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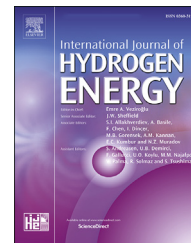
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Effect of selected representative biomass gasification tar compounds on Ni-GDC solid oxide fuel cells

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HIGHLIGHTS

- 15 g/Nm³ benzene or ethylbenzene in simulated biosyngas appear as additional fuels.
- The light tar seems not to harm Ni-GDC SOFC during 100 h non-continuous tests.
- 0.3 g/Nm³ naphthalene and 0.05 g/Nm³ phenanthrene hinder WGS and CH₄ reforming.
- The heavy tar tested affect noticeably also the SOFC electrochemical reactions.
- The negative effects of the heavy tar tested appeared almost completely reversible.

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ABSTRACT

Contaminants as particulate matter, sulfur, chlorine and tar should be removed from biosyngas to avoid damaging solid oxide fuel cells. However, there is no sufficient information on tar effect since they might be potentially used as a fuel, or they might cause performance losses and irreversible damages. Therefore, this study aims to assess whether tar can be reformed inside the SOFC and used as fuel. Short-duration experiments were conducted on Ni-GDC cells operating with simulated biosyngas containing different concentrations of representative tar compounds from biomass gasification. While benzene and ethylbenzene could be regarded as additional fuels even at concentrations as high as 15 g/Nm³, naphthalene and phenanthrene act as contaminants for the SOFC electrochemical and catalytic reactions, even at concentrations of 0.3 and 0.05 g/Nm³. However, the effect on these reactions appeared almost completely reversible. Solid carbon deposited on the SOFC ceramic housing in proximity of the inlet. Post-mortem analysis should be performed to assess the tar effect on the cell anode.

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Nomenclature

Acronyms

ASR	Area Specific Resistance
GC	Gas Chromatograph
GDC	Gadolinium-doped ceria
LSM	Lanthanum strontium manganite
OCV	Open Circuit Voltage
ScSZ	Scandia stabilized zirconia
SEM-EDS	Scanning Electron Microscope and Energy Dispersive X-Ray Spectroscopy
SOFC	Solid Oxide Fuel Cell
YSZ	Yttria stabilized zirconia

Symbols

C_{in}	Inlet carbon molar flow
C_{out}	Outlet carbon molar flow
F	Faraday constant
i	Current density
$P_{O_{2,cat}}$	Equilibrium oxygen partial pressure at cathode
$P_{O_{2,ano}}$	Equilibrium oxygen partial pressure at anode
R	Universal gas constant
S/C_{OCV}	Steam to carbon ratio at OCV condition
$S/C_{current}$	Steam to carbon ratio under current
T	Temperature
V	Voltage
V_{Nernst}	Nernst voltage

Introduction

Fossil fuels can be replaced by biomass for small scale power and heat generation thanks to biomass gasifier solid oxide fuel cells (SOFC) systems. Biomass is first converted in biosyngas, a mixture of H_2 , CO , CH_4 , CO_2 , N_2 and H_2O . However, biosyngas also contains particulate matter, halides, sulfur and tar compounds, which might be contaminants for the SOFC [1]. These gas is therefore clean from these compounds in a gas cleaning step that can be performed at low or high temperature (above 300 °C). The operating temperature and the heat integration network affects the overall efficiency and the complexity of these systems.

Tar compounds, might not be regarded as contaminants for Solid Oxide Fuel Cell (SOFC). These compounds can be reformed and used as additional fuel directly inside the SOFC due to the cell and fuel characteristics: high temperature, nickel catalyst, presence of steam and carbon dioxide. Moreover, the exothermic operation of the SOFC provides the heat required by the reforming reaction. The gas cleaning tar removal stage could be therefore avoided by reforming these compounds, together with volatile organic compounds and light condensable (hereinafter generally named tar), directly inside the SOFC. Moreover, depending on the biosyngas tar content, the overall system efficiency might increase thanks to the use of the additional fuel represented by the hydrogen and carbon atoms contained in tar. An additional efficiency gain might be obtained from the lower power consumption of the air blower thanks to the endothermic reforming reactions

replacing the excess air used to compensate the exothermic behaviour of the SOFC [2]. However, direct internal tar reforming is not yet adopted since tar can cause carbon deposition and lead to performance losses and even irreversible damages to the SOFC [3].

Different authors in the past years have tried to assess the feasibility of direct internal tar reforming, but no decisive conclusion has been reached. Papurello et al. concluded that even only 0.1 g/Nm³ toluene causes a significant performance decrease in anode supported Ni-Yttria stabilized zirconia (Ni-YSZ) cells operated at 750 °C with simulated biosyngas or partially pre-reformed biogas [4,5]. Nonetheless, higher tolerance limits are often found in literature. As an example, Baldinelli et al. did not observe any carbon deposition when testing anode supported Ni-YSZ cells at 800 °C with simulated biosyngas carrying 10 g/Nm³ toluene, despite the low steam content equal to 2.8 vol% [6]. Conversely, 6.3 g/Nm³ toluene in biosyngas led to carbon deposition and performance drop in the experiments performed by Liu et al. with electrolyte supported Ni-YSZ cells operating at 800 °C with simulated biosyngas containing 10 vol% steam [7]. Madi et al. concluded that even 14.4 g/Nm³ toluene in biosyngas do not lead to any significant added degradation for anode supported Ni-YSZ cells at 800 °C fed with simulated biosyngas containing 5 vol % H_2O [8]. Even higher tolerance limits are reported in literature for Ni-Gadolinium doped ceria (Ni-GDC) cells. For instance, Liu et al. did not observe any degradation on an electrolyte supported cell at 800 °C when the biosyngas contained 20 g/Nm³ toluene [9]. This same amount of toluene decreased the cell Area Specific resistance (ASR) and increased the amount of fuel available, thus increasing the cell performance in the experiments of Doyle et al. on electrolyte supported Ni-GDC cells operating at 850 °C and fed with simulated biosyngas. Nonetheless, Scanning Electron Microscope and Energy Dispersive X-Ray Spectroscopy (SEM-EDS) analysis showed the presence of some carbon deposition, and 32 g/Nm³ dramatically affected the ASR [10]. Other tar compounds have also been investigated, including naphthalene [11–13] and benzene [14,15], or lighter compounds as phenol [16,17]. When testing electrolyte supported Ni-GDC symmetric cells in humidified hydrogen at 850 °C, Aravind et al. concluded that a few ppm of naphthalene do not harm the cell [13]. However, Hauth et al. highlighted the absence of methane steam reforming when this tar is present in syngas and fed to electrolyte supported Ni-GDC cells operating at 900 °C [12]. When comparing the effect of light (toluene and benzene) and heavy (naphthalene) tar, Papurello et al. suggested that the former can be regarded as fuel, and the latter as poison for anode supported Ni-YSZ cells operating at 750 °C with 7 vol% H_2O containing simulated biosyngas [11]. However, slightly heavier tar, such as phenol, have been reported to cause coking and carbon formation, thus severely damaging anode supported Ni-YSZ cells even at concentrations as low as 1.5 g/Nm³. The cells were operated at 700 °C with simulated biosyngas containing 50 vol% H_2O [16,17]. In previous studies, also real tar mixtures has been used [18–21]. As an example, in the test conducted by Hofmann et al. feeding an electrolyte supported Ni-GDC cell at 850 °C with biosyngas from a circulating fluidized bed gasifier containing 10 g/Nm³ of tar, the cell performance remained stable [20]. However, in the tests the

biosyngas was humidified to reach around 50 vol% steam. Recently it was shown by Fisher et al. that the cell electrochemical performance might remain stable, while the pressure drop over an anode supported Ni-YSZ SOFC stack kept at 715 °C increases due to formation of carbon on the anode and on the current collector despite a steam content above 40 vol% [22].

The possibility to reform tar directly inside SOFC can reduce the complexity and increase the efficiency of biomass gasifier SOFC systems. However, there is not yet agreement in the scientific community on whether tar compounds damage SOFC. This is due to several factors, including different anode materials, model tar compounds, and operating conditions used. Moreover, the conclusions of a study might be affected by diagnosis tools and evaluation criteria [23]. This study aims therefore to add new evidence on the effect of tar on SOFC. The effect on SOFC with Ni-GDC anode of four different tar compounds representative of biomass gasification were analysed and compared. This study was part of the European “FlexiFuel-SOFC” project, and the results contribute to the technology development of micro-scale biomass gasifier fuel cell systems [24].

Methodology

Setup and equipment

The cells used in the study are IKTS G3 cells with a 16 cm² active area, 165 μm 10SCSZ electrolyte, LSM cathode and Nicmeret anode [25]. A description of the housing used can be found in a previous publication [26]. The furnace temperature was controlled by a thermocouple placed in proximity of the furnace heating element. An additional thermocouple was used to monitor the cell temperature. The furnace temperature was set in order to have an initial cell temperature of 830 °C. The cells were fed with simulated biosyngas with composition 35 vol% H₂O, 2 vol% CO, 20 vol% CO₂, 4 vol% CH₄, 24 vol% H₂ and 16 vol% N₂. Varying concentrations of benzene (3–15 g/Nm³ d.b.), ethylbenzene (3–15 g/Nm³), naphthalene (0.3–1.0 g/Nm³ d.b.) or phenanthrene (0.05–0.15 g/Nm³) were added to the biosyngas. A Controlled Evaporator Mixer (CEM) (Bronkhorst, The Netherlands) was used to add steam to the biosyngas in a steady manner, thus avoiding changes in composition and voltage fluctuations. Differently, due to material compatibility issues, the tar compounds were added by diverging a fraction of the dry hydrogen towards a temperature controlled bath (tar evaporator). The tar evaporator temperature to obtain the desired tar concentration in the gas was calculated with Antoine's equation. Fig. 1 shows a simplified piping and instrumentation diagram of the test station. One cell was used for testing benzene, and another cell was used to test the other three compounds studied. Four parameters were used to evaluate the tar compounds effect on the cell: the voltage (at open circuit and under current), polarisation curves, outlet gas composition, and cell temperature. The gas composition was measured with a micro gas chromatograph (GC).

The cell was kept at a constant current during the tar exposure, and the polarisation curves were recorded 2 h after the tar addition and before removing the tar. When recording the polarisation curves, the maximum current was limited to the current corresponding to the operating voltage. The ASR was calculated as the ratio between difference in voltage and difference in current density, as shown in Equation (1)

$$ASR = \frac{\Delta V}{\Delta i} \quad (1)$$

The expected open circuit voltage (OCV) was calculated the using the Nernst equation formulation shown in Equation (2). The cathode and the anode oxygen partial pressures at equilibrium were calculated using the software FactSage.

$$V_{Nernst} = \frac{RT}{4F} \ln\left(\frac{P_{O_2,cat}}{P_{O_2,ano}}\right) \quad (2)$$

Testing procedure

After having reduced the cells at 930 °C, the oven temperature was decreased to reach a cell temperature of 830 °C. The gas flow rates were set to 1000 NmL/min simulated biosyngas at the anode and 2000 NmL/min simulated air at the cathode. With the second cell, the cathode flow rate was decreased to 1000 NmL/min since the cell performance appeared not to be affected by this change. Before proceeding with the tar

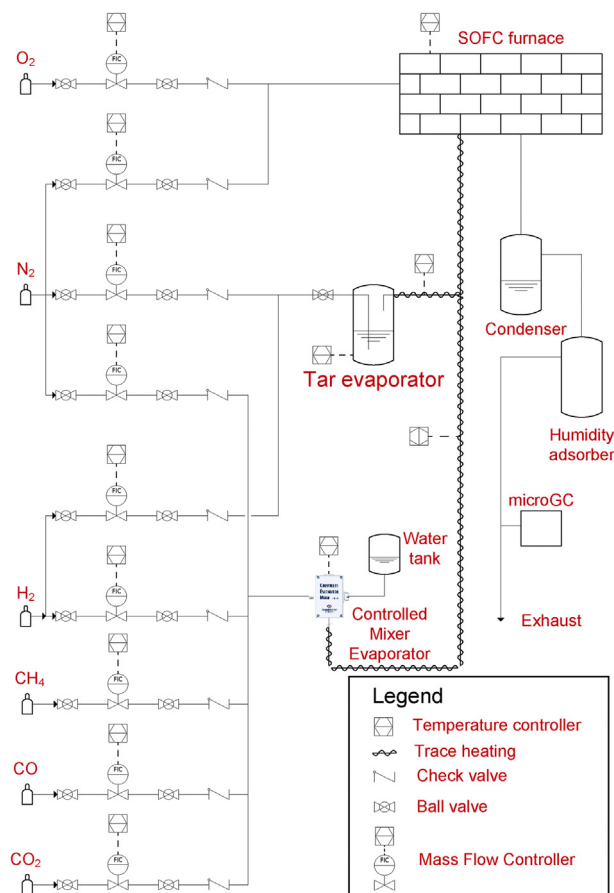


Fig. 1 – Scheme of the test station.

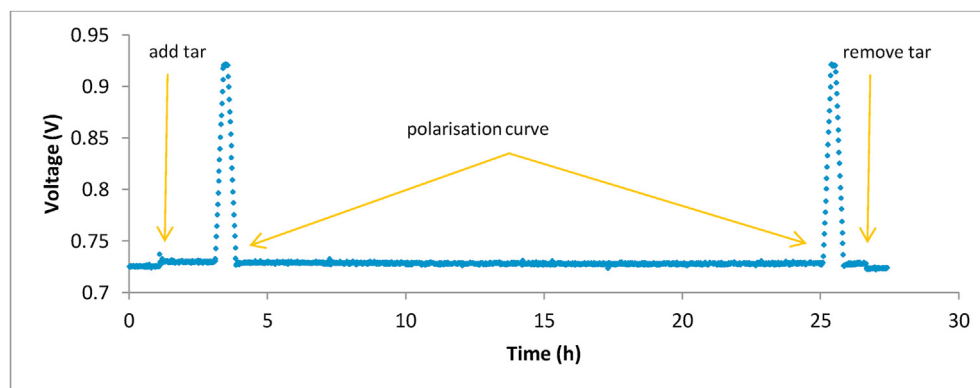

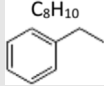
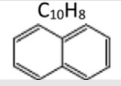
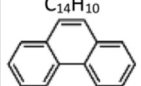


Fig. 2 – Graphic representation of the testing procedure followed for each tar concentration tested.

Table 1 – Summary of the tests performed and the relevant parameters.

Test #	Gas flowrates	Gas composition	Contaminants concentration	Operating conditions	Exposure time
1	A: 1000 NmL/min C: 2000 NmL/min (air)	(35% H ₂ O, 2% CO, 20% CO ₂ , 4% CH ₄ , 24% H ₂ , 16% N ₂)	Benzene: 3, 6, 9, 12, 15 g/Nm ³ d.b.	830 °C 94 mA/cm ² S/C _{OCV} 1.3 S/C _{current} 1.4 up to 1.1 g/Nm ³ d.b. Benzene, 1.3 at higher benzene concentrations	24 h
2.1	A: 1000 NmL/min C: 1000 NmL/min (air)		Ethylbenzene: 3, 9, 15 g/Nm ³ d.b.	830 °C 438 mA/cm ²	
2.2			Naphthalene: 0.3, 0.6, 1.0 g/Nm ³ d.b.	S/C _{OCV} 1.3 S/C _{current} 1.5	
2.3			Phenanthrene: 0.05, 0.10, 0.15 g/Nm ³ d.b.		

Table 2 – Summary of the concentrations of the tar tested in different units.

	g/Nm ³ d.b.	g/Nm ³ w.b.	NmL/min	g/min	ppmv d.b.	ppmv w.b.
Benzene	3.0	1.9	0.6	0.002	856	556
	6.0	3.9	1.1	0.004	1712	1113
	9.0	5.8	1.7	0.006	2568	1669
	12.0	7.8	2.2	0.008	3424	2226
	15.0	9.7	2.8	0.010	4280	2782
Ethylbenzene	3.0	2.0	0.4	0.002	646	420
	9.0	5.8	1.2	0.006	1879	1221
	15.0	9.8	2.1	0.010	3170	2061
Naphthalene	0.3	0.2	0.03	0.0002	53	34
	0.6	0.4	0.07	0.0004	105	68
	1.0	0.7	0.11	0.0006	174	113
Phenanthrene	0.05	0.03	0.006	0.00003	9	6
	0.10	0.07	0.012	0.00007	18	12
	0.15	0.10	0.017	0.00010	27	17

experiments, both cells were kept under current for 100 h and two polarisation curves were measured before and after the 100 h operation to assure no self-degradation of the cell. The ASR of the first cell was significantly higher than expected due to poor contact between the Pt gauzes current collector and the cathode [27]. Therefore, to keep the voltage above 0.8 V, the current during the tests was limited to 94 mA/cm². An additional Pt gauze was used with the second cell to decrease the contact resistance. A current of 438 mA/cm² was drawn during the tests and the cell voltage remained above 0.7 V. The current densities used, especially with the first cell, were quite low and far from the performance these cells normally have (e.g. Refs. [25,27]). Further adjustments are therefore necessary to find the right current collector thickness. However, the tests performed still provide useful insights on the tar behaviour since the negative effects of tar on the cell might be actually mitigated by higher current densities.

After the self-degradation test, the cell voltage was set at 0.8 or 0.7 V. The desired concentration of tar was added to the anode stream and a polarisation curve was measured after 2 h. The cell was then kept 22 h in these same conditions before recording a new polarisation curve. The tar flow was stopped and the cell was left under current for a variable amount of time required to reach a stable operating voltage. In case of full recovery, this value was expected equal to the one measured before the exposure to the tar compound. A higher tar concentration, or a different tar compound was then added and the procedure repeated. The testing procedure described is represented in Fig. 2, and a summary of the tests performed is presented in Table 1. Table 2 shows the tested tar concentrations in different units to facilitate the comparison with other studies in literature.

Results

An OCV of 0.910 V for the first cell and 0.917 V for the second cell tested was measured at 830 °C with the biosyngas

composition tested. The expected OCV, calculated using Equation (2), should be 0.922 V and 0.924 V for the two cells, that were operating at 827 °C and 822 °C. The difference between measured and expected OCV can be mostly ascribed to the incomplete reforming of methane, due to the high flow rate used in the tests. Fig. 3 presents the polarisation curves recorded before and after the 100 h operation for the two cells. The decreased slope between the curves of the two cells clearly indicates the positive effect of the additional Pt gauze. The overlap between the polarisation curves before and after 100 h operation indicates no degradation taking place. For the first cell, the polarisation curve measured before the 100 h operation period shows a non-linear trend. This might be due to the cell not having reached stable operating conditions or to an error in the measurement. However, it is clear that no degradation happened over the 100 h operation.

Benzene

These results have been previously presented in the 16th International Symposium on Solid Oxide Fuel Cells (SOFC-XVI) [26]. Therefore, we present here only a short summary. The results show that benzene is reformed inside the cell and up to 15 g/Nm³ do not negatively affect the cell electrochemical performance during 24 h exposure. The voltage increased when benzene was present and decreased when the tar flow was stopped, in accordance with the voltage values calculated using Equation (2). Adding benzene resulted mostly in an increase of hydrogen and carbon monoxide flow rates and marginally of carbon dioxide and methane flow rates. Methane might be a product of benzene decomposition, as observed in a previous study using toluene as tar [28]. However, it might be possible that benzene occupies some of the methane active sites thus preventing its reforming.

Ethylbenzene

Similar to the case of benzene, also with ethylbenzene the cell did not appear to degrade and the compound was rather used as fuel. Fig. 4, showing the voltage trend with 15 g/Nm³

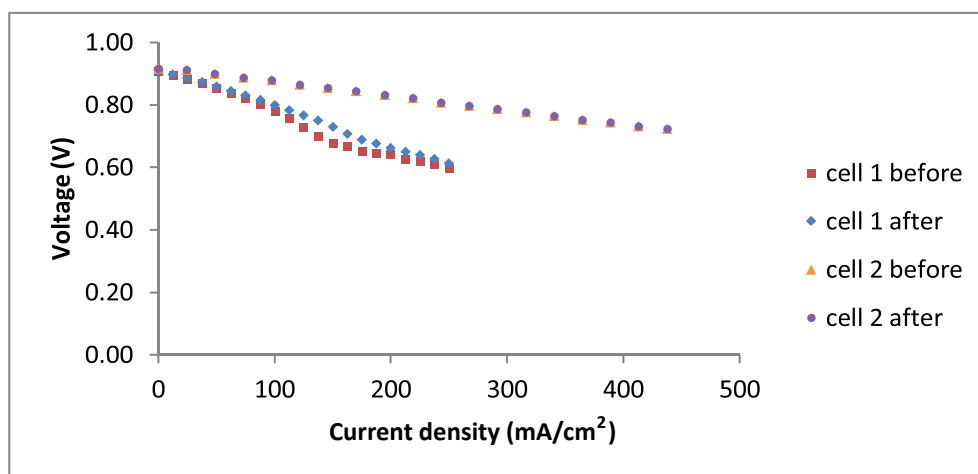


Fig. 3 – Polarisation curves measured before and after 100 h operation at 830 °C, 438 mA/cm² for cell 2 and 94 mA/cm² for cell 1, with simulated biosyngas.

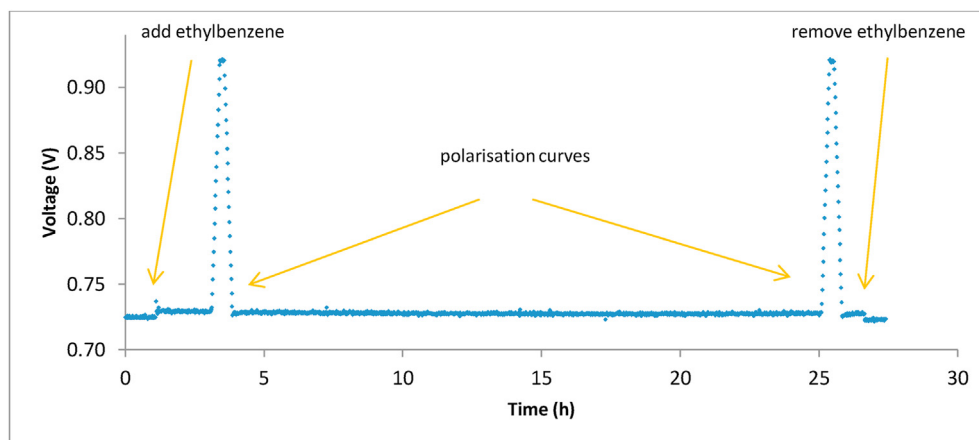


Fig. 4 – Cell operating voltage with 15 g/Nm³ ethylbenzene.

ethylbenzene over 24 h, can be overlapped with Fig. 5, representing the measured cell temperature during the test. The presence of ethylbenzene caused a decrease in the cell temperature of roughly 1 °C. The change in temperature can be ascribed to the endothermicity of the reforming reaction. In the same figure, also the change in temperature due to the recording of the polarisation curves can be observed. The cell ASR, equal to 0.44 Ω·cm², was not affected by the presence of ethylbenzene.

Table 3 presents a comparison between the measured outlet flow rates and the expected flow rates if equilibrium

condition was achieved. Similar to the case of benzene, methane reforming was not complete inside the cell due to the large flowrate used. This also explains the lower OCV measured as compared to the expected value. Also in this case, the presence of the tar resulted in an increase mostly in the hydrogen and carbon monoxide flow rates and to a minor extent in the carbon dioxide and methane flow rates. According to equilibrium calculations results, the presence of ethylbenzene should not cause a visible effect on CO₂ and methane flow rates, with the last one expected to increase from 0.01 NmL/min to 0.02 NmL/min. The increase in the flow

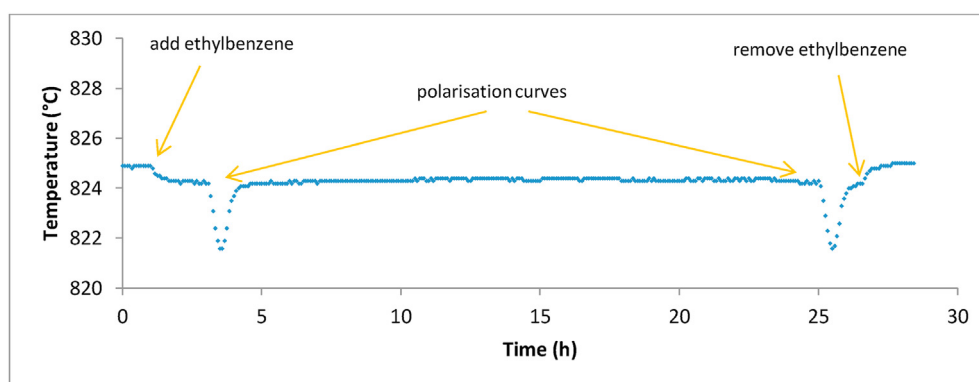


Fig. 5 – Temperature profile during the cell operation with 15 g/Nm³ ethylbenzene.

Table 3 – Measured and equilibrium gas flowrates at the cell outlet (NmL/min), measured and expected cell OCV, and operating voltage with ethylbenzene.

	Ethylbenzene concentration							
	0 g/Nm ³		3.0 g/Nm ³		9.0 g/Nm ³		15.0 g/Nm ³	
	Meas.	Equilib.	Meas.	Equilib.	Meas.	Equilib.	Meas.	Equilib.
H ₂	243	260	243	266	250	276	260	288
CO	88	99	88	102	92	108	98	115
CH ₄	8	0	9	0	10	0	10	0
CO ₂	159	156	162	156	163	156	166	156
OCV measured (V)	0.916		0.916		0.917		0.920	
OCV expected (V)	0.924		0.925		0.928		0.930	
Voltage (V)	0.723		0.723		0.725		0.728	

rates of these compounds can be due to an incomplete conversion of the tar or to the tar occupying Ni active sites and preventing the reforming of CH_4 and the reverse water gas shift reactions in the simulated biosyngas.

Naphthalene

The behaviour of naphthalene was significantly different. The tar caused an immediate decrease in the cell performance with the operating voltage diminishing during the first hours

of exposure and then remaining stable, as visible in Fig. 6. Moreover, the presence of the tar caused a temperature increase of roughly $2\text{ }^\circ\text{C}$, as shown in Fig. 7. Higher concentrations of naphthalene resulted in lower time required to reach a stable voltage and in lower voltages. After the exposure, the voltage returned almost to the initial value in roughly 24 h. Table 4 presents the measured outlet flow rates during the exposure to the different naphthalene concentrations and at the end of the recovery periods. Methane reforming and the reverse water gas shift reactions appeared hindered by the tar,

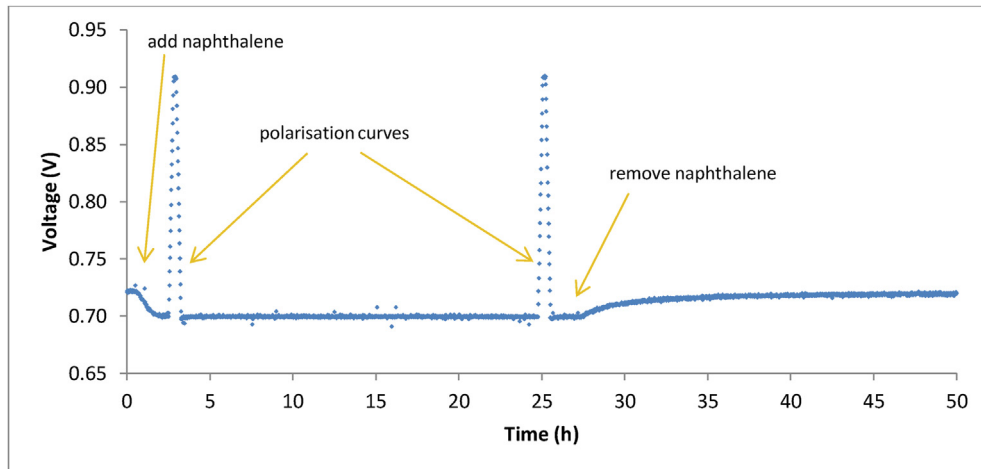


Fig. 6 – Cell operating voltage with 1 g/Nm^3 naphthalene.

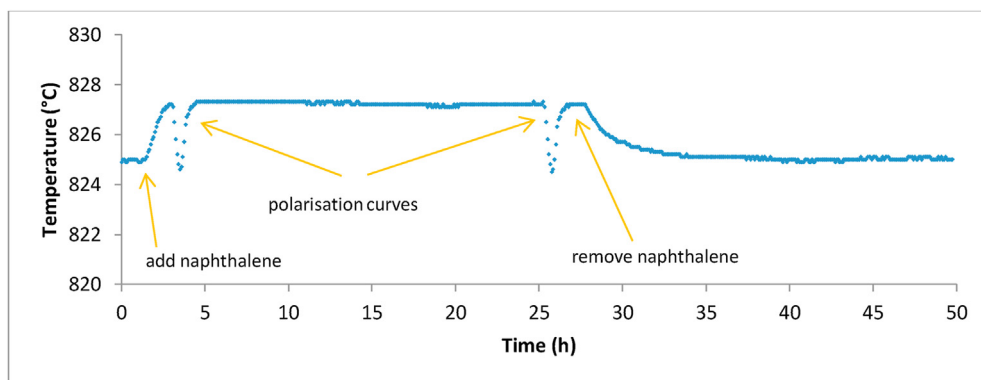


Fig. 7 – Temperature profile during the cell operation with 1 g/Nm^3 naphthalene.

Table 4 – Gas flowrates measured at the cell outlet (NmL/min), measured and equilibrium cell open circuit voltage, and cell operating voltage with naphthalene and after the recovery period.

	Naphthalene concentration							
	Inlet	0 g/Nm ³	0.3 g/Nm ³		0.6 g/Nm ³		1.0 g/Nm ³	
			exposure	recovery	exposure	recovery	exposure	recovery
H ₂	240	243	202	242	197	244	196	244
CO	23	88	65	89	56	91	52	91
CH ₄	36	8	24	8	28	7	29	7
CO ₂	195	159	167	159	172	158	176	159
OCV measured (V)	/	0.916	0.909	0.915	0.908	0.915	0.909	0.915
OCV expected (V)	/	0.924	0.923	0.924	0.923	0.924	0.923	0.924
Voltage (V)	/	0.726	0.705	0.722	0.702	0.722	0.700	0.720

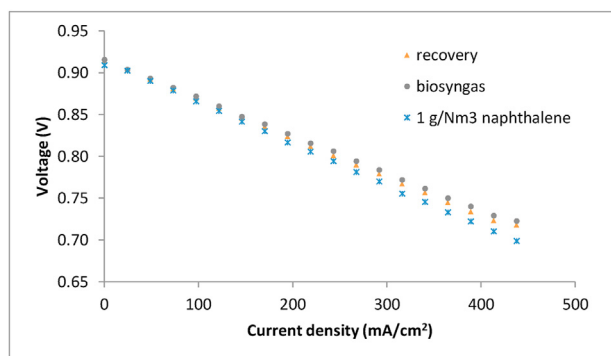


Fig. 8 – Polarisation curves measured before the tests with naphthalene, with 1 g/Nm³ of tar, and at the end of the 24 h recovery period.

and higher concentrations result in more severe effects. The cell temperature increased as a consequence of the tar affecting these endothermic reactions. Naphthalene effect on these reactions is also visible from the measured OCV that decreased when the contaminant was present. The voltage drop caused by the presence of naphthalene is higher when the cell is under current than when the cell is at OCV. This result might indicate that naphthalene is affecting also the cell electrochemical performances and it is confirmed by the increase in the cell ASR that rose from 0.44 to 0.48 $\Omega\cdot\text{cm}^2$. In Table 4, the OCV calculated for naphthalene-containing biosyngas is lower than the OCV calculated for clean biosyngas. This is due to the lower temperature used in the calculation. The recovery period after the end of the test with 1 g/Nm³ naphthalene lasted 24 h, and the cell ASR reached 0.45 $\Omega\cdot\text{cm}^2$, almost equal to the value measured before the exposure to the tar, as visible in Fig. 8.

Phenanthrene

The effect of phenanthrene was more severe than that of naphthalene. The lowest concentration tested of 0.05 g/Nm³ caused the voltage to drop to 0.687 V as opposed to 0.700 V reached with 1 g/Nm³ of naphthalene. Also the cell ASR had a larger increase and reached 0.51 $\Omega\cdot\text{cm}^2$, as visible in Fig. 9,

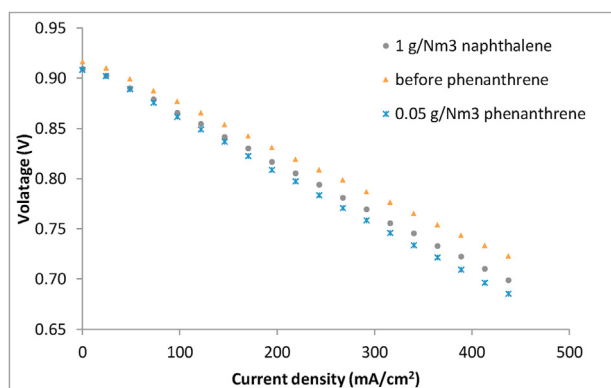


Fig. 9 – Polarisation curves measured before the test with phenanthrene, with 1 g/Nm³ of naphthalene, and with 0.05 g/Nm³ phenanthrene.

Table 5 – Measured and expected cell open circuit voltage, and cell operating voltage with different phenanthrene amounts and at the end of the recovery period.

	Phenanthrene concentration							
	0 g/Nm ³		0.05 g/Nm ³		0.10 g/Nm ³		0.15 g/Nm ³	
	expos.	recov.	expos.	recov.	expos.	recov.	expos.	recov.
OCV measured (V)	0.916	/	0.909	0.914	0.908	0.915	0.907	0.914
OCV expected (V)	0.924	/	0.923	0.924	0.923	0.924	0.923	0.924
Voltage (V)	0.724	0.719	0.687	0.691	0.666	0.693	0.665	0.692

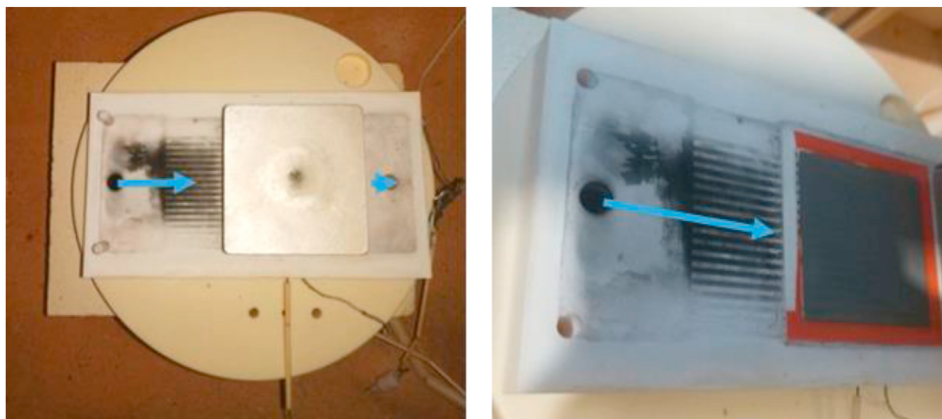


Fig. 10 – Anode compartment of the ceramic housing (left) and cell anode side (right) at the end of the tests with ethylbenzene, naphthalene and phenanthrene. The arrows indicate the gas flow direction.

where the polarisation curves measured with naphthalene, phenanthrene and before adding phenanthrene are presented. However, the effect on the OCV was similar for the two tar compounds and also the gas composition changed accordingly. This might indicate a larger effect of phenanthrene on the electrochemical cell performance. Unfortunately, after the first concentration tested, the cathode oxygen supply had a series of unplanned interruptions while the cell was in operation and this damaged the cell. Therefore, the cell performance after the first concentration were significantly worsened and with a current of 438 mA/cm^2 , a voltage of 0.691 V was measured, as presented in Table 5. Nonetheless, it was decided to continue the test campaign maintaining the same current of 438 mA/cm^2 even if the cell ASR after the accident was higher and equal to $0.51 \Omega \cdot \text{cm}^2$. No significant difference was observed between 0.10 and 0.15 g/Nm^3 phenanthrene, with the cell ASR increasing to $0.56 \Omega \cdot \text{cm}^2$ and the cell operating voltage decreasing to 0.665 V . The poisoning effect of the tar appeared reversible and the cell ASR returned to $0.51 \Omega \cdot \text{cm}^2$ after a recovery of 24 h.

At the end of the tests with the second cell, carbon deposition was observed on the ceramic housing, as visible in Fig. 10. In the picture, the anode compartment is illustrated with (left) and without (right) the anode current collector. However, no carbon deposition was found on the cell anode or on the anode current collector. Due to the test sequence followed, it was not possible to understand which compounds were responsible for the carbon deposited. Nonetheless, in the tests performed with the first cell and in previous tests using the same test rig and naphthalene as tar compound, no carbon deposition was found, thus indicating that carbon deposition might have originated from ethylbenzene or phenanthrene.

Discussion

The results obtained show that lighter tar compounds, such as benzene and ethylbenzene, are reformed in the SOFC and might therefore be considered harmless and, if in significant concentrations, even as additional fuel. This is in agreement with the outcomes of Liu et al. Doyle et al. and Dekker et al.

obtained using toluene as representative tar compound [9,10,29]. Compared to existing knowledge, the present study adds ethylbenzene to the compounds that can be directly reformed inside SOFC, and extends the test duration with benzene to 24 consecutive hours and even to more than 100 h if the 1-h clean biosyngas periods between each concentration are neglected. However, other contaminants present in biosyngas might affect the reforming process, as observed in a previous study [28]. Furthermore, SOFC tolerance to light tar might hold only for Ni-GDC cells, which are expected to have better performances with hydrocarbons containing fuels [30]. In fact, Papurello et al. reported a strong decrease in voltage after 60 h of operation when testing a Ni-YSZ cell with simulated biosyngas containing 24.2 ppmv toluene, and also Liu et al. observed a drop in the operating voltage of a Ni-YSZ cells fed with simulated biosyngas with 6.3 g/Nm^3 toluene [7,11]. Nonetheless, Baldinelli et al. did not observe any degradation when testing Ni-YSZ cells with 10 g/Nm^3 of the same tar compound, although the exposure time was only 1 h [6]. Moreover, a distinction should be made between anode and electrolyte supported cells. The oxygen ions react with the fuel in the anode active layer, while carbon deposition due to the presence of tar is reported to damage the anode support layer by metal dusting. Furthermore, degradation of the Ni/YSZ support due to low tar concentration might not be visible from cell potential and impedance measurements, as observed by Geis et al. with phenol as tar compound [17].

Differently from lighter tar compounds, heavier tar, such as naphthalene and phenanthrene, should be considered as contaminants. The contamination effect seemed to be only a decrease in the cell OCV and an increase in the ASR happening immediately with the addition of the contaminant. The performance remained then stable and an almost complete recovery could be observed. After the initial drop, the voltage remained stable even with concentrations above 100 ppm naphthalene. Differently, Papurello et al. while testing Ni-YSZ anode supported cells at $750 \text{ }^\circ\text{C}$ with 2–10 ppm naphthalene observed a continuous decrease in the cell voltage when the concentration of naphthalene was above 5 ppmv [11]. The higher cell temperature of $830 \text{ }^\circ\text{C}$ and the use of a Ni-GDC anode might explain the difference. In fact, also Dekker

et al. when testing a Ni-GDC cell operating at 850 °C with simulated biosyngas, observed an immediate decrease in performance and then a stable operation for 40 h with 525 ppm naphthalene. They also observed the same behaviour with 22 ppm pyrene during a 100 h test [29]. Compared to the study by Dekker et al. in the present study even lower tar concentrations were investigated. The decrease in OCV observed was caused by naphthalene and phenanthrene hindering the catalytic reactions occurring in the cell, in accordance with literature [12]. This behaviour is expected to be relevant also on the direct internal reforming of the lighter tar compounds, as observed by Hauth et al. who tested the cross-influence of naphthalene and toluene on Ni-YSZ cells operating at 900 °C [31]. Lack of reforming of lighter tar compounds might lead to the formation of heavier tar compounds, as observed by Lorente et al. according to the maturation process proposed by Milne et al. [19,32]. Operating conditions might play a role since higher temperatures promote the reforming and higher current densities might help due to larger amounts of water available for reforming and maybe oxygen reaching the sites where the tar is attached [12,33]. The inhibition of methane reforming reactions might lead to the risk of fuel starvation in some area of the cell close to the outlet and/or if the fuel utilization is not carefully assessed. However, this depends on the concentration of methane in the biosyngas mixture. Interestingly, tests done with real biosyngas containing more than 10 g/Nm³ tar, including 3–5 g/Nm³ and 0.5–1.0 g/Nm³ phenanthrene, did not show a significant drop in voltage of an electrolyte supported Ni-GDC cell over few hours of operation [20]. However, recent studies on Ni-YSZ anode supported cell stack fed with real biosyngas containing around 5 g/Nm³ tar had to be interrupted after only 5 h due to the increased pressure drop caused by carbon accumulation in the anode fuel channels [22,34]. The increase in cell ASR observed in this study suggests a non-negligible effect of larger hydrocarbons also on the electrochemical reactions, and the heavier is the tar, the more severe is the effect. Differently, previous studies by Papurello et al. indicated no remarkable effect of 25 ppmv of naphthalene in a humidified H₂-N₂ mixture on anode supported Ni-YSZ cells, and the polarisation losses increase observed when feeding the cell with simulated biosyngas containing 9.3 ppmv, were mostly due to the low frequency part of the impedance spectrum, probably associated with mass transport phenomena, and only to a minor extent to the high frequency term, related to the electrochemical processes [4]. A similar result was obtained by Aravind et al. when testing electrolyte supported symmetric Ni-GDC anodes in a humidified H₂-N₂ mixture containing up to 110 ppmv naphthalene [4,13]. Also Dekker et al. concluded that the influence of naphthalene (525 and 1050 ppmv) on the cell electrochemical performance is only limited and the tar affects mostly the cell catalytic reactions [29]. However, in this study the observed increase in the cell ASR by 9% and 13% with concentrations as low as 34 and 6 ppmv wet basis of naphthalene and phenanthrene, suggests to bear in mind also the effect of heavy tar on the electrochemical fuel oxidation, and not only on the catalytic reactions. The incomplete recovery observed with naphthalene, despite being minimal, might be an indication of the presence of non-visible carbon deposits, or loss of Ni as observed by

Namioka et al. when testing Ni-ScSZ SOFC fed with humidified hydrogen with 3 g/Nm³ toluene at 800 °C and 500 mA/cm², [35]. The behaviour might have also been caused by the tar incomplete desorption. The results presented in this manuscript can have a significant impact on the design of biomass gasifier SOFC systems. First, it is important to acknowledge that different tar compounds have a different effect on SOFC operation. As a consequence, it is recommended to clearly identify which tar compounds are generated during the gasification process before evaluating the possibility of reforming tar directly in the SOFC. If the tar present in the biosyngas cannot be reformed internally, they can be reformed, at least partially, in an external reformer where the catalyst and the operating conditions allow heavier tar reforming. However, also lighter tar would be reformed, thus losing the advantages of direct internal tar reforming. Since heavier tar compounds hinder methane and lighter tar reforming, a simple external pre-reformer could be used to reform exclusively light tar compounds and methane, thus making their energy content available. This configuration might also help avoid the formation of carbon observed in this and in a previous study where acetic acid was used as tar compound representative of updraft gasifiers [36]. Alternatively, operating the system without any pre-reforming, the presence of heavier tar would result in lower cell voltage and higher ASR, thus in a lower system electrical efficiency. However, this might be compensated by a simpler and cheaper system.

In light of these considerations, a detailed techno-economic analysis focussing on different tar reforming strategies is suggested as part of future work on this topic. Additional work is also necessary to investigate the incomplete performance recovery observed with heavier tar. A detailed post-mortem analysis is advised for verifying the occurring of metal dusting and the presence and form of carbon deposition, which might be the cause of the behaviour observed. Additionally, tests overcoming the 100 h of operation with simulated biosyngas and representative tar compounds and tests with SOFC stacks and tar containing biosyngas should be performed. A more thorough study using electrochemical impedance spectroscopy and distribution of relaxation time is suggested as future work to understand the electrochemical processes occurring during tar exposure and in the recovery period. Post-mortem analysis of the cells via SEM of the anode to determine the effect of the tars on the microstructure and to ensure that there is no permanent degradation. Investigation of the carbon depositions caused by the different tars to compare the amount and type of the depositions caused by the individual tars. Long term tests and tests with full SOFC stacks required.

Conclusions

This work assessed the effects of reforming different tar compounds directly inside SOFC, and the results presented are useful for the design of biomass gasifier solid oxide fuel cell systems. Tar compounds are currently converted in external reformers or directly removed from the raw biosyngas in these systems. However, less complex and more efficient systems can be obtained if tar are reformed directly

inside the SOFC. This study is part of the European project “FlexiFuel-SOFC”, which aim at the development of a highly efficient and fuel flexible biomass gasifier fuel cell systems for the production of heat and power in the micro scale.

Benzene and ethylbenzene can be considered additional fuels for the SOFC since they appeared to be reformed inside the SOFC without causing and performance degradation. The cell voltage increased when the tar compounds were present in the anode mixture and the cell ASR did not vary after 24 h of exposure to concentrations as high as 15 g/Nm³ dry basis. While single ring compounds are not harmful, larger compounds as naphthalene and phenanthrene should be regarded as contaminants and, the higher the number of rings, the worse is the effect. These compounds appeared to hinder the cell catalytic and electrochemical reactions. In fact the cell operating voltage showed a larger decrease than the cell OCV and the ASR increased when the tar were present in the gas mix. Nonetheless, the effect appeared immediately after the introduction of the tar and did not worsen over time. Moreover, the cell performance almost completely recovered after the removal of the tar. The different effect observed depending on the tar compound tested make extremely important the careful evaluation of which compounds are generated in the gasifier. Unfortunately it was not possible to distinguish which tar caused the solid carbon deposited at the ceramic housing inlet.

Direct internal tar reforming can decrease the complexity of solid oxide fuel cell systems coupled with biomass gasifier and can even increase their efficiency. Long term tests, post-mortem analysis and tests with full SOFC stacks are still required to confirm the possibility to operate safely and efficiently SOFC with biosyngas containing some tar compounds. However, the results presented in this paper offer clear and promising insights that can contribute to successfully integrate biomass gasification with SOFC for clean and efficient heat and power production.

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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