred to Saadabadi et al.⁴⁵

2.2 | Experimental procedure

The cells were preheated by heating the furnace to 1000°C at a ramp rate of 50°C h^{-1} with N_2 gas flowing at a rate of 1200 ml min^{-1} to the anode and cathode. At 950°C , the NiO of the anode was reduced by feeding H_2 to the anode and simulated air (O_2 and N_2) to the cathode. During cell reduction, the concentration of H_2 gas was gradually increased from 2% to 100% in 4 h. The current-voltage measurements were carried out after the cell reduction procedure.

The cells were fed with CH_4 , CO_2 and N_2 mixture with different compositions. H_2S injection was carried out by including H_2S in the gas mixtures which was in N_2 bottle. The concentration of H_2S in the fuel gas was varied by changing the flow from H_2S/N_2 (H_2S concentration of 50 ppm) bottle and compensating it with the flow from N_2 bottle to maintain a total of $1200 \text{ Nml min}^{-1}$. The ratio of $CH_4:CO_2$ in this experiment was 2:3. The ratio was chosen to have enough CO_2 which can suppress carbon deposition.^{46,47} After poisoning with H_2S , the cells were recovered using pure H_2 balanced with N_2 gas for 12 h.

To determine the effect of H_2S on dry reforming under current conditions using a Ni-ScSZ cell, a constant current of 2 A (250 A m^{-2}) was drawn from the cell using $CH_4:CO_2$ of 2:3 as fuel at 800°C . Starting with H_2S concentration of 0 ppm, the cell was poisoned with 0.125 ppm and the percentage of CH_4 reformed was

TABLE 1 Studies on sulphur poisoning during methane reforming process

Cell/Catalyst	Fuel	Experimental Conditions	H ₂ S tolerance limit	Ref.
Planar SOFCs with (Ni/YSZ) anode support and an active Ni/YSZ anode, a YSZ electrolyte, and a lanthanum-strontium-manganese (LSM)/YSZ cathode. (Total area 5x5 cm ² , active area 4x4 cm ²)	13–46% H ₂ , 17–29% CH ₄ , 37–58% H ₂ O, 2–9 ppm H ₂ S (57–60% FU)	T = 850°C, OCV and under current load 1 A/cm ²	Under current load, just below 7–9 ppm is feasible for 24-hour period	[16]
Planar SOFC Ten Cell Stack (12x12 cm ²)	11.5% H ₂ , 10.5% CO, 12.5% CO ₂ , 1.5% CH ₄ , 63.2% N ₂	T = 700°C, 800°C	10 ppm at 800°C	[38]
Anode supported SOFCs with Ni/YSZ anodes, YSZ electrolytes and LSM/YSZ cathodes (denoted as Ni, YSZ, LSM). The active area was 4 cm x4 cm	13% H ₂ , 29% CH ₄ , 58% H ₂ O 2–24 ppm of H ₂ S.	T = 850°C. OCV and under 1 A cm ⁻² (0.44)	2 ppm for Ni/Sc-YSZ and less than 2 ppm for Ni/YSZ for 500 h	[15]
Ni/GDC, electrolyte supported, 100 cm ² active area	Different percentages of H ₂ , CO, CH ₄ , CO ₂ , N ₂ , H ₂ O-2 ppm of H ₂ S	T = 850°C, T = 920°C	Less than 2 ppm of sulphur deactivates the Ni/GDC anodes for methane reforming but not for oxidation of H ₂ and CO	[26]
Ni-YSZ (uncoated and coated with Ni-CeO) button cells	32% CH ₄ , 48% H ₂ O, 20% CO ₂ , 200 ppm of H ₂ S	T = 850°C, at 0.5A cm ⁻²	20 ppm caused irreversible loss for uncoated cell and reversible loss for the coated loss	[33]
Anode supported cells with Ni/YSZ anodes, YSZ electrolyte and LSM/YSZ cathodes, 5x5 cm ²	26% H ₂ , 32% H ₂ O, 20% CO, 22% CO ₂ at 850°C and 27% H ₂ , 31% H ₂ O, 19% CO and 23% CO ₂	T = 750°C and T=850°C, at 0.25–0.5 A cm ⁻²	Less than 8 ppm was possible for CO-containing fuel and less up to 90 ppm for H ₂ /H ₂ O fuel	[39]
LSV, La _{0.7} Sr _{0.3} VO ₃ /YSZ and LSV/GDC	24.1% H ₂ , 28.6% CO, 3.2% N ₂ , 12% CO ₂ , 27.1% H ₂ O, 300 ppm	T = 800°C, T = 900°C, electro-catalytic conditions	LSV/GDC showed significant difference between H ₂ and syngas/H ₂ S gas as compared to LSV/SYZ under similar conditions	[40]
La _{0.4} Sr _{0.5} Ba _{0.1} TiO ₃ (LSBT) anode-based solid oxide fuel cell/SYZ electrolyte YSZ (LSBT powders)	0.5% H ₂ S, CH ₄ (C:H ration 1.9–2.5), 3% H ₂ O	T = 900 K–1100 K	In the presence of H ₂ O, H ₂ S appear to increase the effect of carbon deposition.	[35]
Ni/8YSZ planar anode supported SOFC 5x5.8 cm (active area 4x4 cm)	31% H ₂ , 42% CO, 12% CO ₂ , 12% N ₂ , 3% H ₂ O (H ₂ O was increased from 3–10%), 12.5 ppm	T = 800°C	CO ₂ and H ₂ O content appear to be beneficial to mitigate the H ₂ S poisoning effect. However, the effect is higher as compared to H ₂ /N ₂ fuel	[41]
Ni/YSZ, 12.5x12.5 cm (121 cm ² active area)	25%, 35%, 50% DIR of CH ₄ with H ₂ O, 1 ppm H ₂ S	T = 750°C, CD = 0.5 A cm ⁻² fuel utilisation and air utilisation 60% and 35% respectively.	1 ppmv of H ₂ S caused increased degradation as the percentage of direct internal reforming (DIR) increases.	[4]

(Continues)

TABLE 1 (Continued)

Cell/Catalyst	Fuel	Experimental Conditions	H ₂ S tolerance limit	Ref.
Ni/8YSZ cermet with LSCF cathode with CGO inter diffuser barrier	11.43–15.8% H ₂ , 9.12–11.82% H ₂ O, 44.75–55.15% N ₂ , 14.12–16.24% CO, 10.18–11.39% CO ₂	T = 750°C, CD = 1 A cm ⁻²	0.1 ppm of H ₂ S caused a 20% performance loss. There was performance degradation delay of 20 h followed by stabilised performance of the cell after 20 h.	[23]
Ni/8YSZ anode with LSCF cathode and CGO inter layer (50 x 50 mm ²)	0.15% H ₂ , 0.15% H ₂ O, 0.13% CO ₂ and 0.45% N ₂	T = 800°C, pO ₂ cathode = 0.12 atm	With 0.1 ppm H ₂ S in the gas, no significant degradation of the polarisation was observed for 100 h. However, for 0.5 ppm H ₂ S, considerable increase in the polarisation resistance of the cell was observed. A decrease in the water gas shift reaction is reported.	[42]
[Ni]/8YSZ with La _{1-x} Sr _x MnO ₃ /YSZ cathode (4 x 4) cm active area	4% CH ₄ , 5% CO, 13% CO ₂ , 48% H ₂ , 30% H ₂ O, H ₂ S 2 ppm	T = 800°C, OCV and CD = 0.625A cm ⁻²	At 2 ppm of H ₂ S, methane reforming process was inhibited both at OCV and under current conditions	[43]
Ni/YSZ powder catalyst (250 mg)	5% CH ₄ , 10% H ₂ O, 35% N ₂ and 50% He, 5% CO ₂ , 5% O ₂ , 40% N ₂ , 50% He	T = 700°C	50 ppm caused a drop in methane reforming under catalytic conditions; however, the effect of H ₂ S on methane reforming is more severe under steam reforming as compared to dry conditions.	[34]
Electrolyte supported Ni-ScSZ cermet	CH ₄ /CO ₂ = 1.5	T = 1000°C, CD = 200 mA cm ⁻²	1 ppm of H ₂ S caused 9% voltage drop and about 40% decrease in the reaction rate of internal dry reforming.	[32]
Anode supported Ni-ScSZ with LSM cathode	S/C = 1.5 (also octane fuel)	T = 800°C, CD 40 mA cm ⁻² for 5 h	5 ppm of H ₂ S in the gas increased the methane concentration in the anode off gas from less than 10% to 40%	[44]
Reformax [*] 250	58% CH ₄ , 39% CO ₂	T = 650°C–850°C	0.5 mol % of H ₂ S cause a decrease in reforming from 67% to 19%	[36]

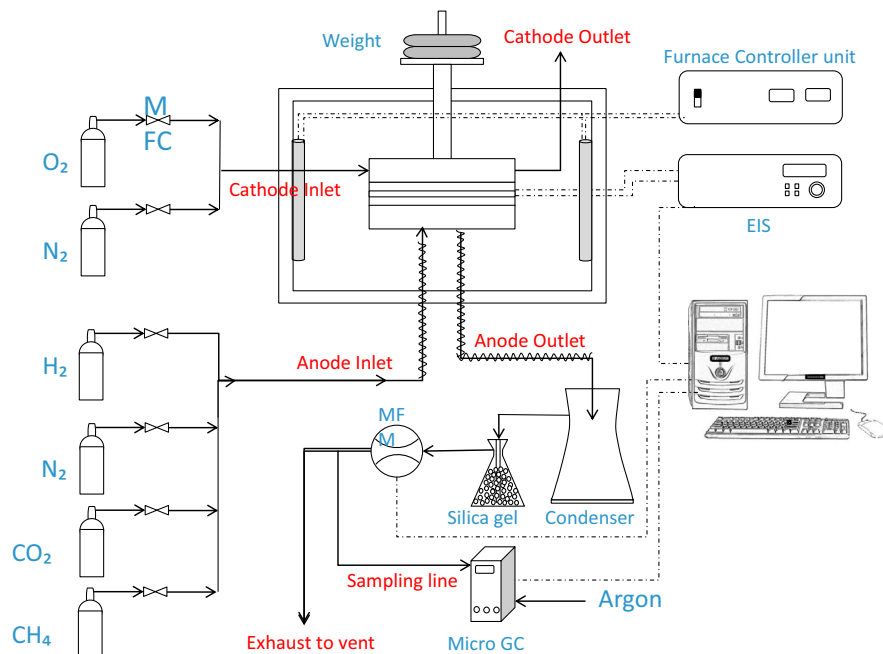


FIGURE 1 Schematic of the experimental test station (Reproduced with permission from Saadabadi et al.⁴⁵)

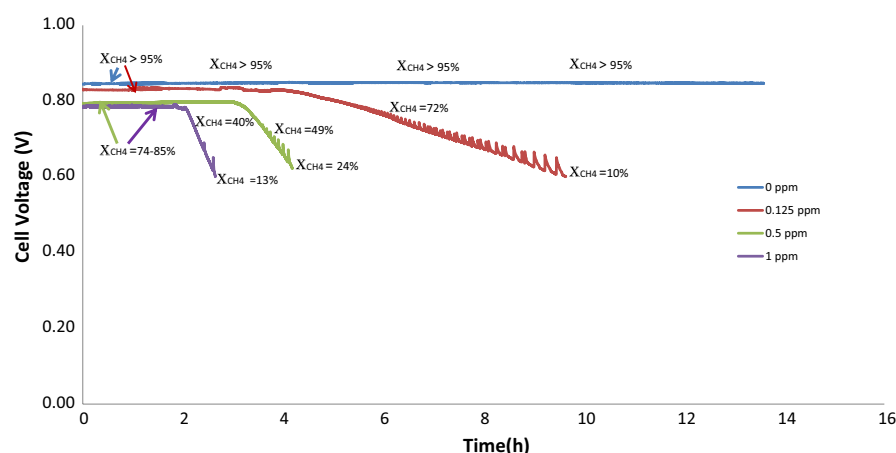


FIGURE 2 The effects of H_2S on dry reforming (X_{CH_4} is percentage of CH_4 reformed) and performance of the Ni-ScSZ cell under current of 2 A at 800°C and $\text{CH}_4:\text{CO}_2$ of 2:3

monitored by samples analysed in the Agilent 490 micro-GC columns until the cut-off voltage of 0.6 V which was monitored by Gammy FC-350. The percentage of CH_4 reformed was calculated based on the carbon balance of outlet gas composition described in Saadabadi et al.⁴⁵ The experiment was repeated by increasing the H_2S concentration to 0.5 ppm and 1 ppm. To determine the effect of H_2S on dry reforming under OCV conditions (purely dry conditions), the experimental conditions were maintained and the cell was poisoned by H_2S concentration of 0.125 ppm.

In order to determine the contribution of the cell material (catalyst) to the H_2S effects on reforming, the experiment was repeated using dummy cell mica (thermiculite) sheet. The effect of H_2S on reforming was evaluated at $\text{CH}_4:\text{CO}_2$ of 2:3 and at 800°C dummy cell temperature.

3 | RESULTS AND DISCUSSION

3.1 | Effect of H_2S on dry reforming on Ni-ScSZ under current

Using the Ni-ScSZ electrolyte-supported cell under a current of 2 A (250 A m^{-2}) at 800°C cell temperature and $\text{CH}_4:\text{CO}_2$ ratio of 2:3, it was observed that with no H_2S in the fuel gas (0 ppm), CH_4 reforming was more than 95%. If H_2S is gradually introduced in the gas, then the reforming efficiency (methane conversion) is reduced with time. Figure 2 shows how the concentration of H_2S in the gas affected both the cell voltage and the dry reforming process. With H_2S concentration of 0.125 ppm in the gas, there was no effect observed in the percentage of CH_4 reforming (X_{CH_4}) for 4 h. Also, the cell voltage was stable for the first 4 h, After 4 h,

CH₄ reforming started decreasing and a decrease in the cell voltage was observed. Between 4 and 10 h, a gradual decrease in the CH₄ reforming process and a decrease in cell voltage were observed. At the cut-off voltage of 0.6 V, CH₄ reforming process had decreased to 10%. The decrease in cell voltage can be attributed to the decrease in CH₄ reforming. These results suggested that the effect of H₂S is more pronounced at the reforming sites. A similar trend was observed when the H₂S concentration in the gas was increased to 0.5 ppm and 1 ppm but in a shorter period. This trend suggested that the decrease in cell voltage resulted from a reduction in H₂ and CO due to the reduced percentage of CH₄ reformed. It was reported that sites for reforming (catalytic sites) are different from electro-chemical sites.³⁸ It seems that under dry reforming conditions, H₂S is adsorbed to the reforming sites. Similar to steam reforming, H₂S has an effect on the electro-chemical activity during dry reforming.^{16,38} These results have a good agreement with what was reported by Shiratori et al.³² They observed that H₂S can affect the reforming and electro-chemical performance of the cell, but the performance of the cell was tolerant to 1 ppm at 1000°C. However, our present research has revealed that 1 ppm of H₂S is not feasible in internal dry reforming at temperatures of 800°C. Results showed that H₂S concentration in the gas as low as 0.125 ppm

can affect the cell voltage and the internal dry reforming process in SOFCs operating at 800°C within only 4 h of operation.³²

It was also observed that after poisoning the cell with 0.125 ppm of H₂S, the initial cell voltage slightly dropped (Figure 2). This can be attributed to incomplete sulphur desorption during cell recovery. The current-voltage (IV) curves were obtained with pure H₂ after recovering the cell and before the next reforming process. The IV curves (Figure 3) showed that H₂S caused a small drop in performance.

3.2 | Effect of H₂S on dry reforming on Ni-ScSZ at OCV

The experiment was repeated when the cell was at OCV. A decrease in the CH₄ reforming process was observed after two hours of injecting 0.125 ppm of H₂S in the fuel gas (Figure 4). The CH₄ reforming process and cell OCV decreased from 47% to 4% and 0.96 V to 0.85 V respectively in 3 h. When H₂S injection was stopped, methane reforming and OCV were recovered from 4% to more than 41%. This is also in agreement with Chattanathan et al.³⁶ who observed that 0.5 mol% of H₂S caused a decrease in dry reforming to 19% using a Reformax 250 catalyst

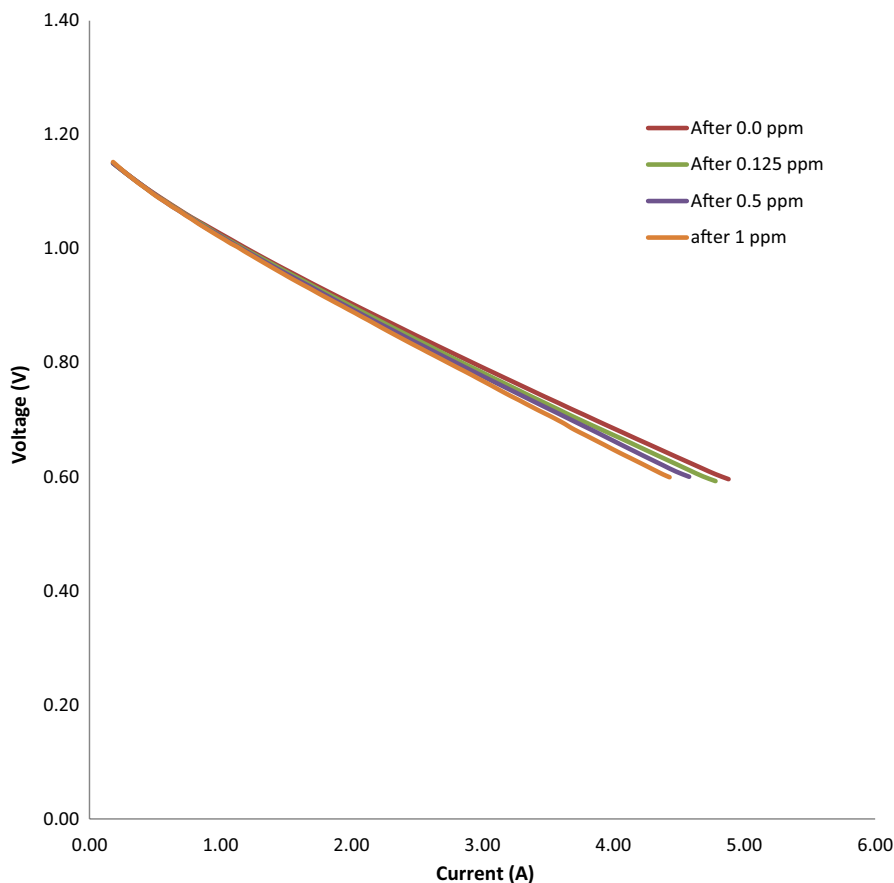


FIGURE 3 Current-voltage curves of the cell during different points of the experiment at 800 °C and CH₄:CO₂ of 2:3

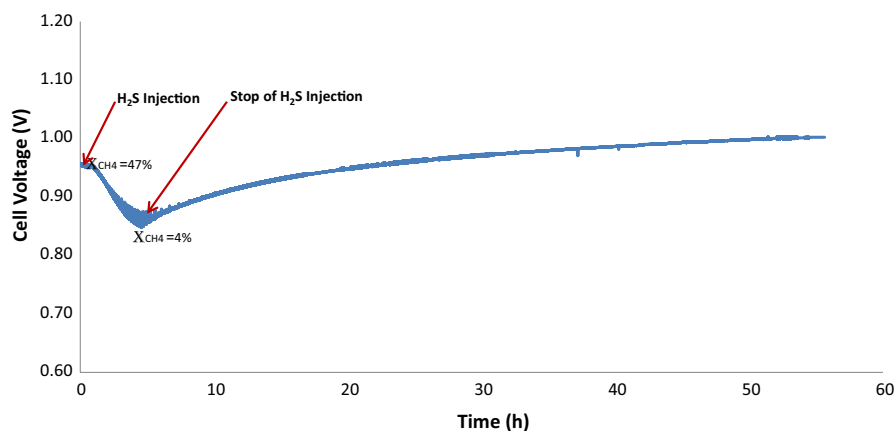


FIGURE 4 The effect of 0.125 ppm H_2S on dry reforming and performance of the cell with a Ni-ScSZ cell at OCV at 800°C and $\text{CH}_4:\text{CO}_2$ of 2:3

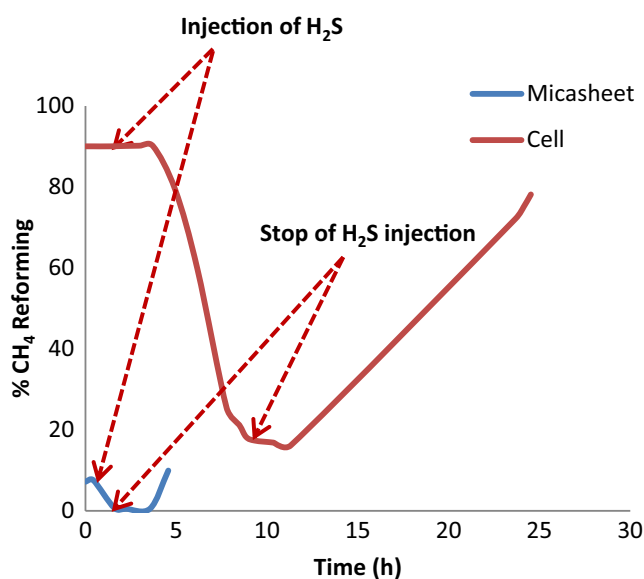


FIGURE 5 Effect of H_2S on CH_4 reforming without and with a catalyst at 850°C

in a bed reactor. This research has revealed that even at purely catalytic conditions, H_2S as low as 0.125 ppm causes a severe decrease in dry reforming at operating conditions of SOFCs. While Johnson et al.²² has reported that 25 ppm affects dry reforming on crashed anode catalyst (Ni-ScYSZ and Ni-ScYSZ/Pd-CGO), we report that even 0.125 ppm can affect dry reforming on an electrochemically performing complete solid oxide fuel cell with Ni-ScSZ anode.

3.3 | H_2S effect on dry reforming with and without a catalyst

Reforming has been assumed to take place on the cell and to a small extent on the current collector.⁴⁸ However, it is possible that other process equipment such as

stainless steel may contribute to catalytic dry reforming.⁴⁹ Therefore, to test the catalytic reforming effect of H_2S purely on the cell, the experiment was carried out using the mica sheet (dummy cell) and the real cell without a current corrector.

To test the reforming and the effect of H_2S on reforming without catalysts (Ni-ScSZ cell and Pt current collector), the experiment was conducted using a dummy cell (mica sheet) in a ceramic block without platinum mesh (as the current collector) at 800°C . The same procedure was repeated using a real cell in a ceramic block without platinum mesh for comparison. It was observed that even when the cell was taken out (with mica sheet as a dummy cell), CH_4 dry reforming took place though lower than in presence of the cell. Figure 5 shows the effects of H_2S on dry reforming with and without the cell. With a dummy cell, the percentage of CH_4 reformed (X_{CH_4}) was 8%. When 0.125 ppm H_2S was injected, X_{CH_4} decreased to 0.5% in 1 h. These could imply that H_2S could also affect the reforming reaction even without a cell. However, when H_2S was stopped, the CH_4 reforming was recovered. A similar trend was observed when a real cell (without platinum wire mesh) was used. A percentage of over 90% of CH_4 reforming was observed before injection of 0.125 ppm of H_2S in the fuel gas. When H_2S was injected, the X_{CH_4} decreased to below 20% and it was recovered when H_2S injection was stopped.

From Table 1, it appears from different authors that 1–2 ppm H_2S concentration is feasible for steam reforming using carbon-containing fuels. Also, Johnson et al.²² observed that dry reforming was more tolerant to H_2S poisoning than steam reforming. However, from this research, dry reforming is greatly reduced by H_2S poisoning even at very low ppm levels, that is a 0.125 ppm H_2S concentration in the gas resulted in a significant decrease in the reforming process. This suggests that H_2S as low as 0.125 ppm affects the catalyst on the reforming sites of SOFCs.

4 | CONCLUSIONS

It has been observed that methane dry reforming in biogas-fuelled SOFC is affected by H₂S even at concentrations as low as 0.125 ppm H₂S in biogas with Ni-ScSZ cell. This H₂S concentration is far below the threshold of 1 ppm which is normally reported in literature. H₂S appeared to influence the reforming in the cell chamber even when the mica sheet (dummy cell) was used. Therefore, if biogas is to be used as fuel for SOFCs and internal dry reforming is envisaged, a stringent cleaning system is required, which can clean the gas to nearly zero ppm of H₂S level. With up to over 2000 ppm of H₂S concentration in biogas reported in literature, such a stringent gas cleaning system needs to be carefully designed to meet the conditions of internal dry reforming in SOFCs. Otherwise, an external reformer for dry reforming of CH₄ is required.

While we present the results obtained by our experiments, it appears that the influence of H₂S on different types of anodes under different fuel conditions including dry reforming needs detailed studies. Therefore, further studies are required to investigate the effect of H₂S in the presence of hydrocarbon fuels to facilitate SOFC systems design for real-life applications and material selection for systems components.

ACKNOWLEDGEMENTS

The authors would like to give special thanks to Mr. Alessandro Cavalli for his valuable comments.

ORCID

Henry Wasajja  <https://orcid.org/0000-0001-5001-1670>

REFERENCES

- Larminie J, Dicks A. *Fuel Cell Systems Explained*, 2nd ed. John Wiley & Sons; 2003.
- Wang Y, Yao L, Wang S, Mao D, Hu C. Low-temperature catalytic CO₂ dry reforming of methane on Ni-based catalysts: a review. *Fuel Process Technol.* 2018;169:199-206. doi:10.1016/j.fuproc.2017.10.007
- EG&G Technical Services, I. *Fuel Cell Handbook*; U.S. Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory, 2004; Vol. 7 Edition; ISBN 0442319266.
- Smith TR, Wood A, Birss VI. Applied Catalysis A: general effect of hydrogen sulfide on the direct internal reforming of methane in solid oxide fuel cells. *Appl Catal A.* 2009;354:1-7. doi:10.1016/j.apcata.2008.10.055
- Saadabadi SA, Thallam Thattai A, Fan L, Lindeboom REF, Spanjers H, Aravind PV. Solid Oxide Fuel Cells fuelled with biogas: potential and constraints. *Renew Energy.* 2019;134:194-214. doi:10.1016/j.renene.2018.11.028
- Thiruselvi D, Kumar PS, Kumar MA, et al. A critical review on global trends in biogas scenario with its up-gradation techniques for fuel cell and future perspectives. *Int J Hydrogen Energy.* 2021;46:16734-16750. doi:10.1016/j.ijhydene.2020.10.023
- Lu Q, Hou Y, Laraib SR, et al. Electro-catalytic steam reforming of methane over Ni-CeO₂/Γ-Al₂O₃-MgO catalyst. *Fuel Process Technol.* 2019;192:57-64. doi:10.1016/j.fuproc.2019.04.021
- Goula G, Kioussis V, Nalbandian L, Yentekakis IV. Catalytic and electrocatalytic behavior of Ni-based cermet anodes under internal dry reforming of CH₄ + CO₂ mixtures in SOFCs. *Solid State Ionics.* 2006;177:2119-2123. doi:10.1016/j.ssi.2006.03.040
- Lanzini A, Leone P, Guerra C, Smeacetto F, Brandon NP, Santarelli M. Durability of anode supported Solid Oxides Fuel Cells (SOFC) under direct dry-reforming of methane. *Chem Eng J.* 2013;220:254-263. doi:10.1016/j.cej.2013.01.003
- Trendewicz AA, Braun RJ. Techno-economic analysis of solid oxide fuel cell-based combined heat and power systems for biogas utilization at wastewater treatment facilities. *J Power Sources.* 2013;233:380-393. doi:10.1016/j.jpowsour.2013.01.017
- Schubert SK, Kusnezoff M. Sulphur Poisoning of Sofc Anodes. 2nd International Workshop on Degradation Issues on Fuel Cells, Thessaloniki. 2011.
- Staffell I, Green R. The cost of domestic fuel cell micro-CHP systems. *Int J Hydrogen Energy.* 2013;38:1088-1102. doi:10.1016/j.ijhydene.2012.10.090
- Aravind PV, De Jong W. Evaluation of high temperature gas cleaning options for biomass gasification product gas for Solid Oxide Fuel Cells. *Prog Energy Combust Sci.* 2012;38:737-764. doi:10.1016/j.pecs.2012.03.006
- Abatzoglou N, Boivin S. A review of biogas purification processes. *Biofuels, Bioprod Biorefin.* 2012;6:246-256. doi:10.1002/bbb
- Hagen A, Rasmussen JFB, Thydén K. Durability of solid oxide fuel cells using sulfur containing fuels. *J Power Sources.* 2011;196:7271-7276. doi:10.1016/j.jpowsour.2011.02.053
- Rasmussen JFB, Hagen A. The effect of H₂S on the performance of SOFCs using methane containing fuel. *Fuel Cells.* 2010;10:1135-1142. doi:10.1002/fuce.201000012
- Niakolas DK. Sulfur poisoning of Ni-based anodes for Solid Oxide Fuel Cells in H/C-based fuels. *Appl Catal A.* 2014;486:123-142. doi:10.1016/j.apcata.2014.08.015
- Guerra C, Lanzini A, Leone P, Santarelli M, Brandon NP. Optimization of dry reforming of methane over Ni / YSZ anodes for solid oxide fuel cells. *J Power Sources.* 2014;245:154-163. doi:10.1016/j.jpowsour.2013.06.088
- Kyocera News Releases. 2017. Available online: https://global.kyocera.com/news/2017/0702_bnfo.html (accessed on Jul 3 2018).
- Elcogen Solid Oxide Fuel Cell Stacks. Available online: <https://elcogen.com/products/solid-oxide-cell-stacks/> (accessed on Jul 9, 2019).
- WATT ImperiumTM - Watt Fuel Cell Available online: <https://www.wattfuelcell.com/portable-power/watt-imperium/> (accessed on Jul 2, 2018).
- Johnson GB, Hjalmarrsson P, Norrman K, Ozkan US, Hagen A. Biogas catalytic reforming studies on nickel-based solid oxide fuel cell anodes. *Fuel Cells.* 2016;16:219-234. doi:10.1002/fuce.201500179
- Weber A, Dierickx S, Kromp A, Ivers-Tiffée E. Sulfur poisoning of anode-supported SOFCs under reformate operation. *Fuel Cells.* 2013;13:487-493. doi:10.1002/fuce.201200180
- Tremblay JP, Marquez AI, Ohn TR, Bayless DJ. Effects of coal syngas and H₂S on the performance of solid oxide fuel

- cells: single-cell tests. *J Power Sources*. 2006;158:263-273. doi:10.1016/j.jpowsour.2005.09.055
25. Papadam T, Goula G, Yentekakis IV. Long-term operation stability tests of intermediate and high temperature Ni-based anodes' SOFCs directly fueled with simulated biogas mixtures. *Int J Hydrogen Energy*. 2012;37:16680-16685. doi:10.1016/j.ijhydene.2012.02.147
 26. Ouweltjes JP, Aravind PV, Woudstra N, Rietveld G. Biosyngas utilization in solid oxide fuel cells with Ni / GDC anodes. *J Fuel Cell Sci Technol*. 2006;3:495-498. doi:10.1115/1.2349535
 27. Yun JW, Yoon SP, Park S, Kim HS, Nam SW. Analysis of the regenerative H₂S poisoning mechanism in Ce_{0.8}Sm_{0.2}O₂-coated Ni/YSZ anodes for intermediate temperature solid oxide fuel cells. *Int J Hydrogen Energy*. 2011;36:787-796. doi:10.1016/j.ijhydene.2010.10.060
 28. Kavurucu Schubert S, Kusnezoff M, Michaelis A, Bredikhin SI. Comparison of the performances of single cell solid oxide fuel cell stacks with Ni/8YSZ and Ni/10CGO anodes with H₂S containing fuel. *J Power Sources*. 2012;217:364-372. doi:10.1016/j.jpowsour.2012.06.020
 29. Zha S, Cheng Z, Liu M. Sulfur poisoning and regeneration of Ni-based anodes in solid oxide fuel cells. *J Electrochem Soc*. 2007;154:B201. doi:10.1149/1.2404779
 30. Jayaprakash S, Dewangan N, Jangam A, Kawi S. H₂S-resistant CeO₂-NiO-MgO-Al₂O₃ LDH-derived catalysts for steam reforming of toluene. *Fuel Process Technol*. 2021;219:106871. doi:10.1016/j.fuproc.2021.106871
 31. Cavalli A, Bernardini R, Del Carlo T, Aravind PV. Effect of H₂S and HCl on solid oxide fuel cells fed with simulated biosyngas containing primary tar. *Energy Science and Engineering*. 2019;7:2456-2468. doi:10.1002/ese3.434
 32. Shiratori Y, Oshima T, Sasaki K. Feasibility of direct-biogas SOFC. *Int J Hydrogen Energy*. 2008;33:6316-6321. doi:10.1016/j.ijhydene.2008.07.101
 33. Xu C, Zondlo JW, Gong M, Elizalde-blancas F, Liu X, Celik IB. Tolerance tests of H₂S-laden biogas fuel on solid oxide fuel cells. *J Power Sources*. 2010;195:4583-4592. doi:10.1016/j.jpowsour.2010.02.078
 34. Lakshminarayanan N, Ozkan US. Applied Catalysis A: general effect of H₂O on sulfur poisoning and catalytic activity of Ni – YSZ catalysts. "Applied Catalysis A: General". 2011;393:138-145. doi:10.1016/j.apcata.2010.11.034
 35. Cui S, Li J, Jayakumar A, et al. Effects of H₂S and H₂O on carbon deposition over La_{0.4}Sr_{0.5}Ba_{0.1}TiO₃/YSZ perovskite anodes in methane fueled SOFCs. *J Power Sources* 2014, 250, 134-142. doi:10.1016/j.jpowsour.2013.10.124
 36. Chattanathan SA, Adhikari S, McVey M, Fasina O. Hydrogen production from biogas reforming and the effect of H₂S on CH₄ conversion. *Int J Hydrogen Energy*. 2014;39:19905-19911. doi:10.1016/j.ijhydene.2014.09.162
 37. Gao Y, Jiang J, Meng Y, Yan F, Aihemaiti A. A review of recent developments in hydrogen production via biogas dry reforming. *Energy Convers Manage*. 2018;171:133-155. doi:10.1016/j.enconman.2018.05.083
 38. Rostrup-Nielsen JR, Hansen JB, Helveg S, Christiansen N, Jannasch A-K. Sites for catalysis and electrochemistry in solid oxide fuel cell (SOFC) anode. *Appl Phys*. 2006;A 85:427-430. doi:10.1007/s00339-006-3702-1
 39. Hagen A. Sulfur poisoning of the water gas shift reaction on anode supported solid oxide fuel cells. *J Electrochem Soc*. 2013;160:111-118. doi:10.1149/2.060302jes
 40. Cooper M, Channa K, De Silva R, Bayless DJ. Comparison of LSV / YSZ and LSV / GDC SOFC anode performance in coal syngas containing H₂S. *J Electrochem Soc*. 2010;157:1713-1718. doi:10.1149/1.3489380
 41. Li J, Fu X, Luo J, Chuang KT, Sanger AR. Application of BaTiO₃ as anode materials for H₂S-containing CH₄ fueled solid oxide fuel cells. *J Power Sources*. 2012;213:69-77. doi:10.1016/j.jpowsour.2012.03.106
 42. Kromp A, Dierickx S, Leonidea A, Webera A, Ivers-Tiffée E. Electrochemical analysis of sulphur-poisoning in anode-supported SOFCs under reformate operation. *ECS Trans*. 2012;41:161-169. doi:10.1149/1.3702423
 43. Li TS, Xu M, Gao C, et al. Investigation into the effects of sulfur on syngas reforming inside a solid oxide fuel cell. *J Power Sources*. 2014;258:1-4. doi:10.1016/j.jpowsour.2014.02.041
 44. Sasaki K, Haga K, Yoshizumi T, Minematsu D, Yuki E, Liu R. Chemical durability of solid oxide fuel cells: influence of impurities on long-term performance. *J Power Sources*. 2011;196:9130-9140. doi:10.1016/j.jpowsour.2010.09.122
 45. Saadabadi SA, Illathukandy B, Aravind PV. Direct internal methane reforming in biogas fuelled solid oxide fuel cell; the influence of operating parameters. *Energy Science and Engineering*. 2021;9(8):1232-1248. doi:10.1002/ese3.887
 46. Goula G, Kiouis V, Nalbandian L, Yentekakis I. V Catalytic and electrocatalytic behavior of Ni-based cermet anodes under internal dry reforming of CH₄ + CO₂ mixtures in SOFCs. *Solid State Ionics*. 2006;177:2119-2123. doi:10.1016/j.ssi.2006.03.040
 47. Lanzini A, Leone P. Experimental investigation of direct internal reforming of biogas in solid oxide fuel cells. *Int J Hydrogen Energy*. 2010;35:2463-2476. doi:10.1016/j.ijhydene.2009.12.146
 48. Usman M, Wan Daud WMA, Abbas HF. Dry reforming of methane: Influence of process parameters - a review. *Renew Sustain Energy Rev*. 2015;45:710-744. doi:10.1016/j.rser.2015.02.026
 49. De Oliveira-Vigier K, Abatzoglou N, Gitzhofer F. Dry-reforming of ethanol in the presence of a 316 stainless steel catalyst. *Can J Chem Eng*. 2005;83:978-984. doi:10.1002/cjce.5450830607

How to cite this article: Wasajja H, Saadabadi SA, Illathukandy B, Lindeboom REF, van Lier JB, Vellayani Aravind P. The effect of H₂S on internal dry reforming in biogas fuelled solid oxide fuel cells. *Energy Sci Eng*. 2021;00:1–10. doi:[10.1002/ese3.1021](https://doi.org/10.1002/ese3.1021)