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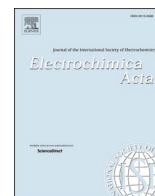
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Solid oxide fuel cells (SOFCs) fed with biogas containing hydrogen chloride traces: Impact on direct internal reforming and electrochemical performance

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ABSTRACT

This study is particularly aimed at investigating the influence of hydrogen chloride traces in biogas on direct internal reforming in solid oxide fuel cells (SOFCs). The experiments are performed with simulated biogas containing methane to carbon dioxide ratio of 3:2, the usual average proportion in biogas. To the best of our knowledge, there are no reported studies that investigated the effect of hydrogen chloride on direct internal reforming by clearly establishing the effect of reforming with outlet gas composition measurements. The experiments at SOFC operating temperature of 850 °C reveals no negative effect on reforming or cell performance, with 4, 8, and 12 ppm(v) of hydrogen chloride in biogas. At 800 °C, there is no visible performance degradation, but a negligible amount of methane (~ 1%) is detected in the anode off gas. Both the reforming and electrochemical performance are marginally affected at 750 °C. Further, post-test analyses (FESEM-EDS, XRD) of the used SOFC reveals no damage to the cell at microstructure level or chlorine poisoning. All the experiments are performed in the context of utilizing the biogas generated from sewage treatment plants in an SOFC system. The reported level of chlorine traces in biogas generated from sewage sludge is < 10 ppm(v) and hence the limit set for experiments is at par with this value.

1. Introduction

Biogas is a versatile renewable energy source which can replace fossil fuel consumption in the areas such as thermal/heating applications, gaseous fuel for engines/fuel cells, and enriched biogas as a replacement for natural gas in chemical production. It possess a higher calorific value (HCV) of about 35 MJ/kg and when enriched by separating out the carbon dioxide (CO₂) this value reaches upto 52 MJ/kg, which is comparable with that of the natural gas [1]. Biogas production through anaerobic digestion (AD) possesses the following advantages [2,3]: (i) it helps to process the organic waste efficiently as well as generate/recover energy out of it; (ii) the AD process requires less energy input and

maintenance expenses; (iii) it is environmentally friendly as it helps in reducing the greenhouse gas (GHG) emissions; and (iv) digestate slurry, the by-product during biogas production, is a good organic manure which can replace or reduce the use of chemical fertilizers. In general, biogas production through AD is a promising solution from the multiple perspectives of energy production as well as waste management and is a sustainable option for decentralized and low carbon emission based energy economy [4].

It is apparently evident that organic wastes, if not treated properly, may end up in the emission of methane (CH₄) into the atmosphere and its impact on climate change is very high as compared to CO₂. As per the fifth assessment report of the intergovernmental panel on climate change (IPCC), the global warming potential (GWP) of CH₄ for a time

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Nomenclature

AD	anaerobic digestion
CEM	controlled evaporator mixer
CHP	combined heat and power
DIR	direct internal reforming
DR	dry reforming
EDS	energy-dispersive spectroscopy
FESEM	field emission scanning electron microscope
GC	gas chromatograph
GDC	gadolinium doped ceria
GHG	greenhouse gas
GWP	global warming potential
HRT	hydraulic retention time
IPCC	intergovernmental panel on climate change
LFG	landfill gas

LHV	lower heating value
LSCF	lanthanum strontium cobalt ferrite
LSM	lanthanum strontium manganite
MFC	mass flow controller
OCV	open-circuit voltage
ppm(v)	parts per million by volume
RSD	relative standard deviation
sccm	standard cubic centimeters per minute
ScSZ	scandia stabilized zirconia
SDC	samarium doped ceria
SOFC	solid oxide fuel cell
SR	steam reforming
SRT	solids retention time
WWTP	wastewater treatment plant
XRD	X-ray diffraction analysis
YSZ	yttria stabilized zirconia

horizon of 100 years is 28 times as compared to CO₂ [5]. The importance of effectively capturing the methane from organic waste sources is self-explanatory from the former statement, and AD appears to be an effective method for treating organic waste with high water content. As reported by Kuo et al. [6], adopting appropriate technologies for waste-to-energy conversion generates renewable energy, solves many environmental issues and, most importantly, plays a key role in developing a sustainable circular economy.

Anaerobic units possess small footprints (area requirements), and the power requirements and operating costs are much lower than aerobic systems [7–9]. For decentralised wastewater systems, a combination of technologies, i.e., initially treat it anaerobically to reduce the organic load to 60 to 70 percent and then refine it using aerobic systems will be a possible solution. D'silva et al. [10], based on an intensive performance assessment of 36 sewage treatment plants in Northern India concluded that anaerobic followed by microaerobic treatment imparts effective pollutant (organics and nutrients) removal. Meanwhile, this will also result in sustainable wastewater treatment plants (WWTPs). According to Babu [11], this would be the best strategy as the wastewater that reaches a treatment plant in Delhi, India is a mixture of domestic and industrial waste. LOTUS^{HR} [12,13] is one such project that focuses on local treatment of urban sewage and energy recovery through biogas generation and the subsequent use of biogas in SOFCs for power generation. Rayner et al. [14] mentioned that the integration of AD and SOFC technology is an environmentally sustainable and cost-effective method for simultaneous waste management and energy production. High electrical efficiency, multifuel capability, and environmental compatibility are listed as the major advantages of SOFCs [15]. In a recent article, Tian and Milcarek [16] mentioned the importance of recovering and utilizing biogas in an SOFC-combined heat and power (CHP) system, which otherwise is flared off from most of the waste water treatment plants. DEMOSOFC [17], an industrial sized biogas-fed SOFC demonstration plant in Europe, successfully utilized the biogas for power generation after passing it through a stringent gas cleaning system. The project was successful in demonstrating it at the SMAT Collegno WWTP in Italy and reported that about 25–30 % of the electrical requirements and almost the entire thermal needs at the WWTP can be met from this. The prime motive behind the study mentioned in this manuscript, as an associate/team member of the LOTUS^{HR} project [12], is also to recover energy from waste streams, produce biogas and utilize it in an SOFC system to generate power.

1.1. Biogas–SOFC system: a promising option for power generation

Biogas is emerging as a potential fuel for SOFCs. Even though anaerobic digestion is a slow process, it is attractive owing to its simple,

cost-effective, and eco-friendly nature. Also, AD is a promising method to recover energy from wastewater streams, especially for the warm-climate regions on account of the favourable environmental conditions that prevail almost throughout the year [18]. Biogas seems to be an attractive option for power generation through direct conversion in SOFCs owing to its high efficiency and broad versatility [14,19–21], and this will concurrently help to reduce the global warming potential [14, 22]. Biogas, after partial pre-reforming, can be fed to SOFC as internal reforming is possible due to the presence of nickel (Ni) at the anode surface and the inherent/desirable temperature inside the SOFC [23–27]. Depending upon the proportion of CH₄ and CO₂, the option of dry reforming (DR), steam reforming (SR), or a combination of DR and SR can be employed. However, the trace impurities in biogas still pose a major challenge to employing it as a direct fuel for SOFCs [28]. So, the trace contaminant levels in biogas should be properly controlled, for which the upper tolerance limits are to be arrived at based on detailed experimental studies.

SOFC is considered as the most fuel flexible fuel cell as it can accommodate various types of fuels as well as electrochemically oxidize both hydrogen (H₂) and carbon monoxide (CO) at the anode [22,29–31]. Even though it is fuel flexible, minute quantities of contaminants in the fuel can cause an adverse effect on its performance. Li et al. [15] reported that the main challenges and hurdles for the bio-syngas SOFC systems are the Ni anode degradation due to carbon deposition, nickel re-oxidation, and trace contaminants in the fuel, as this will affect the stable long term operation of SOFCs. Utmost priority should be given to eliminate this problem by properly identifying the tolerance limits of contaminants and gas purification methods (if needed), to safely integrate and operate the biogas-SOFC systems.

Most of the studies on chlorine contamination used H₂ or syngas generated through gasification as the fuel for SOFC. The reason might be due to the fact that syngas is found to have higher levels of chlorine contaminants as compared to other carbonaceous fuels like biogas. It is worth noting that fuel activation, surface chemistry, and conversion efficiencies differ with respect to the fuels (H₂ or carbon containing fuels) fed to SOFC [32]. Definitely, there will be differences in the degradation mechanisms and catalyst deactivation when experiments are conducted with such fuels contaminated with chlorine. Reeping et al. [19] reported that there are only very few studies on the toxic effects in SOFC's with chlorine contamination in carbon-based fuels compared with those of H₂ based fuels. A research article published in the year 2019 by Escudero and Serrano [33] also reported that most of the studies to find the degradation effect by HCl on SOFCs were mainly studied with H₂ or syngas as fuel in nickel-yttria stabilized zirconia (Ni-YSZ) anode SOFCs. So, more investigations are still needed with appropriate combinations and compositions of such fuels and

contaminants. Also, there are not much experimental studies on DIR of biogas in SOFC. Hence, studies to investigate the impact of chlorine traces in biogas on DIR will help to arrive at well-engineered systems for the future.

2. An overview of the trace contaminant studies

Biogas generated from treatment plants and landfills contains a wide range of trace contaminants such as siloxanes, sulphur compounds, halogens, tar compounds, etc [34]. Similarly, biogas generated from the excrement of livestock or sewage from human life may contain traces of chlorine, siloxanes, ammonia, etc [35]. Also, chlorine added to the tap water for disinfection may reach the waste/sewage treatment plants and finally the biogas generated from it [36]. So, the level of contaminants in biogas may vary from site to site. As of now, quite a good number of research publications are available for the contaminant tolerance studies with hydrogen sulphide (H_2S) in the fuel gas fed to SOFC [28]. This study is focused on identifying the effects of HCl traces on methane reforming and electrochemical performance of SOFCs. Hence, an effort is made to sum up the relevant observations and findings from the published research articles.

Paolini et al. [37], based on their study at a WWTP in Italy for converting the sewage sludge to biogas, reported that an average concentration of chlorine at the rate of 26.8 mg/m^3 (i.e., 9.24 ppm(v)) was observed in the produced biogas. This is high when compared to the EU limit of 1 mg/m^3 in biogas [37]. The probable reasons stated for the presence of chlorine traces in biogas are the degradation of organochlorine compounds during AD, and the presence of chlorinated clarifying agents. Dechlorination can be attained with the use of carbon filters consisting of activated charcoal and alkaline carbon. Alkaline carbon is found to be more effective for the removal of acidic species [38,39], and an HCl removal efficiency of 99.6% was observed.

Reeping et al. [19] examined the degradation of nickel-based anodes in SOFCs operating on biogas fuel with 110 ppm Cl (either as CH_3Cl or HCl) at 650 and 700 °C. It is found that chlorine immediately suppresses the carbon deposition but results in a slow and steady degradation of the cell. But continuous exposure to 110 ppm chlorine ends up in rapid and irreversible failure. It is also reported that the cell degradation rates with biogas are faster than with either H_2 or methane alone.

Papurello and Lanzini [34] conducted a study with syngas as fuel to determine the threshold tolerance limits of various contaminants, i.e., the concentration at which the SOFC performance is reversible. The effect of HCl was investigated in galvanostatic mode to determine the ohmic and diffusive polarization resistance. Only very slight impact observed with 1–20 ppm(v) HCl, and total cell performance recovery (back to starting voltage) was achieved on removal of the contaminant. The electrochemical process is affected by HCl concentrations above 40 ppm(v). The polarization losses due to the electrochemical process increased by 53%, when HCl concentration varied from zero to 1000 ppm(v).

Syngas produced from gasification of coal or biomass may contain HCl in the range of 10–500 ppm, and this might lead to poisoning of SOFCs through chlorine adsorption on the Ni surface or $NiCl_2$ formation [40]. Blesznowski et al. [40] conducted a study about the trace level presence of HCl in syngas and its effect on an anode supported solid oxide fuel cell (AS-SOFC) with Ni-YSZ cermet anode. They performed 113 h HCl-free operation followed by 48 h with 1 ppm HCl, and another 48 h with 3 ppm HCl. After the experiments, the SOFC is operated on clean fuel for 5 h and finally with 10 ppm HCl for 67 h. A voltage drop of 10 mV was observed with 10 ppm HCl in syngas. However, this drop was found to be reversible on the removal of chlorine. Scanning electron microscopy (SEM) analysis did not show any adverse effects on the microstructure. The energy dispersive spectroscopy (EDS) result did not show any traces of chlorine on the surface or cross-section of the cell.

Sasaki et al. [31] conducted tests using Ni-ScSZ SOFC at 800 °C with chlorine concentrations ranging from 5 ppm to 1000 ppm in humidified

H_2 for 150 h at a constant current density of 0.2 A/cm^2 . They observed that sublimation of $NiCl_2(g)$ was predominant in this case. It is suggested that Cl_2 species are moderately reactive to the Ni-based anodes and hence proper care should be taken to control them below their tolerant concentrations.

Haga et al. [36] conducted detailed thermochemical calculations, microstructural analysis, and electrochemical characterization to arrive at the poisoning effects of chlorine compounds (Cl_2 and HCl) on Ni-based electrolyte-supported SOFC with Ni-ScSZ cermet anode. The degradation rates in cell voltage were ca. 3%/1000 h for H_2 containing 5 ppm Cl_2 as compared to that of ca. 2%/1000 h for pure H_2 as fuel. Both adsorption-type and sublimation-type ($NiCl_x$ formation at high temperatures) poisoning mechanism is attributed to the said degradation.

Escudero and Serrano [33] used biogas ($CH_4:CO_2:H_2$ in the ratio 70:25:5) in a W-Ni-Ce/SDC/LSCF type single cell at 750 °C. They observed only a slight dip in open circuit voltage (OCV). But there were some major oscillations in the power density values under load demand. The maximum power density diminished by ~22% and the maximum current density by ~29% after 29 h of operation with 250 ppm HCl, in comparison with the performance of SOFC with contaminant-free biogas. The W-Ni-Ce/SDC/LSCF type SOFC is found to be inferior to that of SOFCs based on Ni-YSZ or Ni-ScSZ anodes, while operating with HCl contaminated H_2 or syngas. The cell recovery with pure H_2 was only marginal. The post-test SEM-EDS study did not show any cracks or delamination. The presence of chlorine was detected on both the Ni and Ce particles of the anode, and nothing on the electrolyte. The degradation in SOFC performance is on account of the adsorption of chlorine and carbon formation (even though cannot be identified as carbon itself is coated on the anode for the SEM analysis) on active sites. Also, commented that CO_2 and H_2O might have aided the oxidation of Ni and CeO_{2-x} .

Reeping et al. [32] mentioned the “palliative” effect of a small amount of molecular hydrogen supplemented with carbonaceous fuels contaminated with chlorine traces. They used 5 % H_2 along with the carbon fuel and found that the presence of H_2 masks the deterioration in the catalytic activity of nickel. It also helps to remove the adsorbed chlorine from Ni surface thereby resulting in the methane cracking reaction to continue, although at a slower pace. When H_2 is removed, chlorine occupies the methane/biogas reforming sites and cell failure happens immediately.

Cavalli et al. [41] observed that among the different publications related to HCl contamination, no unison is found in the suggested tolerance levels, and this points to the need to carry out more studies for better understanding. It is seen that only the corrosion effect by HCl to the stainless steel piping, interconnects, and ancillary units is the common factor in all the reported cases. Varying results are observed from different studies, and the relevant ones with the details of SOFC, fuel type, contaminant level, operating temperature, observations, and reasons for failure are summarised in a concise form in Table 1.

3. Motivation

Biogas seems to be an attractive alternative fuel for SOFCs. But the wide usage of biogas is limited due to the presence of trace contaminants. Hence, contaminant tolerance studies and effective biogas cleaning based on these studies are a must for overcoming such challenges. Even though there are a lot of results available to find out the limits of H_2S and siloxanes, only very limited studies and results are available for the effect of chlorine in biogas on SOFCs performance. Of these limited studies on chlorine contamination, H_2 was the primary fuel for SOFCs and very minimal attention was given to explore its harmful effects in predominantly carbon-containing fuels [19,49]. The degradation rate and mechanism will be different with carbon-containing fuels when compared to hydrogen [41]. Also, there are still differing results in terms of performance loss, reversibility, and microstructure changes of the cell with studies pertaining to HCl traces in the fuel gas to

Table 1

The impact of chlorine contaminants on the performance of SOFCs: details in a nutshell.

Refs.	Type of cell /Experiment details	Gas composition & operating conditions	Observations/findings reported	Reasons listed / Remarks
Trembly et al. [42]	ESC - button type Ni-YSZ Tested potentiostatically at 0.7 V	Coal syngas with 20 and 160 ppm HCl at 800 and 900 °C.	17.4 and 26.1% degradation in current density at 800 °C during 100 h with 20 ppm and 160 ppm respectively. And 13.3 and 51.8 % at 900 °C. The effect was reversible on removal of HCl.	Adsorption of chlorine onto the Ni surface. No traces of NiCl ₂ observed. Suggested additional testing at lower temp. (approx. 750 °C) and at lower HCl levels.
Aravind et al. [43]	Ni/GDC anode (22 mm dia, 35 µm thick) printed to a 3YSZ electrolyte (25 mm dia., 130–140 µm thick).	Humidified H ₂ with 4.2 vol% moisture. H ₂ bottle containing a fixed fraction of HCl Anode test at 850 °C	No significant change in performance after 90 min of exposure to 9 ppm(v) HCl. Impedance spectra did not show any variation in the resistance values of any of the circuit elements	No chemical interaction between HCl and anode materials (Ni and ceria) Anode composition & structure is unaltered.
Haga et al. [35]	Electrolyte-supported cells with ScSZ (10 mol % Sc ₂ O ₃ – 1 mol % CeO ₂ – 89 mol % ZrO ₂) and Ni–ScSZ cermet anodes. Double anode layer of 20 mm dia. Electrolyte of 200 µm thickness	3% humidified H ₂ at a flow rate of 20 mL min ^{−1} and pure dry N ₂ (carrier gas) with a flow rate of 20 mL min ^{−1} . All experiments at 5 – 1000 ppm, 800 °C, 0.2 A cm ^{−2} & 5% FU.	Degradation in voltage per 100 h: ~0.2% for pure H ₂ ~0.3% for H ₂ with 5 ppm Cl ₂ ~1.7% for H ₂ with 100 ppm Cl ₂ ~9.4% for H ₂ with 1000 ppm Cl ₂ Increased degradation rate with increased chlorine level. Poisoning is partially reversible.	Adsorption-type (reversible) and Sublimation-type (irreversible) degradation. Reaction of Ni and Cl ₂
Bao et al. [44]	Ni-YSZ/YSZ/LSM cell from InDec B. V., Netherlands. 2.5 cm diameter electrolyte: 4–6 µm, anode layer: 5–10 µm, porous anode support layer (NiO–YSZ) of 465–555 µm, cathode layer of 30–60 µm thick. The cathode is open to dry air.	Synthetic coal gas with 40 ppm HCl at 750 & 800 °C Overall fuel flow rate is approx. 100 mL/min (30.6% H ₂ , 30.0% CO, 27.6% H ₂ O & 11.8% CO ₂).	No degradation up to 100 h with HCl at 750 & 800 °C. But, power density dropped from 182 to 173 mWcm ^{−2} (degradation rate: ~0.15 mWcm ^{−2} h ^{−1}) with CH ₃ Cl at 850 °C after ~ 60 h	Surface adsorption on Ni or some bulk effect on supported YSZ.
Marina et al. [45]	Nickel/zirconia ASC with 2 cm ² active area Anode support: ~ 900 µm thick and 30 vol.% porous, comprised of Ni/YSZ bulk layer with 40/60 vol.% ratio. Anode active layer: 5 µm thick 50/50 vol.% Ni/YSZ. Electrolyte: 9 µm thick 8YSZ. After tests, the cells were analyzed using SEM-EDS and Auger electron spectroscopy (AES).	Synthetic coal gas (55 parts by vol. H ₂ and 45 parts by vol. of CO ₂) with up to 800 ppm(v) HCl. Temp: 650–850 °C	Reversible poisoning of anode. Poisoning decreased with increase in temp. Performance loss increased with HCl up to 100 ppm(v), beyond which it was insensitive to concentration. Cell voltage or current density did not have any effect on the extent of poisoning. Performance change is electrodic (temporary) only. No long-term degradation or microstructural changes.	Adsorption of chlorine species. Chlorine adsorption is reversible which indicates that the strength of this bond is not so high.
Xu et al. [46]	A five layered Ni-YSZ anode-supported cell (MSRI make) Anode support: 0.8–0.9 mm Ni-8YSZ Interlayer: 25 µm Ni-8YSZ Electrolyte: 20 µm thick 8YSZ Interlayer: 25 µm LSM-8YSZ Current collection layer: 50 µm thick LSM Cell effective area: 2 cm ² Chemical and structural change analyses by SEM, XRD, and XPS.	Syngas with 100 ppm HCl at 800 and 850 °C. Current load: 0.5 A/cm ² Total syngas flow rate: ~ 200 ± 2 sccm Air flow rate: ~300±2 sccm	100 ppm HCl in syngas for 400 h resulted in a performance loss of about 3%. Avg. voltage degradation of 0.033 mV/h at 800 °C at 0.5 A/cm ² . At 850 °C, a higher degradation in performance with an average rate of 0.1 mV/h. Consistent OCV: 0.942 V at 800 °C and 0.925 V at 850 °C.	Chlorine adsorption on the Ni surface and loss of Ni. Permanent changes on the anode (Ni particles) microstructure. Corrosion to tubing and interconnects, a great concern while using coal syngas.
Sasaki et al. [31]	Ni-ScSZ / ScSZ/ LSM single cell. Long-term poisoning tests followed by microstructural observations (FESEM micrographs).	Effect of Cl ₂ from 5 to 1000 ppm at 800 °C in 3% humidified H ₂ fuel Const. current load of 0.2 A/cm ² for 150 h. Temp: 750 & 850 °C Galvanostatic mode at 250 mA/cm ² Fuel: Hydrogen 1 to 10 ppm HCl added at the rate of 1 ppm per hour.	Continuous degradation. Approx. 9.4% per 100 h for 3% humidified H ₂ fuel with 1000 ppm Cl ₂ . (Typical degradation rate of this cell was ca. 0.3%/1000 h). Partially recoverable on removal of Cl ₂ . No effect due to HCl concentrations of 8 ppm at 850 °C and 10 ppm at 750 °C.	Sublimation of NiCl ₂ (g)
Li et al. [47]	Anode supported cell Cell active area: 4 × 4 cm ² Ni-YSZ active layer of 10 µm and Ni-YSZ support 400 µm; YSZ electrolyte of 10 µm thick; Double cathode: LSM current collector of 30 µm and LSM-YSZ functional layer of 25–30 µm.			
Blesznowski et al. [40]	Ni/YSZ anode Supported SOFC of 5 × 5 cm ² . Experiments conducted with single contaminants (H ₂ S, HCl).	50% H₂ and 50% N₂ humidified with 3% H ₂ O, 1 – 10 ppm HCl T = 750 °C I = 0.25 A/cm ²	Upto 10 ppm of HCl does not affect the AS-SOFC operation at 750 °C.	During long term tests, adsorption on to the anode surface might impede/hinder the H ₂ reaction sites.
Madi et al. [48]	Ni-YSZ anode supported single and short stacks. Single cells: Circular, active area - 7.5	1 – 1000 ppm(v) HCl in H ₂ /syngas at 750 °C. Fuel for stack: a gas mix that	Severe poisoning of single cells with H ₂ as compared to syngas. At higher current densities, the effect due to HCl	Adsorption of chlorine. Ruled out the possibility of secondary phase of nickel

(continued on next page)

Table 1 (continued)

Refs.	Type of cell /Experiment details	Gas composition & operating conditions	Observations/findings reported	Reasons listed / Remarks
	cm ² (Topsoe Fuel Cells, Denmark) & 80 mm dia., active area - 47 cm ² (SOLIDpower, Italy) Short stack: 11 ASC from Topsoe Fuel Cells, Denmark	simulates the steam-reformed biogas or H ₂ -rich syngas.	will be more due to diffusion limitations. No degradation in short stacks except the corrosion of anode exhaust pipe.	chlorine.
Reeping et al. [19]	Electrolyte supported cell 50 μm thick Ni-YSZ cermet and an approx. 5 μm thick Ni-GDC interlayer	Synthetic biogas (50% CH ₄ 50% CO ₂) 110 ppm Cl (either as CH ₃ Cl or HCl) at 650 and 700 °C	Chlorine immediately suppresses the carbon accumulation. Slow and steady degradation of the cell and continual exposure to Cl ends up in rapid and irreversible failure. Significant performance loss with carbon containing fuels	Continuous chlorine exposure inhibits CH ₄ cracking and dry reforming. Note: Details of reforming are not reported. Chlorine poisoning of the C-H bond activation mechanisms.
Reeping et al. [32]	Fuel Cell Materials make SOFC. Diameter: 25.4 mm Anode: 50 μm thick Ni-YSZ cermet and approx. 5 μm thick Ni-GDC functional anode layer. Cathode: 50 μm thick LSM layer with an approx. 5 μm thick LSM-GDC interlayer cathode. Electrolyte: 250–300 μm thick “Hionic” material.	110 ppm CH ₃ Cl in CH₄ / biogas at 650 and 700 °C. The fuel mix is supplemented with 5% H ₂		
Papurello and Lanzini [34]	ASC700 (SOLIDpower, Italy) Anode: Ni-YSZ Cathode: GDC/LSCF 80mm dia FU - 30% (due to seal-less cell)	Syngas (% mol: H ₂ -50.8, CO-19.5, CO ₂ -9.1, CH ₄ -0.7, H ₂ O-19.9) with 1 – 1000 ppm(v) HCl. Steam/Carbon = 2 T = 750 °C, I = 0.21 A/cm ²	Upto 20 ppm(v), total cell performance recovery (back to starting voltage) is achieved. Electrochemical process affected when HCl is above 40 ppm(v)	HCl affected the TPB zone
Escudero and Serrano [33]	W-Ni-Ce/SDC/LSCF single cell Active area - 0.25 cm ² , Electrolyte - 11 mm dia & ~0.4 mm thick. 250 ppm HCl from a H ₂ /HCl gas bottle with 1 % HCl Anode flow – 50 ml/min, Cathode – open air	Simulated biogas (CH ₄ /CO ₂ /H ₂ ratio of 70/25/5) with 3 % moisture at 750 °C. 89 mA/cm ² for 40 h without HCl & 71 mA/cm ² for 29 h with HCl.	250 ppm (typical value of halogenic compounds in landfill biogas) of HCl caused important oscillations in the potential and performance loss under load demand.	Adsorption of chlorine and carbon formation on active sites.
Papurello et al. [21]	Short stack comprising six anode supported Ni-YSZ/8YSZ/LSM-YSZ SOFCs. Active cell area – 80 cm ² FU – 75 %	Technical gases – H ₂ , CO, CO ₂ , N ₂ & CH ₄ . 750 °C 20 ppm(v) HCl in H ₂ as carrier gas	Ceramic sealant rupture and reoxidation of the cell	Reaction between HCl and the glass ceramic sealant resulted in rupture and reoxidation of the cell

SOFC.

This particular study is focused on performing experiments with chlorine traces in carbon containing fuels where the proportion of CH₄:CO₂ is maintained throughout as 3:2, which is the most commonly found average value in biogas generated from sewage treatment plants. The intention is to investigate its immediate effect on direct internal reforming as well as the electrochemical performance of the SOFC.

4. Materials and methods

This study is executed in three stages. Initially, the thermochemical calculations are done to identify the carbon deposition risk. This analysis helps to arrive at the safe operating condition for SOFC in terms of operating temperature, fuel mix, and steam to methane ratio. Based on these results, direct internal reforming experiments are performed with contaminant-free biogas. This is followed by contaminant tolerance study of SOFC with various levels of HCl in the feed biogas, at different temperatures. Finally, post-test analyses are also performed to investigate the microstructure of anode surface and cross section of the SOFC. Field emission scanning electron microscope (FESEM), energy-dispersive spectroscopy (EDS), and x-ray diffraction analysis (XRD) are used for this purpose. These are further illustrated in the following sections.

4.1. Thermochemical analysis

The thermochemical calculation software and database package, FactSage (Version 8.0, developed by Thermfact/CRCT (Montreal, Canada) and GTT-Technologies (Aachen, Germany)), is used to calculate the thermodynamic equilibrium composition of the biogas mixture at various temperatures and atmospheric pressure. These calculations are needed to identify the risk of carbon deposition at equilibrium compositions of fuels at the operational temperature and pressure of the SOFC. FactSage software gives the chemical equilibrium composition based on Gibbs free energy minimization. The ternary (C-H-O) diagram prepared based on these calculations is found to be extremely useful in identifying the safe operating conditions for the biogas-fuelled SOFC. It is worth noting that there is still a chance that experimental findings may differ from the equilibrium predictions due to anode catalyst types, size of nickel/catalyst crystallites, fuel flow rates, etc [50].

The following combinations of fuel mixtures are used for the thermochemical calculations:

- Biogas DR1; ii) Biogas DR2; iii) Biogas SR1; iv) Biogas SR2; v) Biogas SR3. The composition details are appended below in Table 2.

A ternary diagram prepared based on multiple thermochemical calculations with these different fuel mixes at the SOFC operating conditions is shown in Fig. 1.

It can be seen that the dry reforming operation with low CO₂

Table 2

Composition of the different fuel mix considered preliminarily for the study.

Fuel mix	Proportion of the constituents			
	CH ₄	CO ₂	H ₂	H ₂ O
Biogas DR1	3	2	-	-
Biogas DR2	3	2	0.5	-
Biogas SR1	3	2	-	2
Biogas SR2	3	2	-	3
Biogas SR3	3	2	0.5	3

concentrations results in carbon deposition as the number of moles of CO₂ available is always less than that of the CH₄ present in the biogas. As this is the most common scenario of CH₄ to CO₂ (3:2) composition in raw biogas, dry reforming alone is not a possible option for direct internal reforming (DIR) in the SOFC. Either extra CO₂ captured from other processes should be available or extra steam must be added, thereby making this a combined SR and DR process, for a safe operation of the SOFC. Saadabadi et al. [51] based on their experiments at 850 °C and current density ≥ 2000 A/m² reported that an equimolar ratio of CH₄ and CO₂ is required for safe and optimal performance, if dry reforming is the choice. This resulted in no carbon deposition and, at the meantime, delivered maximum power density. Biogas SR1 containing steam to methane ratio of 0.67 is just lying on the 750 °C temperature line, whereas both the Biogas SR2 and Biogas SR3 with steam to methane ratio of one are well within the safe region. Biogas SR3, the one with 5% H₂, is marginally safer than Biogas SR2, and hence this composition is considered for the experiments. Additionally, in actual biogas, varying levels of H₂ are found most of the time. Garcia et al. [52] reported that the biogas generated from wastewater treatment plants contain CH₄ (50–70%), CO₂ (20–50%), H₂ (0–5%), H₂S (0–1%) and various other trace contaminants. Cigolotti et al. [53] mentioned that the biogas composition may vary considerably depending on the feedstock, the

process conditions and the type of digester used, but a generally applicable composition is CH₄: 55–65%, CO₂: 30–45%, N₂: 1–5%, H₂: 1–5%, H₂S: 80–4000 ppm and other pollutants in trace levels (<1000 ppm). Also, Reeping et al. [32] mentioned about the “palliative” effect of 5 % H₂ in carbonaceous fuels to mask the deterioration in the catalytic activity of nickel. Fan et al. [54] used nearly 8 % H₂ in their study on methane steam reforming kinetics and mentioned that addition of a small amount of hydrogen ensures a reducing environment for the SOFC anode. All these findings prompted us to stick on to Biogas SR3 for the experiments.

The equilibrium compositions of reformed biogas at various temperatures and atmospheric pressure with Biogas SR3 as the input fuel to SOFC is shown in Fig. 2. This is plotted based on the results obtained from the multiple runs on FactSage software at temperatures ranging from 400 to 1000 °C and 1.013 bar. From Fig. 2, it is clear that there is only a slight variation in the composition of reformed gases beyond 750 °C. The CH₄ is completely reformed, and the composition is almost steady after 800 °C. Hence, all the experiments were conducted with the SOFC operating temperature set between 750 and 850 °C.

4.2. Experimental

The details of SOFC, experimental test bench, fuel-mix, and the description of test procedures adopted are elaborated in the subsequent sections.

4.2.1. SOFC details

An electrolyte-supported Ni-YSZ cermet anode SOFC (Keracell 1) with 8YSZ electrolyte made by Kerafol, Germany is used for the experiments. The cell had an overall dimension of 100 × 100 mm with an active area of 90 × 90 mm.

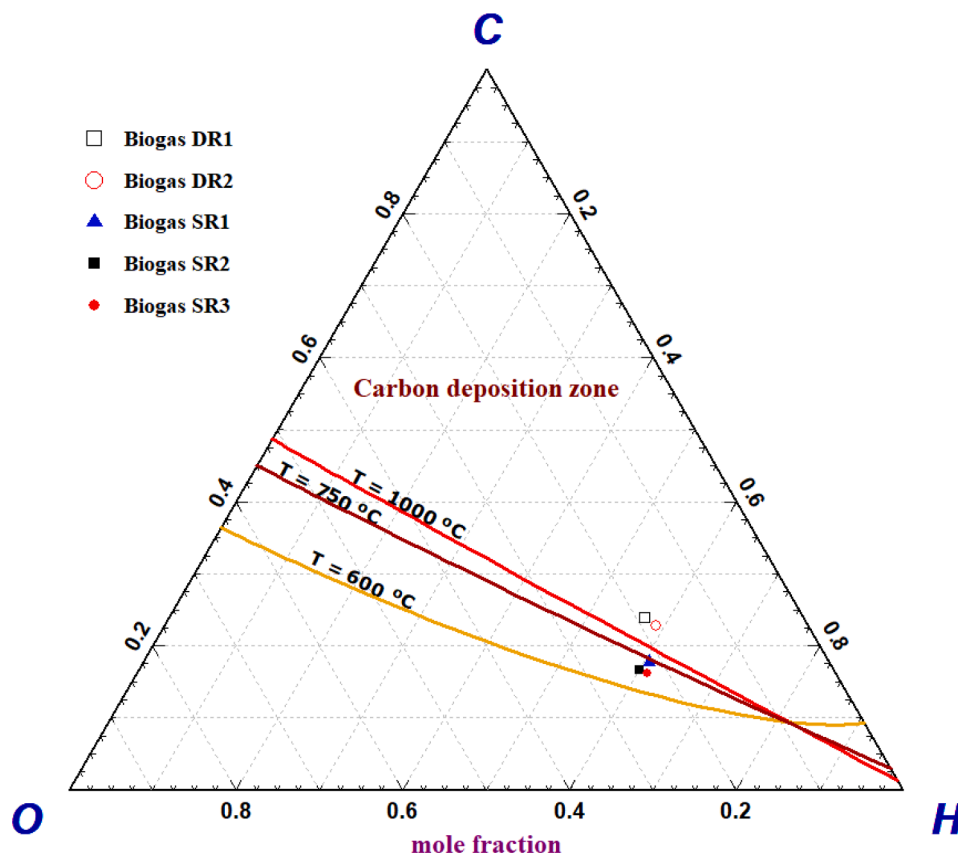


Fig. 1. C-H-O diagram to ascertain the carbon deposition risk of various fuel compositions at different operating temperatures of SOFC.

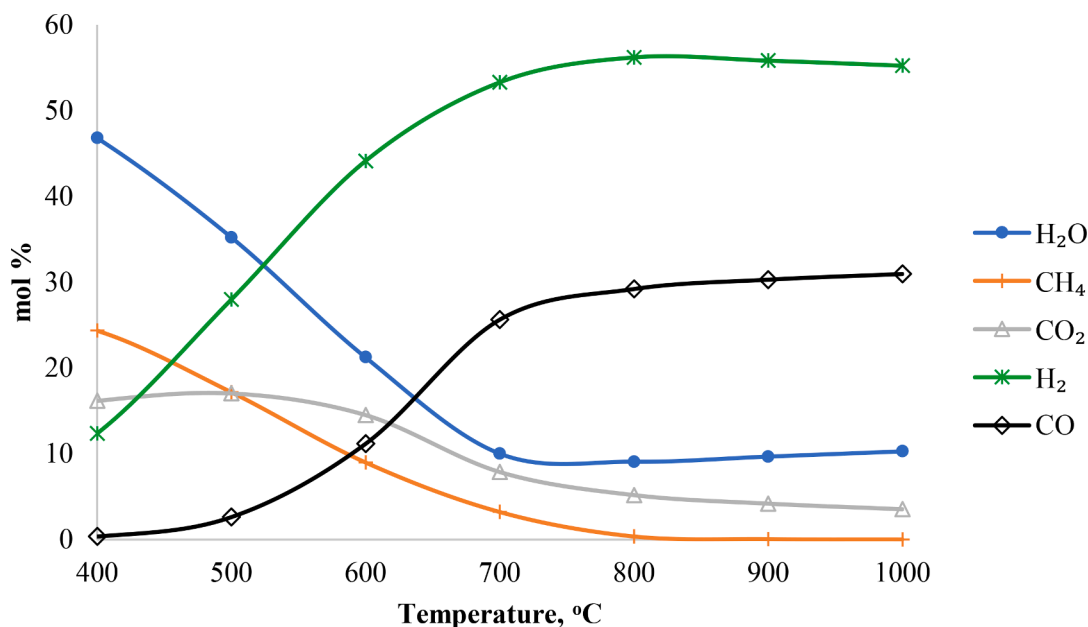


Fig. 2. Equilibrium composition of Biogas SR3 at various SOFC operating temperatures.

4.2.2. Set-up description

The electrolyte supported SOFC is placed inside an alumina testing house, sandwiched between platinum meshes at both the anode and cathode sides. These meshes allow the gas flow from the grooved channels in the alumina housing to the SOFC, as well as act as the current collectors. To ensure proper gas tightness, mica (thermiculite) sheets are used as sealants between the fuel cell and the alumina housing. A four-wire testing configuration is adopted for drawing current and voltage measurements. The required gas composition is simulated by mixing the individual gases in the appropriate ratios. Bronkhorst high-tech b.v mass flow controllers (MFC) are used for setting and controlling the gas flow. A Low- ΔP -Flow series mass flow controller suitable for corrosive gas service is used for adding the HCl/N₂ mixture to the anode inlet gas. A controlled evaporator mixer system (CEM) by Bronkhorst is used to simultaneously generate the steam and mix it with the anode inlet gas. The CH₄ to CO₂ ratio is always maintained at 60:40, which is the expected average value in biogas generated from sewage treatment. The total flow rate of anode inlet gas is maintained throughout the entire set of experiments at 1000 Nml.min⁻¹. Simulated air by mixing appropriate proportions of N₂ (79%) and O₂ (21%) is used at the cathode side.

The anode inlet as well as the outlet fuel lines are preheated to 130 °C by means of trace heaters to avoid any steam condensation inside the fuel pipelines. The outlet gas from the anode is passed through a steam condenser unit operating at ambient conditions. This gas is further dried by passing through a silica gel based gas cleaning unit to completely remove the moisture. A stream of this dried gas is sent to the gas chromatography (Agilent 490 Micro GC Biogas Analyzer) system through a sampling pipe while the remaining part is vented out. This GC consists of two columns; a 10-meter CP-Molsieve 5A with argon as carrier gas (for excellent sensitivity and linearity for hydrogen), and a 10-meter CP-PoraPLOT U column with helium as carrier gas. A Bronkhorst high-tech b.v mass flow meter (MFM) is connected just after the drier unit and prior to the tapping for micro GC sampling. This MFM is used to check the gas tightness of the assembly/testing house. All the electrochemical measurements are done with the Gamry make potentiostat/galvanostat (Gamry Reference 3000). It can perform general physical electrochemistry experiments at high voltages and high currents for batteries, fuel cells, or supercapacitors. Also, a Gamry Reference 30K Booster is interfaced with the Gamry Reference 3000 to enable it for high current applications. For monitoring the SOFC operating

temperature, a K-type thermocouple (RS PRO, -50 °C / +1200 °C) is inserted through the anode side alumina block and placed very close (< 2 mm) to the anode surface. This thermocouple is connected to a temperature logger (Model: USB-TC01, Make: National Instruments) for continuous measurement and recording of the SOFC temperature. The schematic of the test station is shown in Fig. 3.

4.2.3. Fuel-mix

Based on the thermochemical calculations, Biogas SR3 containing CH₄, CO₂, H₂O, and H₂ in the ratio 3:2:3:0.5 is used for all the experiments. The required level of HCl is added to the SOFC fuel line, after the CEM outlet and just before the inlet to the SOFC by means of a premixed standard gas cylinder containing N₂ and HCl mixture. In order to vary the HCl level in the inlet gas, the flowrate from this premixed cylinder as well as the normal N₂ inlet line are adjusted to maintain the required ppm(v) level and the total inlet flow. The anode inlet flow, keeping the CH₄:CO₂ ratio at 3:2, is steadily maintained 1000 Nml.min⁻¹ throughout so as to have a constant residence time for all the set of experiments.

4.2.4. Test procedures

The SOFC is heated from room temperature to 900 °C at a uniform ramping rate of 50 °C/h with N₂ as the inlet gas at both the anode and cathode. After reaching the set temperature, the flow rate of N₂ is gradually lowered and H₂ is proportionally increased at the anode side until the whole N₂ is replaced with the H₂ gas. Simultaneously, the N₂ gas at the cathode side is switched completely to simulated air mixture. This process enables the nickel oxide (NiO) to get reduced to Ni. The SOFC is maintained at this temperature on pure H₂ for a few hours. On attaining a steady OCV, the cell is switched to galvanostatic mode. After several hours of stable operation in galvanostatic mode, the measurements / experiments with biogas are started. The polarization (I-V) curve is plotted at the start and end of the experiments and compared to find out the deterioration/degradation of the SOFC. Experiments were conducted at various ppm(v) levels (upto 12 ppm(v)) of HCl and temperatures of 850, 800 and 750 °C.

It is understood that errors may get introduced due to various elements during a measurement process. An error analysis helps in understanding and evaluating the uncertainties in measurement [55]. Any measurement, however carefully made, cannot be completely free from uncertainties. Hence, an uncertainty analysis is performed based on the guidelines given in the books by Holman [56] and Taylor [55]. The

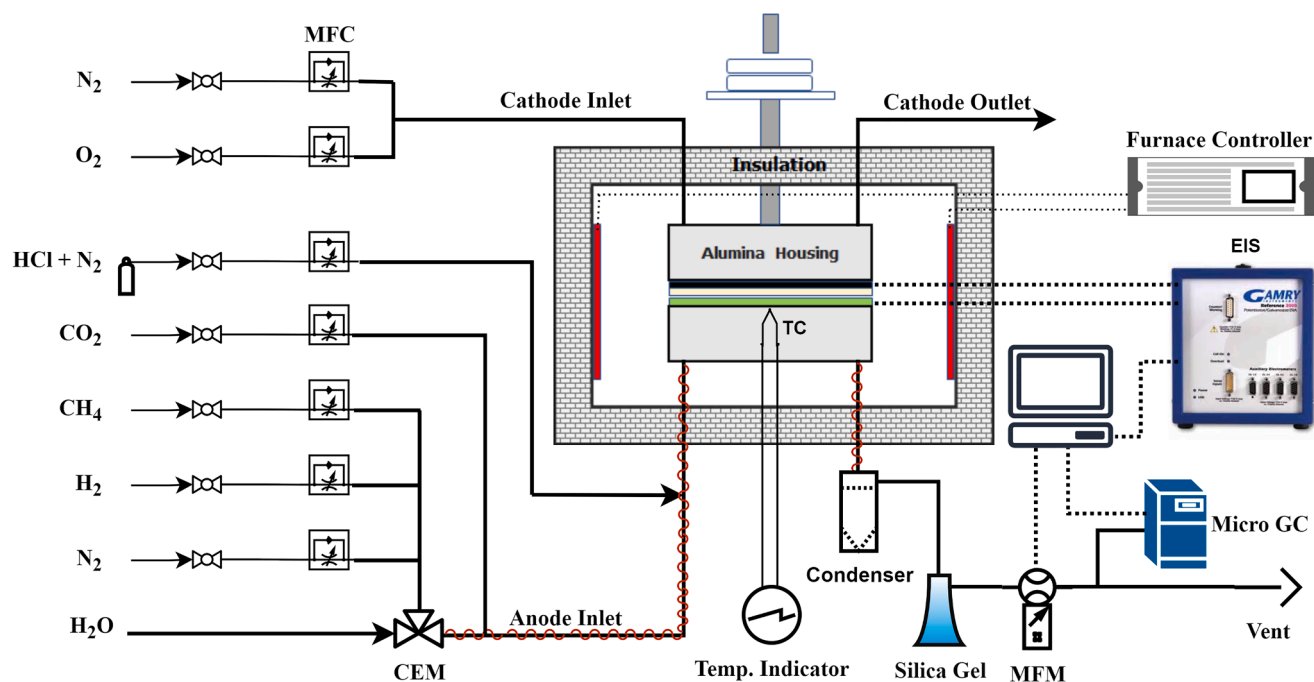


Fig. 3. Schematic diagram of the test setup used for SOFC experiments.

uncertainty in anode gas flow measurements related to CH_4 , CO_2 , H_2 & N_2 are $\pm 0.4\%$, $\pm 0.4\%$, $\pm 2.0\%$ and $\pm 1.1\%$, respectively. The flow measurements at the cathode side have an uncertainty of $\pm 0.8\%$ for O_2 and $\pm 0.9\%$ for N_2 gas. The MFC used for adding the HCl/N_2 mixture possess an uncertainty of $\pm 1.1\%$. The temperature measurement (SOFC operating temperature) is expected to have an uncertainty of $\pm 0.4\%$. The Gamry Ref 3000 and 30 k booster used to measure the cell performance is calibrated using the calibration cell (provided by the manufacturer) prior to the experiments. The uncertainty in DC characteristics (Current & Voltage measurements) is within $\pm 0.2\%$. The gas chromatography measurements of the anode outlet gas composition have a peak area repeatability (RSD%) of < 0.5 .

4.3. Post-test analyses

After the electrochemical experiments, microstructural analysis is performed on the cell using a JEOL JSM-7800F Prime Field Emission Scanning Electron Microscope (FE-SEM/EDS) along with an Oxford make EDS detector. Samples of both the anode surface and the anode-electrolyte cross-section are examined. The XRD analysis is performed on the anode surface of the used cell with the PANalytical make X'pert Pro X-ray diffractometer.

5. Results & discussions

This section illustrates and presents the effects of varying concentrations (4–12 ppm(v)) of HCl in biogas on the direct internal reforming and the electrochemical performance of SOFC. The same set of experiments were conducted at three different operating temperatures: initially at 850°C , then at 800°C and finally at 750°C .

5.1. Effect of HCl on DIR at various temperatures: anode outlet gas measurement results

To study the effect of HCl on direct internal reforming of biogas at various temperatures, the SOFC operating temperature is varied through 850°C to 750°C by 50°C . At 850°C , there is hardly any unreformed methane in the anode outlet gas in the closed-circuit condition. The

composition of the anode outlet gas when operating the SOFC at $500\text{ A}/\text{m}^2$ with zero ppm(v), 4 ppm(v), 8 ppm(v), and 12 ppm(v) concentration of HCl in the feed gas is depicted in Fig. 4 below.

The results show marginal difference/dip in reforming at the SOFC operating temperatures of 800°C and 750°C . It can be seen from Fig. 4 that at 800°C the unreformed methane in the dry anode outlet gas is less than 1 % and that at 750°C it varied from 2.94 % to 3.52 %. This change is probably due to the effect of temperature on reforming and not that of the poisoning of the anode/ Ni catalyst due to the HCl traces in biogas. We observed similar results, when experiments were performed without HCl traces in biogas. This trend is also seen in the thermochemical calculation (Fig. 2), where there is slight presence of methane at 750°C .

5.2. Effect of HCl on the electrochemical performance of SOFC

The SOFC is operated at 850°C in galvanostatic mode at a current density of $500\text{ A}/\text{m}^2$. The cell voltage vs time for the same is shown in Fig. 5 (a) below. After about 4 h of operation on Biogas SR3 with a steam to methane ratio of one, 4 ppm(v) HCl is added to the fuel inlet line by proportionally mixing the required quantity of standard concentration $\text{HCl}-\text{N}_2$ gas from a cylinder. Anode outlet gas samples are analysed at regular intervals of 30 min in a micro GC. After 3 h, the HCl is removed and the cell is operated for about an hour on clean biogas mix, and then with 8 ppm(v) HCl in biogas for another 3 h. Again, HCl removed, the cell is operated on clean biogas mix for 2 h and repeated the experiment with 12 ppm(v) HCl in biogas.

After completing all the tests at 850°C , the polarization curve is plotted, and this is compared with the one taken prior to performing the trials with HCl contamination. Fig. 5(b) shows that both these curves are almost identical/overlapping, and hence it can be concluded that there is no significant degradation in cell performance.

After the test with 12 ppm(v) HCl in biogas fuel at 850°C , the cell is flushed with humidified (3%) hydrogen, kept in open circuit condition for a few hours, and then the same cell is used to perform similar set of experiments with biogas at SOFC operating temperature of 800°C and finally at 750°C . While switching from humidified H_2 fuel to biogas, a drop in temperature of about $18\text{--}20^\circ\text{C}$ is observed. This is on account of the *in situ* endothermic reforming reactions. It can be seen from Fig. 6(a)

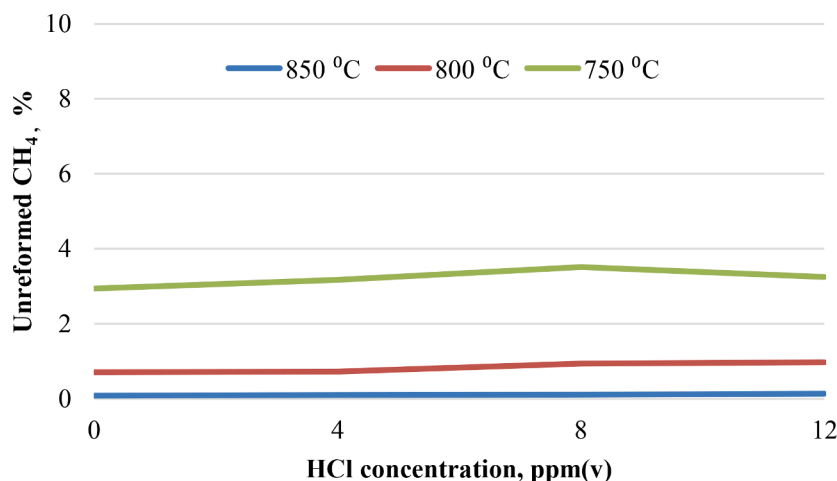


Fig. 4. Unreformed methane in the dry anode outlet gas when the SOFC is operated under a current load of 500 A/m^2 at various temperatures.

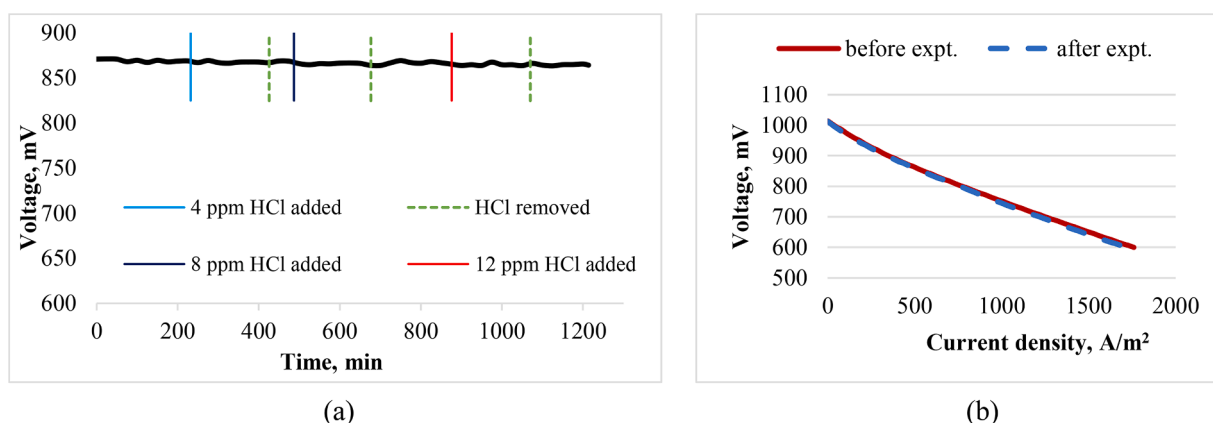


Fig. 5. (a) Cell voltage during galvanostatic mode at 850°C with HCl (4–12 ppm(v)) in biogas; (b) Polarisation curve without HCl (before expt.) and after the experiment with HCl traces in biogas at SOFC operating temperature of 850°C .

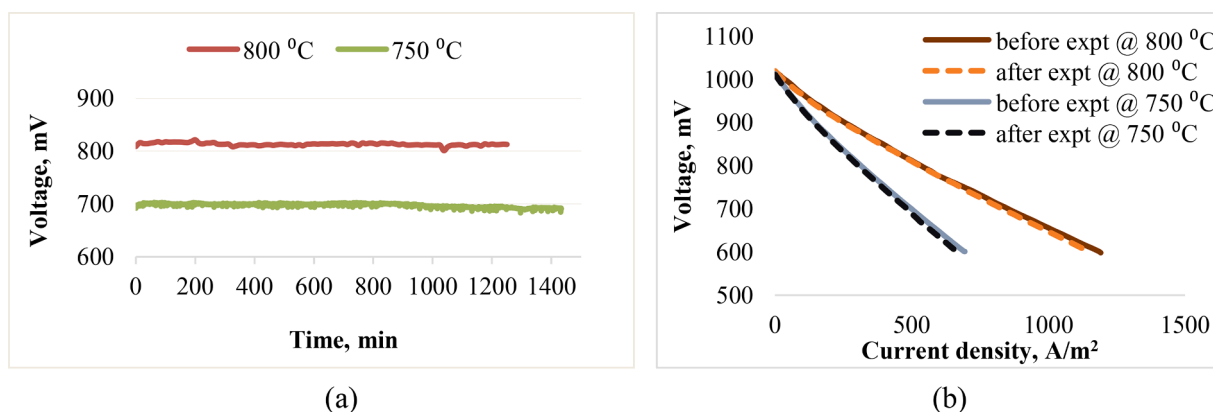


Fig. 6. (a) Comparison of cell voltage during galvanostatic mode at 750 and 800°C with HCl traces upto 12 ppm(v) in biogas; (b) Polarisation curve, before and after the experiments with HCl traces, at 750 and 800°C .

that there is no significant performance drop at 800°C , but a drop in voltage is observed during the experiments at the SOFC operation temperature of 750°C . A dip of about 8–10 mV, compared to the initial voltage, is observed in this case. This might be due to the presence of unreformed methane (3–4 %) and carbon accumulation on the anode inlet area at this temperature.

The I-V curves (Fig. 6(b)) at various SOFC operating temperatures

(750 & 800°C) taken before and after the experiments with trace HCl levels in biogas shows that there is no noticeable deterioration in performance except the minor deviation observed with the one at 750°C . So, with this composition ($\text{CH}_4/\text{CO}_2 = 3/2$ & $\text{CH}_4/\text{H}_2\text{O} = 1$) of fuel to anode, it is recommended to operate the SOFC at 850°C , for complete internal reforming as well as safe long term operation of the cell.

5.3. Post-test analyses of SOFC

The post-test analyses are performed after the entire set of experiments (with 0–12 ppm(v) HCl at 850, 800, and 750 °C). The images from the FESEM-EDS analysis done for the SOFC after performing the final set of chlorine contamination experiments are detailed below in Fig. 7. There are hardly any changes in the microstructure, and sufficient bonding between the anode and the electrolyte is observed. The cross-sectional SEM images of the anode-electrolyte area is shown in Fig. 7(a).

Fig. 7(b) shows the area mapping of nickel particles in the anode-electrolyte cross-section while Fig. 7(c) displays the microstructure and the elemental line mapping of the anode surface of the SOFC. From these images and the elemental data based on the EDS spectra, it can be interpreted that the Ni catalyst is intact in the microstructure. Fig. 8(a) shows the EDS spectra obtained during an elemental area mapping done on the anode surface.

The presence of carbon of about 5% (wt.) is detected on the anode surface. This might have occurred during the SOFC operation at 750 °C, wherein about 3–4 % of unreformed methane is observed in the anode outlet gas. It is good to note that the presence of chlorine is not detected

on the anode surface, and only negligible traces (0.01 to 0.08 wt%) is found in the cross section (anode-electrolyte) area.

The SOFC sample after the experiments with HCl is analysed to check for NiCl_2 formation, if any. Fig. 8(b) shows the X-ray diffraction pattern obtained for the anode surface of the SOFC. In comparison with the results of NiCl_2 peaks from the literature [57], it is interpreted that there is no deposition/presence of NiCl_2 on the SOFC when *in situ* reforming is performed by direct feeding of biogas containing HCl levels of upto 12 ppm(v).

5.4. SOFC fed with biogas containing HCl traces: implications on system design

It is found that complete internal reforming is possible when the biogas-fed SOFC is operated at 850 °C. This is true while operating with clean biogas as well as with biogas containing HCl traces (up to 12 ppm (v)). The electrochemical performance of the cell also is found to be stable while operating at 850 °C. There is no noticeable degradation in voltage when the SOFC is operated under galvanostatic mode. Also, the polarization curve before and after the experiments with biogas

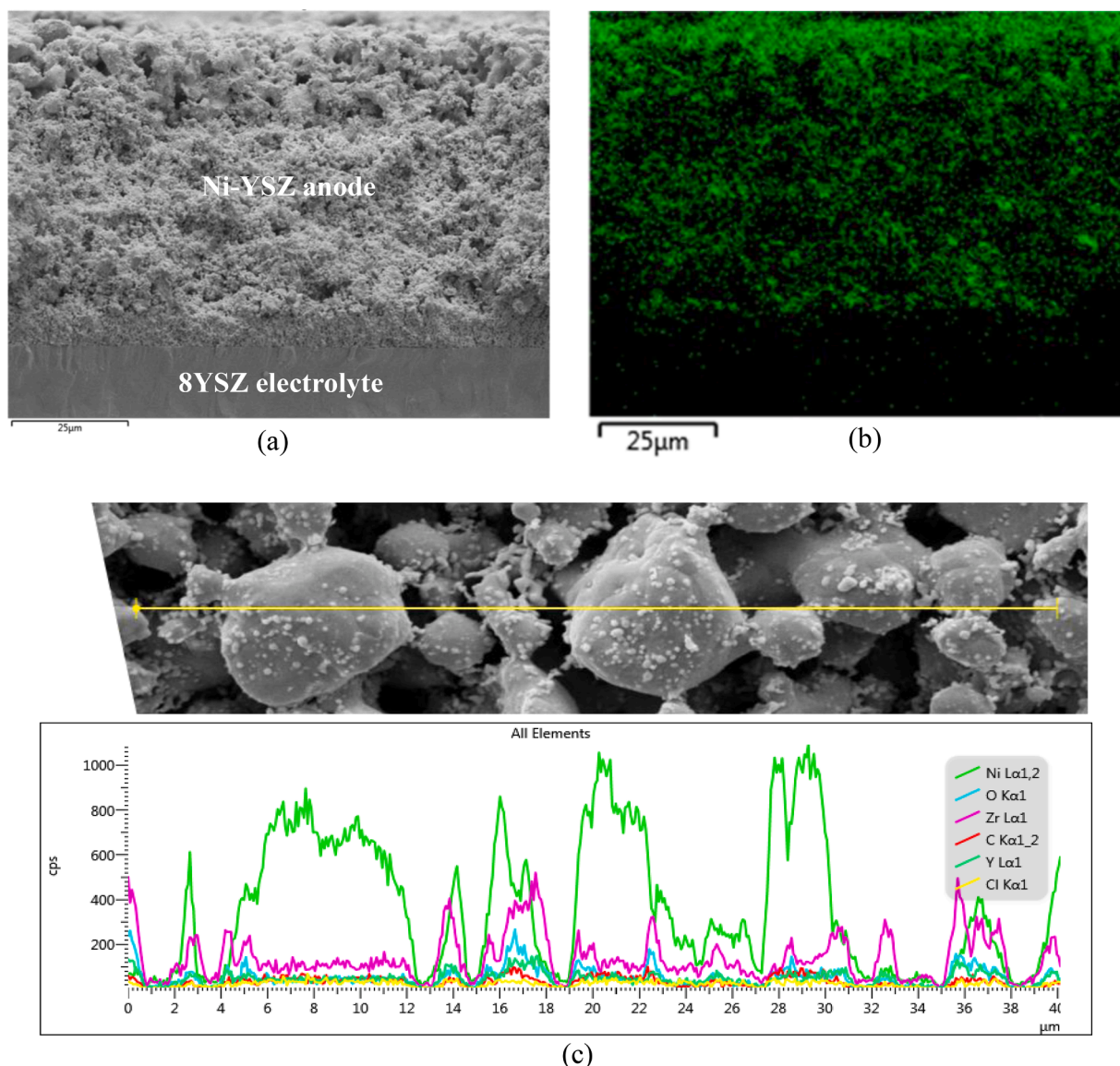


Fig. 7. FESEM-EDS images of: (a) Anode–electrolyte cross-section; (b) Mapping of Ni particles at the anode-electrolyte cross-section; (c) Line mapping and elemental composition of the anode surface of SOFC.

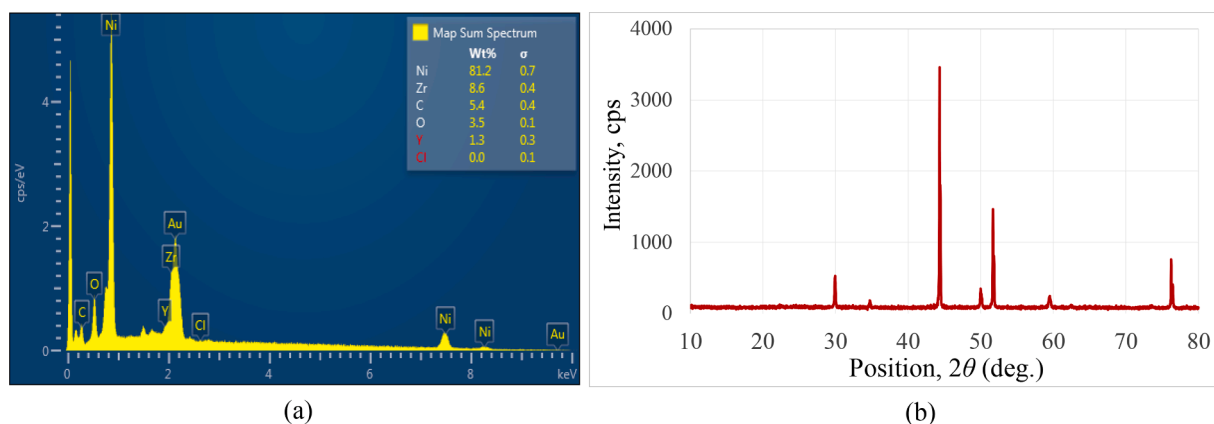


Fig. 8. (a) Elemental composition from the EDS measurements performed on the anode surface of the SOFC; and (b) X-ray diffraction pattern of the SOFC sample.

containing HCl traces did not show any signs of deterioration. Hence, it can be inferred that these findings will help in eliminating or minimizing the expenses related to the gas cleaning (as far as only HCl is considered) and external methane reforming units while opting for an integrated biogas-SOFC system for sewage treatment plants.

6. Conclusions

This work is exclusively focused on evaluating the direct internal reforming and the electrochemical performance of a Ni-YSZ electrolyte supported SOFC fed with biogas containing HCl traces. The relevant findings are:

1) Direct internal reforming and cell performance remains unaffected when SOFC is operated at 850 °C with biogas containing HCl traces (upto 12 ppm(v)).

2) At 800 °C, negligible amount (~ 1%) of unreformed methane is present in the anode off-gas while no degradation in cell performance is observed.

3) Both DIR and cell performance are marginally affected at 750 °C.

4) A reduction in SOFC temperature of 18–20 °C is observed when the fuel is switched from humidified H₂ to biogas. This is due to the endothermic nature of the reforming reaction.

5) Complete reforming of methane is attained at 850 °C. This eliminates the need for an external reformer, provided the biogas is free of other contaminants (sulphur, siloxanes, etc.).

It is observed that most of the studies pertaining to the degradation effect by HCl on SOFCs mainly used H₂ or syngas as the fuel. The fuel used in this study contains methane to carbon dioxide ratio of 3:2, the usual average proportion in biogas. Since the cells are susceptible to carbon deposition at the inlet region (during current load) or throughout the cell (at OCV) during dry reforming, combined steam and dry reforming is used in this case by maintaining a steam to methane ratio of 1:1.

At 850 °C, both the I-V curve and the voltage vs time curve under galvanostatic mode are not indicating any signs of performance deterioration. At 800 °C, the unreformed methane in the dry outlet gas is less than 1 % and that at 750 °C it varied from 2.94 % to 3.52 %. No degradation in electrochemical performance is observed at 800 °C whereas a dip of about 8–10 mV in the operational voltage is observed towards the end of the experiment at 750 °C. The presence of unreformed methane and carbon deposition on the anode surface at this operating temperature might be affecting the SOFC. The elemental composition from the EDS measurements performed on the anode surface of the SOFC also indicated the presence of about 5 % (wt.) of carbon. The FESEM-EDS results reveals that there are no microstructural changes, chlorine infiltration, and Ni catalyst erosion due to HCl traces upto 12 ppm(v) in the biogas fuel. Also, the results from XRD analysis rules out the presence of NiCl₂ and the associated degradation of SOFC.

This study is aimed at finding out the safe operation conditions when biogas generated from sewage is employed as a fuel for SOFC, and hence the HCl level selected for the experiments are based on those expected lines. Based on the experiments with this biogas composition (CH₄/CO₂ = 1.5 & H₂O/CH₄ = 1) and HCl traces upto 12 ppm(v), it is found to be safe to operate the SOFC at 850 °C, for complete internal reforming as well as safe and stable operation of the cell. We are under the expectation that these findings will help further in eliminating or minimizing the expenses related to the gas cleaning (as far as only HCl is considered) and external methane reforming units while opting for an integrated biogas-SOFC system for sewage treatment plants that normally contains CH₄:CO₂ = 3:2 and HCl traces of less than 10 ppm(v) in the generated biogas. As per the details available, the level of HCl is far high for biogas generated from land fill gas (LFG), syngas, etc., and hence these results may not serve as a suitable guideline when using such fuels. Also, this study needs to be extended further for higher current densities, extended durations, and with different sealant materials.

CRediT authorship contribution statement

Biju Illathukandy: Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft. **S. Ali Saadabadi:** Conceptualization, Writing – review & editing. **Po-Chih Kuo:** Methodology, Writing – review & editing. **Henry Wasajja:** Writing – review & editing. **Ralph E.F. Lindeboom:** Project administration, Writing – review & editing. **V.K. Vijay:** Supervision, Writing – review & editing. **P.V. Aravind:** Supervision, Conceptualization, Resources, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] I. Ullah Khan, M. Hafiz Dzarfan Othman, H. Hashim, T. Matsuura, A.F. Ismail, M. Rezaei-DashtArzhandi, I. Wan Azelee, Biogas as a renewable energy fuel – a review of biogas upgrading, utilisation and storage, *Energy Convers. Manag.* 150 (2017) 277–294, <https://doi.org/10.1016/j.enconman.2017.08.035>.
- [2] T.C. D' Silva, A. Isha, R. Chandra, V.K. Vijay, P.M.V. Subbarao, R. Kumar, V. P. Chaudhary, H. Singh, A.A. Khan, V.K. Tyagi, K.L. Kovács, Enhancing methane production in anaerobic digestion through hydrogen assisted pathways – a state-of-the-art review, *Renew. Sustain. Energy Rev.* 151 (2021), <https://doi.org/10.1016/j.rser.2021.111536>.
- [3] R. Chandra, H. Takeuchi, T. Hasegawa, Methane production from lignocellulosic agricultural crop wastes: a review in context to second generation of biofuel production, *Renew. Sustain. Energy Rev.* 16 (2012) 1462–1476, <https://doi.org/10.1016/j.rser.2011.11.035>.
- [4] G. Shah, E. Ahmad, K.K. Pant, V.K. Vijay, Comprehending the contemporary state of art in biogas enrichment and CO₂ capture technologies via swing adsorption, *Int. J. Hydrog. Energy* 46 (2021) 6588–6612, <https://doi.org/10.1016/j.ijhydene.2020.11.116>.
- [5] Anthropogenic, Natural Radiative Forcing, *Clim.Chang. in. 2013 – Phys. Sci. Basis*, Cambridge University Press, 2014, pp. 659–740, <https://doi.org/10.1017/CBO9781107415324.018>.
- [6] P.C. Kuo, B. Illathukandy, C.H. Kung, J.S. Chang, W. Wu, Process simulation development of a clean waste-to-energy conversion power plant: thermodynamic and environmental assessment, *J. Clean. Prod.* 315 (2021), 128156, <https://doi.org/10.1016/j.jclepro.2021.128156>.
- [7] Y.J. Chan, M.F. Chong, C.L. Law, D.G. Hassell, A review on anaerobic-aerobic treatment of industrial and municipal wastewater, *Chem. Eng. J.* 155 (2009) 1–18, <https://doi.org/10.1016/j.cej.2009.06.041>.
- [8] V. Stazi, M.C. Tomei, Enhancing anaerobic treatment of domestic wastewater: state of the art, innovative technologies and future perspectives, *Sci. Total Environ.* 635 (2018) 78–91, <https://doi.org/10.1016/j.scitotenv.2018.04.071>.
- [9] A.G. Capodaglio, G. Olsson, Energy issues in sustainable urban wastewater management: use, demand reduction and recovery in the urban water cycle, *Sustainability* (2020) 12, <https://doi.org/10.3390/su12010266>.
- [10] T.C. D'Silva, M. Ahmad, M. Nazim, M.W. Mirza, T. Arafat, M.A. Ashraf, M. N. Hasan, R.Z. Gaur, V.K. Tyagi, P.K. Mutiyar, R.G. Lew, B. Lew, A. Ali Khan, Performance and sustainability assessment of full-scale sewage treatment plants in northern india using multiple-criteria decision-making methods, *J. Environ. Eng.* 147 (2021) 1–11, [https://doi.org/10.1061/\(asce\)ee.1943-7870.0001941](https://doi.org/10.1061/(asce)ee.1943-7870.0001941).
- [11] Suresh Babu.S.V, Delhi's sewage, DowntoEarth. (2004.). <https://www.downtoearth.org.in/news/delhis-sewage-12161> (accessed January 7, 2021).
- [12] Local Treatment of Urban Sewage for Healthy Reuse, <https://lotushr.org/projects/technology-behind-project-2/> (accessed February 24, 2021).
- [13] P.V. Aravind, A. Cavalli, H.C. Patel, M. Recalde, A. Saadabadi, A.N. Tabish, G. Botta, A.T. Thattai, A. Teodoru, S. Hajimolana, P. Chundru, T. Woudstra, Opportunities and challenges in using SOFCs in waste to energy systems, *ECS Trans.* 78 (2017) 209–218, <https://doi.org/10.1149/07801.0209ecst>. ©The Electrochemical Society.
- [14] A.J. Rayner, J. Briggs, R. Tremback, R.M.C. Clemmer, Design of an organic waste power plant coupling anaerobic digestion and solid oxide fuel cell technologies, *Renew. Sustain. Energy Rev.* 71 (2017) 563–571, <https://doi.org/10.1016/j.rser.2016.12.084>.
- [15] Y. Li, Y. Pang, H. Tu, F. Torrigino, S.M.A. Biollaz, Z. Li, Y. Huang, X. Yin, F. Grimm, J. Karl, Impact of syngas from biomass gasification on solid oxide fuel cells: a review study for the energy transition, *Energy Convers. Manag.* 250 (2021), 114894, <https://doi.org/10.1016/j.enconman.2021.114894>.
- [16] J. Tian, R.J. Milcarek, Investigating the degradation mechanism of the solid oxide fuel cell nickel-yttria stabilized zirconia anode under siloxane contamination, *J. Power Sources* 480 (2020), 229122, <https://doi.org/10.1016/j.jpowsour.2020.229122>.
- [17] M. Gandiglio, A. Lanzini, M. Santarelli, M. Acri, T. Hakala, M. Rautanen, Results from an industrial size biogas-fed SOFC plant (the DEMOSOF project), *Int. J. Hydrog. Energy* 45 (2020) 5449–5464, <https://doi.org/10.1016/j.ijhydene.2019.08.022>.
- [18] C.A.L. Chernicharo, Post-treatment options for the anaerobic treatment of domestic wastewater, *Rev. Environ. Sci. Biotechnol.* 5 (2006) 73–92, <https://doi.org/10.1007/s11157-005-5683-5>.
- [19] K.W. Reeping, J.A. Bohn, R.A. Walker, Chlorine-induced degradation in SOFCs operating with biogas, *Sustain. Energy Fuels* 1 (2017) 1320–1328, <https://doi.org/10.1039/C7SE00156H>.
- [20] S.A. Saadabadi, A. Thallam Thattai, L. Fan, R.E.F. Lindeboom, H. Spanjers, P. V. Aravind, Solid oxide fuel cells fuelled with biogas: potential and constraints, *Renew. Energy* 134 (2019) 194–214, <https://doi.org/10.1016/j.renene.2018.11.028>.
- [21] D. Papurello, S. Silvestri, S. Modena, Biogas trace compounds impact on high-temperature fuel cells short stack performance, *Int. J. Hydrog. Energy* 46 (2021) 8792–8801, <https://doi.org/10.1016/j.ijhydene.2020.11.273>.
- [22] D. Papurello, A. Lanzini, D. Drago, P. Leone, M. Santarelli, Limiting factors for planar solid oxide fuel cells under different trace compound concentrations, *Energy* 95 (2016) 67–78, <https://doi.org/10.1016/j.energy.2015.11.070>.
- [23] H. Wasajja, S.A. Saadabadi, B. Illathukandy, R.E.F. Lindeboom, J.B. van Lier, P. Vellayani Aravind, The effect of H₂S on internal dry reforming in biogas fuelled solid oxide fuel cells, *Energy Sci. Eng.* 10 (2022) 374–383, <https://doi.org/10.1002/ese3.1021>.
- [24] V. Somano, D. Ferrero, M. Santarelli, D. Papurello, CFD model for tubular SOFC directly fed by biomass, *Int. J. Hydrog. Energy* 46 (2021) 17421–17434, <https://doi.org/10.1016/j.ijhydene.2021.02.147>.
- [25] D. Papurello, D. Canuto, M. Santarelli, CFD model for tubular SOFC stack fed directly by biomass, *Int. J. Hydrog. Energy* 47 (2022) 6860–6872, <https://doi.org/10.1016/j.ijhydene.2021.12.015>.
- [26] E. Pieratti, M. Baratieri, S. Ceschini, L. Tognana, P. Baggio, Syngas suitability for solid oxide fuel cells applications produced via biomass steam gasification process: Experimental and modeling analysis, *J. Power Sources* 196 (2011) 10038–10049, <https://doi.org/10.1016/j.jpowsour.2011.07.090>.
- [27] H. Zhang, W. Liu, J. Wang, J. Yang, Y. Chen, W. Guan, S.C. Singhal, Power generation from a symmetric flat-tube solid oxide fuel cell using direct internal dry-reforming of methane, *J. Power Sources* 516 (2021), 230662, <https://doi.org/10.1016/j.jpowsour.2021.230662>.
- [28] H. Wasajja, R.E.F. Lindeboom, J.B. van Lier, P.V. Aravind, Techno-economic review of biogas cleaning technologies for small scale off-grid solid oxide fuel cell applications, *Fuel Process. Technol.* 197 (2020), 106215, <https://doi.org/10.1016/j.fuproc.2019.106215>.
- [29] B.C.H. Steele, A. Heinzel, Materials for fuel-cell technologies, *Nature* 414 (2001) 345–352.
- [30] K. Sasaki, K. Watanabe, K. Shiosaki, K. Susuki, Y. Teraoka, Multi-fuel capability of solid oxide fuel cells, *J. Electroceram.* (2004) 669–675, <https://doi.org/10.1007/s10832-004-5174-z>.
- [31] K. Sasaki, K. Haga, T. Yoshizumi, D. Minematsu, E. Yuki, R. Liu, C. Uryu, T. Oshima, T. Ogura, Y. Shiratori, K. Ito, M. Koyama, K. Yokomoto, Chemical durability of solid oxide fuel cells: influence of impurities on long-term performance, *J. Power Sources* 196 (2011) 9130–9140, <https://doi.org/10.1016/j.jpowsour.2010.09.122>.
- [32] K.W. Reeping, J.M. Bohn, R.A. Walker, Palliative effects of H₂ on SOFCs operating with carbon containing fuels, *J. Power Sources* 372 (2017) 188–195, <https://doi.org/10.1016/j.jpowsour.2017.10.071>.
- [33] M.J. Escudero, J.L. Serrano, Individual impact of several impurities on the performance of direct internal reforming biogas solid oxide fuel cell using W-Ni-CeO₂ as anode, *Int. J. Hydrog. Energy* 44 (2019) 20616–20631, <https://doi.org/10.1016/j.ijhydene.2019.06.028>.
- [34] D. Papurello, A. Lanzini, SOFC single cells fed by biogas: experimental tests with trace contaminants, *Waste Manag.* 72 (2018) 306–312, <https://doi.org/10.1016/j.wasman.2017.11.030>.
- [35] K. Haga, S. Adachi, Y. Shiratori, K. Itoh, K. Sasaki, Poisoning of SOFC anodes by various fuel impurities, *Solid State Ion.* 179 (2008) 1427–1431, <https://doi.org/10.1016/j.ssi.2008.02.062>.
- [36] K. Haga, Y. Shiratori, K. Ito, K. Sasaki, Chlorine poisoning of SOFC Ni-cermet anodes, *J. Electrochem. Soc.* 155 (2008) B1233, <https://doi.org/10.1149/1.2980521>.
- [37] V. Paolini, F. Petracchini, M. Carnevale, F. Gallucci, M. Perilli, G. Esposito, M. Segreto, L.G. Occulti, D. Scaglione, A. Ianniello, M. Frattoni, Characterisation and cleaning of biogas from sewage sludge for biomethane production, *J. Environ. Manag.* 217 (2018) 288–296, <https://doi.org/10.1016/j.jenvman.2018.03.113>.
- [38] P. Luekittisup, V. Tanboonchaui, J. Chumee, S. Predapitakun, R.W. Kiatkomol, N. Grisdanurak, Removal of chlorinated chemicals in H₂ feedstock using modified activated carbon, *J. Chem.* (2015), <https://doi.org/10.1155/2015/959012>, 2015.
- [39] M.T. Lee, Z.Q. Wang, J.R. Chang, Activated-carbon-supported NaOH for removal of HCl from reformer process streams, *Ind. Eng. Chem. Res.* (2003) 6166–6170, <https://doi.org/10.1021/ie020705s>.
- [40] M. Blesznowski, J. Jewulski, A. Zieleniak, Determination of H₂S and HCl concentration limits in the fuel for anode supported SOFC operation, *Cent. Eur. J. Chem.* 11 (2013) 960–967, <https://doi.org/10.2478/s11532-013-0228-1>.
- [41] A. Cavalli, B. Bernardini, T. Del Carlo, P.V. Aravind, Effect of H₂S and HCl on solid oxide fuel cells fed with simulated biosyngas containing primary tar, *Energy Sci. Eng.* 7 (2019) 2456–2468, <https://doi.org/10.1002/ese3.434>.
- [42] J.P. Trembly, R.S. Gemmen, D.J. Bayless, The effect of coal syngas containing HCl on the performance of solid oxide fuel cells: investigations into the effect of operational temperature and HCl concentration, *J. Power Sources* 169 (2007) 347–354, <https://doi.org/10.1016/j.jpowsour.2007.03.018>.
- [43] P.V. Aravind, J.P. Ouweltjes, N. Woudstra, G. Rietveld, Impact of biomass-derived contaminants on SOFCs with Ni/gadolinia-doped ceria anodes, *Electrochem. Solid State Lett.* 11 (2008) B24–B28, <https://doi.org/10.1149/1.2820452>.
- [44] J.E. Bao, G.N. Krishnan, P. Jayaweera, J. Perez-Mariano, A. Sanjurjo, Effect of various coal contaminants on the performance of solid oxide fuel cells: part I. accelerated testing, *J. Power Sources* 193 (2009) 607–616, <https://doi.org/10.1016/j.jpowsour.2009.04.034>.
- [45] O.A. Marina, L.R. Pederson, E.C. Thomsen, C.A. Coyle, K.J. Yoon, Reversible poisoning of nickel/zirconia solid oxide fuel cell anodes by hydrogen chloride in coal gas, *J. Power Sources* 195 (2010) 7033–7037, <https://doi.org/10.1016/j.jpowsour.2010.05.006>.
- [46] C. Xu, M. Gong, J.W. Zondlo, X.B. Liu, H.O. Finklea, The effect of HCl in syngas on Ni-YSZ anode-supported solid oxide fuel cells, *J. Power Sources* 195 (2010) 2149–2158, <https://doi.org/10.1016/j.jpowsour.2009.09.079>.
- [47] T.S. Li, C. Xu, T. Chen, H. Miao, W.G. Wang, Chlorine contaminants poisoning of solid oxide fuel cells, *J. Solid State Electrochem.* 15 (2011) 1077–1085, <https://doi.org/10.1007/s10008-010-1166-x>.
- [48] H. Madi, A. Lanzini, D. Papurello, S. Diethelm, C. Ludwig, M. Santarelli, J. Van herle, Solid oxide fuel cell anode degradation by the effect of hydrogen chloride in

- stack and single cell environments, *J. Power Sources* 326 (2016) 349–356, <https://doi.org/10.1016/j.jpowsour.2016.07.003>.
- [49] K.W. Reeping, *Chlorine Induced Degradation of SOFCs Operating on Carbon Containing Fuels*, Montana State University, Bozeman, Montana, 2017.
- [50] S.A. Saadabadi, N. van Linden, A. Heinsbroek, P.V. Aravind, A solid oxide fuel cell fuelled by methane recovered from groundwater, *J. Clean. Prod.* 291 (2021), <https://doi.org/10.1016/j.jclepro.2021.125877>.
- [51] S.A. Saadabadi, B. Illathukandy, P.V. Aravind, Direct internal methane reforming in biogas fuelled solid oxide fuel cell; the influence of operating parameters, *Energy Sci. Eng.* 9 (2021) 1232–1248, <https://doi.org/10.1002/ese3.887>.
- [52] M. Garcia, D. Prats, A. Trapote, Presence of siloxanes in the biogas of a wastewater treatment plant separation in condensates and influence of the dose of iron chloride on its elimination, *Int. J. Waste Resour.* 06 (2016) 1–6, <https://doi.org/10.4172/2252-5211.1000192>.
- [53] V. Cigolotti, S. McPhail, A. Moreno, S.P. Yoon, J.H. Han, S.W. Nam, T.H. Lim, MCFC fed with biogas: experimental investigation of sulphur poisoning using impedance spectroscopy, *Int. J. Hydrog. Energy* (2011) 10311–10318, <https://doi.org/10.1016/j.ijhydene.2010.09.100>.
- [54] L. Fan, L. Van Biert, A. Thallam Thattai, A.H.M. Verkooyen, P.V. Aravind, Study of methane steam reforming kinetics in operating solid oxide fuel cells: influence of current density, *Int. J. Hydrog. Energy* 40 (2015) 5150–5159, <https://doi.org/10.1016/j.ijhydene.2015.02.096>.
- [55] J.R. Taylor, *An Introduction to Error Analysis*, 2nd ed., University Science Books, 1996.
- [56] J.P. Holman, *Experimental Methods for Engineers*, 8th ed., Mc Graw Hill, 2011.
- [57] A. Baba, H. Ouahbi, A. Hassine, J. Sebt, L. Laasri, S. Sebt, Efficient reduction of aromatic nitro compounds catalyzed by nickel chloride supported on natural phosphate, *Mediterr. J. Chem.* 7 (2018) 317–327, <https://doi.org/10.13171/mjc751911281520ss>.