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Sulfur poisoning in Ni-anode Solid Oxide Fuel Cells (SOFC):
deactivation in single cells and a stack

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Abstract

The most thermodynamically stable sulfur compound in the anode electrode at SOFC temperature is H$_2$S, which dissociates on a nickel (Ni) surface according to a chemisorption mechanism. In this study, SOFC performance losses have been quantified in the presence of H$_2$S contamination. The deactivation process has been well quantified by correlating it to Ni surface coverage by sulfur through a Temkin-like isotherm adsorption process. The detailed microscopic features of an Ni-based electrode have been taken into account to quantitatively predict atomic sulfur adsorption on the Ni surface. The results show that, in anode-supported cells, the entire available Ni surface is affected by sulfur contamination and not just the three-phase-boundary (TPB) region.

Experiments on both commercial single-cells and on a stack have been described in this work. The H$_2$S concentration was varied from 0.8 to 6.5 ppm(v) in the single-cell experiments, and between 0.01 and 25 ppm(v) in the stack experiment. The time-to-coverage evaluation has been established on the basis of the relationship between the sulfur capacity of the Ni anode and the sulfur flow rate through the fuel feed.

Keywords

Sulfur coverage, coverage time, SOFC, biogas, Nickel anodes, H$_2$S.

Introduction

Solid oxide fuel cells (SOFCs) are electrochemical devices that are able to directly convert the free energy of a chemical reaction into useful electrical and thermal energy [1],[2]. However, several fuel mixtures (natural gas, digester gas, landfill gas, etc.) can contain several trace compounds that can act as nano-contaminants for the SOFC anode electrode, especially as far as Ni-based anodes concerned. Nano-contaminants can segregate at nickel active sites thus increasing the contaminant
coverage at the three-phase-boundary, which results in an increased charge transfer polarization [3].

Among the various (fuel) contaminants that can be found in a fuel, sulfur compounds are the most abundant. Different sulfur compounds can be found in the biogas obtained from the organic fraction of municipal solid waste: from H₂S to heavier thiols (e.g. C₄H₁₀S). This wide variety of trace compounds has been observed in real pilot plants [4,5] and [6].

Several studies have analyzed the influence of H₂S on SOFC anodes as a function of temperature, partial pressure in the anode stream and current density [6–8] and [9]. Sulfur poisoning on the anode electrode can essentially influence the fuel cell performance in two degradation ways, which are generally referred to as to short-term and long-term effects. The fast physisorption and chemisorption of sulfur with a deactivation of the three phase boundary are included among the short-term-effects. Structural modifications and nickel migration phenomena can be considered among the long-term sulfur effects: the main effects on long-term sulfur exposure are related to micro-structural changes, such as Ni-particle coarsening or nickel migration, in addition to the formation of bulk nickel sulfide [3]. The effect of sulfur on the performance is reduced when the operating temperature is increased. As reported by Brightman et al., (2011), a smaller increase in polarization resistance occurs at higher temperatures [9]. The impact on the SOFC performance is a rapid “passivation” or deactivation, followed by a quasi-stable cell voltage profile. As observed by Rasmussen and Hagen (2009) and Hauch et al., (2014) [8], [10], sulfur poisoning can be represented as a two-step process: an initial voltage drop followed by a constant voltage or a voltage degradation/increase depending on the test parameters. The initial cell voltage degradation is very significant in terms of instantaneous voltage reduction, i.e., a sudden short-term effect, which is potentially much more critical than the subsequent long-term degradation. Zha et al., (2007) [11] attributed the initial voltage drop to a rapid adsorption of S on the Ni surface, which in turn blocks the active hydrogen adsorption and oxidation sites. Schubert and Kusnezoff, (2011) described the
first voltage drop through the chemisorption mechanism of sulfur compounds on nickel active sites [12].

The magnitude of the drop is related to the number of blocked sites. It first increases sharply with increasing $H_2S$ concentration until $\sim40$ ppm(v). A relatively quick performance recovery is observed within the first 50 h of the test, thus clearly indicating that the interaction of $H_2S$ with the Ni catalyst is an adsorption mechanism [8].

Short-term effects, even though less dangerous from the detrimental point of view, require attention due to their fast SOFC performance de-activation rate. As previously mentioned, the sulfur poisoning at the short-term exposure level is regulated by the sulfur chemisorption on Nickel. This can be investigated taking in consideration the sulfur capacity of nickel sites, considering microscopic features of the electrode (i.e., the Ni surface area exposed to the gas phase, etc.). The correlation between the short-term performance losses of the SOFC to the surface coverage of sulfur on nickel was first proposed by Alstrup et al., (1981) [13], for catalysts used for steam gasification, and by Hansen (2008), who used Ni contained in an SOFC. Hansen (2008) [14] reported a semi-empirical derived isotherm for the calculation of the sulfur coverage on Ni surfaces at given temperature and relative $H_2S$ pressure conditions with respect to the $H_2$ fuel. A relationship between $H_2S/H_2$ on the fuel cell performance drop has also been found.

Critical conditions for an SOFC generator, fed by biogas, arise when the sulfur concentration begins to be greater than 1 ppm(v). This condition can be representative of a partial failure of the gas cleaning section, where the sulfur breakthrough is above the threshold concentration for an SOFC [15].

So far, no attempts have been made to quantitatively correlate the anode microscopic features of the anode structure to the impact of $H_2S$ in terms of performance drop. The link between the microstructure of an anode and sulfur time-to-coverage has been established in this work. This
coverage time was used to predict, with a known and variable amount of H₂S in the biogas fuel mixture, the time at which the cell voltage reaches an almost equilibrium polarization (i.e., the time at which the initial short-term impact of sulfur poisoning reaches an equilibrium point). The coverage time was experimentally evaluated and compared with theoretical values. The theoretical values were estimated on the basis of experimental tests considering the sulfur capacity of an electrode and the sulfur flow rate of a typical biogas mixture. The coverage time was calculated taking into account both the geometrical and microscopic features of the Ni anode, the operating temperature, and the \( p_{\text{H}2S}/p_{\text{H}2\text{eq}} \) ratio in the anode feed.

**Sulfur chemisorption mechanism on an Ni surface**

Sulfur compounds are known to interact with Ni catalysts and reversibly or irreversibly decrease the cell performance, depending on the temperature, current density, H₂S concentration, fuel mixture and duration of the sulfur exposure [8,9], and [15,16]. The effects of the above mentioned variation on SOFCs have been clearly summarized in the work by Rasmussen and Hagen, (2009) and Hauch et al., (2014) [8], [10].

It is generally accepted that at least two different types of reactions can take place on Ni catalyst particles:

**Chemisorption:**

\[
H_2S(g) \leftrightarrow HS_{(ads)} + H_{(g/ads)} \leftrightarrow S_{(ads)} + H_2(g/ads)
\]  \( \text{(1)} \)

**Sulfidation:**

\[
Ni + H_2S \leftrightarrow NiS + H_2 \]  \( \text{(2)} \)

\[
3Ni + xH_2S \leftrightarrow Ni_xS_x + xH_2 \]  \( \text{(3)} \)
Literature studies [16,17] and [18,19] show how reaction (1) is the dominating one at 700-800 °C for H₂S concentrations below 50 ppm(v). Higher H₂S concentrations affect the fuel cell performance through nickel sulfide formation, and reactions (2-3) become the relevant ones. It is worth mentioning that the situation of a high H₂S concentration in the anode feed is of rather limited practical interest, as a sulfur polishing step should always be foreseen in SOFC plants. In fact, reformer catalysts are generally poisoned by sulfur thus imposing the requirement of a relatively clean fuel even in the case of sulfur tolerant SOFC anodes.

By increasing the operating temperature, the adsorption of H₂S on nickel become more reversible [20]. Bartholomew et al., (1982) reported that the nickel-sulfur bonds of adsorbed sulfur are much stronger than those in bulk nickel sulfides [21]. Owing to this strength between sulfur-metal bonds, sulfur adsorption is not uniform, as it grows as islands with a well-defined structure [20].

It is important to understand how electrochemical behavior influences sulfur adsorption on Ni. According to Vivet et al., (2011) [22], electrochemical poisoning by sulfur is described as:

\[
H_2S(g) + O^{2-} \rightarrow H_2O(g) + S_{(an\,Ni-TPB)} + 2e^-_{(an\,Ni)}
\]  (4)

The previous reaction is different from the chemisorption of S at any other Ni point:

\[
H_2S(g) \rightarrow H_2(g) + S_{(on\,Ni)}
\]  (5)

When operating a fuel cell, it is important to understand whether the S will be more prone to adsorb at the TPB than on the Ni in the anode support. A large amount of the Ni catalyst area is available, especially for the anode-supported cells, but only a relatively small portion is in the TPB zone. If sulfur adsorbs selectively on the TPB, a very rapid degradation would result. Otherwise, Ni in the support could act as a sulfur trap, thus delaying the time necessary to yield equilibrium coverage. In
this study, the entire Ni catalyst area appears to be affected by sulfur coverage, thus determining a sulfur trap. As will be explained in more detail in the next section, an equilibrium condition exists for sulfur adsorption on Ni, which is called equilibrium sulfur coverage. When the H\textsubscript{2}S concentration starts to reach the anode electrode, sulfur deposits on the Ni sites and forms a monolayer. The saturation level of the available Ni surface depends on the equilibrium sulfur coverage. During this saturation process, performance degradation occurs as fewer Ni sites are available for the electrochemical reactions (at constant current operation the voltage has a decreasing trend). The time to reach the saturated condition is known as the ‘time-to-coverage’. In this study, the ‘time-to-coverage’ was calculated assuming that the entire anode electrode volume was affected by sulfur poisoning. The calculated time-to-coverage values correlate well with the time at which degradation stabilizes.

**Correlation of sulfur coverage on nickel surfaces**

More details on the sulfur chemisorption on nickel active sites can be found in [13], [20], [20], [22] and [24]. Sulfur adsorbed on an Ni (100) crystal surface forms a p(2x2) structure in which one nickel atom is bonded to four sulfur atoms, and a 0.25 monolayer coverage is therefore formed, as demonstrated by Alstrup et al., (1981) and Bartholomew et al., (1982)[13,21]. The arrangement changes to a c(2x2) structure, due to the coverage increases to a 0.5 monolayer, where each nickel atom is now bonded to only two sulfur atoms. Below a certain H\textsubscript{2}S/H\textsubscript{2} ratio, the saturation layers become unstable, and the equilibrium coverage is dependent on the H\textsubscript{2}S/H\textsubscript{2} ratio and temperature. This phenomenon can be described in terms of an adsorption isotherm and an isosteric heat of chemisorption. Expression (Eq. 6) can be used to evaluate the H\textsubscript{2}S/H\textsubscript{2} equilibrium ratio: this isotherm contains an enthalpy value that linearly depends on the coverage and an entropy value that is independent of the coverage. It was suggested and proved that the absence of a coverage dependence on the entropy term is due to subsurface chemisorption (Alstrup et al., (1981) [13]).
As in the classical Temkin isotherm, the heat of adsorption varies linearly with coverage in Eq. 6, but it differs from any of the classical theories as the entropy is independent of the coverage. Constant entropy instead resembles gas-solid solution equilibrium.

The equation reported above represents the Temkin-like isotherm proposed by Alstrup et al., (1981) [13], and later used by Hansen (2008) to correlate data on sulfur coverage on nickel surfaces in a H\textsubscript{2} environment [14]. The study by Alstrup et al., (1981) took into account Ni for the steam reforming process while Hansen (2008) took into account Ni for SOFC related applications. In comparison to the steam reforming case, where only chemical reactions occur, electrochemical reactions also take place in fuel cells. The following values have been determined by means of a nonlinear least-square fit on experimental data [13]: \( \Delta H_0^0 = -289 \) kJ mol\(^{-1}\), \( \Delta S_0^0 = -19 \) J mol\(^{-1}\) K\(^{-1}\) and \( a = 0.69 \), thus resulting in Eq. (7).

\[
\frac{p_{H_2S}}{p_{H_2}} = e^{\frac{\Delta H^0(1-a\theta_s)RT-\Delta S^0}{RT}} \tag{6}
\]

\[
\theta_S = 1.45 - 9.53 \cdot 10^{-5}T + 4.17 \cdot 10^{-5}T \ln \left( \frac{p_{H_2S}}{p_{H_2,eq}} \right) \tag{7}
\]

Unlike the work by Hansen (2008), the expression in Eq. (7) has been used in the present study for a biogas or syngas mixture, and not only for a pure hydrogen stream. The \( p_{H_2,eq} \) considers the available electrochemical fuel reported on an equivalent hydrogen basis. In fact, it contributes to electrochemical fuel carbon monoxide and methane in addition to hydrogen. Rostrup-Nielsen et al., (2006) studied how sulfur compounds affect SOFC performance and found that they mainly act on Ni active sites and reduce the internal biogas reforming activity due to blocking of the Ni sites. The reforming activity decreases with S coverage to the 3\textsuperscript{rd} power [25]. As investigated by Hansen (2008), expression (7) was adopted to evaluate not only the dependency of the cell performance
drop on the Ni surface coverage because of sulfur chemisorption, but also the time required for the equilibrium coverage. Details of the calculation of the time-to-coverage are described hereafter.

**Modeling the time-to-coverage of sulfur on an Ni surface**

The main assumptions adopted to define our simplified sulfur adsorption model are reported hereafter:

- each Ni atom is bonded to four sulfur atoms;
- the sulfur atoms form a monolayer on the nickel surface;
- the sulfur adsorption on the nickel surface is governed by a Temkin-like adsorption isotherm;
- the adopted Temkin isotherm equation implies that the entropy of adsorption is independent of the sulfur coverage;
- the coverage time was calculated by observing and then quantifying the period required to accomplish the first deactivation phase during which a fast performance loss was attained;
- the contribution of methane and carbon monoxide was evaluated on the basis of an equivalent hydrogen contribution: that is methane counts four times hydrogen while carbon monoxide only once (this is based on the assumption that both CH\(_4\) and CO will be converted to H\(_2\) fuel in the fuel electrode thus contributing to the overall current production);

The coverage time is given by:

\[
\tau_s = \frac{\Lambda_s}{m_s} \quad (8)
\]

where \(m_s \text{ (g/h)}\) is the sulfur flow rate across the anode electrode.
The H$_2$S in the anode feed of an SOFC will decompose on the Ni surface to H$_2$(g) and atomic sulfur will be adsorbed on the Ni as monolayer Eq. (5).

According to the work proposed by Alstrup et al., (1981) [13], the chemisorption of sulfur on the Ni surface is governed by Temkin-like equilibrium adsorption isotherms, and equilibrium coverage, $\theta_S$, occurs when the temperature, T and the H$_2$S concentration are varied.

The time-to-coverage is defined as the time required for sulfur atoms to fully occupy the available Ni sites, according to the equilibrium coverage condition (i.e., only the fraction $\theta_S$ of the overall Ni surface area is involved in sulfur adsorption).

The coverage of Ni surface atoms by chemisorbed elemental sulfur in the anode of an SOFC is clearly a dynamic process toward an equilibrium state, whose velocity depends on the amount of H$_2$S in the anode feed.

The basic expression used to calculate the time-to-coverage is given below. First, the overall specific sulfur capacity of the anode catalyst, indicated as $C_S$, must be calculated according to the following expression:

$$C_S = \frac{\Gamma_S}{N_A} \cdot MW_S$$  \hspace{1cm} (9)

where $\Gamma_S$ represents the number of sulfur atoms that can stick to a monolayer of the Ni surface area (which is equal to $8 \times 10^{14}$ S atoms per Ni cm$^2$ [16]), $N_A$ is the Avogadro number ($6.022 \times 10^{23}$ atoms mol$^{-1}$) and $W_S$ is the atomic weight of S.

The equilibrium sulfur capacity, $\Lambda_S$ – expressed as the amount in grams of sulfur that can accumulate on the Ni anode surface according to the Temkin-like adsorption isotherms – is given by:

\hspace{1cm}
\[ \Lambda_s = C_S \cdot S_{Ni} \cdot \theta_S \]  

where \( S_{Ni} \) is the overall Ni surface area (cm\(^2\) Ni) that is exposed to the gas phase.

The anode catalytic surface area (\( S_{Ni} \)) is evaluated by taking into account the amount of available Ni (\( W_{Ni} \)) and the nickel specific surface (\( Ni_{BET} \)) as reported in the study by Vivet et al. (2011) and calculated by means of a focused ion beam tomography technique [22]. In order to verify the nickel specific surface that was reported by Vivet et al., (2011), a BET analysis was conducted on a sample of the anode electrode that was used in the present experiment [22]. The \( \text{N}_2 \) adsorption-desorption isotherm of the anode is type II, according to the IUPAC classification, which is typical of a non-porous adsorbent. The measured BET specific surface area is 1.2 m\(^2\)/g. The lack of a hysteresis loop for the isotherm suggests the absence of significant intra-particles porosity with a non-uniform size and/or shape.

\[ S_{Ni} = W_{Ni} \cdot Ni_{BET} \cdot 10^4 \]  

The value of the specific surface area that was calculated from the BET analysis was in agreement with the value obtained by Vivet et al., (2011) [22]. The nickel mass was found to be around 1.488 g for the SOLIDpower cell and 1.288 g for an H.C. Starck cell.

Finally, the sulfur flow rate that reaches the anode through the biogas stream can be calculated on the basis of the sulfur concentration in the anode feed gas, as expressed in Eq. (11):

\[ \dot{m}_s = \dot{V}_S \cdot MW_S = H_2S_{ppmv} \cdot \dot{n}_{fuel,in} \cdot MW_S \]
The time-to-coverage evaluation of sulfur poisoning on Ni-sites is based on the relationship between the sulfur capacity of the nickel anode and the sulfur flow rate through the fuel feed (a simulated biogas mixture, in the present case).

The novelty of this work concerns the study and further clarifications of the fate of H$_2$S in an Ni-SOFC and the quantification of the performance loss observed in several experiments, spanning from a single cell to a stack. The coverage time that is required to reach full sulfur saturation in commercial Ni-anodes has been predicted and quantified well by correlating it to the Ni surface coverage by sulfur through a Temkin-like isotherm adsorption process. The detailed microscopic features of the Ni-based electrode have been taken into account to quantitatively predict the sulfur capacity of the Ni anode. The results show that the region that is affected by sulfur contamination is in fact the whole available Ni surface and not just the three-phase-boundary (TPB) region.

**Material and methods**

Planar SOFCs (47 cm$^2$ surface area) were used for the experimental test session, and were fed with synthetic biogas and syngas obtained by mixing pure gas feeds from CH$_4$ and CO$_2$ cylinders and CH$_4$, CO$_2$, CO and H$_2$ cylinders (SIAD, Italy), respectively. A variable concentration of H$_2$S was added to the fuel stream by diluting and thus mixing the pure CO$_2$ feed with a stream from a cylinder containing 76.8 ppm(v) of H$_2$S in CO$_2$. The H$_2$S concentration was varied from 0.8 ppm(v) to 6.4 – 6.8 ppm(v).

The SOLIDpower cell (ASC700) was tested for almost 300 h with a simulated syngas mixture obtained, for example, from a wood gasifier power plant. The considered syngas mixture was: 20% vol. H$_2$, 18% vol. CO, 9% vol. CO$_2$, 2% vol. CH$_4$, 51% vol. N$_2$ (syngas).
The H.C. Starck cell (ASC4) was tested for almost 300 h with a simulated biogas mixture (CH₄/CO₂ = 1.5), where half of the electrochemical fuel flow was reformed externally with a steam reformer, while the remaining part was reformed directly in the cell through direct internal reforming (DIR). The adopted gas mixture was: 70.6% vol. H₂, 11.8% vol. CO₂, 17.6% vol. CH₄ (DIR50%).

The oxidant flow (air) at the cathode side was 0.5 Nl min⁻¹ during the start-up and shut-down procedures, otherwise it was fixed at 1.2 Nl min⁻¹ for all the performed experiments. The fuel gas mixtures, contained in certified gas bottles (Siad spa, Italy), were fed to the anode and regulated by means of mass flow controllers (Bronkhorst, The Netherlands). The cell was first activated with hydrogen. The fuel mixture was restored to a clean condition after each sulfur poisoning phase in order to study the sulfur coverage versus cell performance drop, as reported in tables 1 and 2. Sulfur poisoning tests were performed with a fuel utilization (FU) of 30%. A biogas mixture of 50% internally reformed biogas and 50% from an external reforming section was sent to the furnace for the H.C. Starck cell (table 2) while, as can be seen in table 1, a syngas was used for the SOLIDpower cell. The electrochemical characterization of the fuel cell was carried out with an electronic load (Kikusui Electronics Corp., Japan) in conjunction with an additional power supply in current-following mode (Delta Elektronica, The Netherlands). The oven temperature was kept constant at 750 °C.

Two planar circular type seal-less anode supported cells, with a diameter of 80 mm and a screen printed cathode of 78 mm, were used for the experiments:

1. the ASC700 (SOLIDpower, Italy) cell consists of a 240-260 μm porous Ni/8YSZ anode support, a 8-10 μm dense electrolyte YSZ and a 50-60 μm porous GDC/LSCF cathode bilayer.

2. the ASC4 (H.C. Starck, Germany) cell consists of a 465-555 μm porous NiO/YSZ anode support with a 5-10 μm NiO/YSZ porous active layer, a 4-6 μm dense electrolyte YSZ and a 2-4 μm YDC blocking layer plus a 30-60 μm porous LSCF cathode layer.
Nickel and platinum double meshes were used for current collection at the anode and cathode electrodes, respectively. Nitrogen adsorption-desorption measurements were performed at 77 K using a Quantachrome Autosorb 1 (Quantachrome corp., USA). The anode specific surface area was determined by means of the Brunauer–Emmet–Teller (BET) method in the 0.04 – 0.1 relative pressure range, see figure 1. The anode was out-gassed at 150 °C for 2 h before the analysis.

Table 1 - Gas mixture adopted for the sulfur adsorption test on the SOLIDpower cell (ASC 700).

<table>
<thead>
<tr>
<th>Syngas reformate clean</th>
<th>H₂S 0.8 ppm(v)</th>
<th>H₂S 0.9 ppm(v)</th>
<th>H₂S 1.3 ppm(v)</th>
<th>H₂S 1.69 ppm(v)</th>
<th>H₂S 2.4 ppm(v)</th>
<th>H₂S 4.04 ppm(v)</th>
<th>H₂S 5.4 ppm(v)</th>
<th>H₂S 6.4 ppm(v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ (Nml/min)</td>
<td>151.5</td>
<td>151.5</td>
<td>151.5</td>
<td>151.5</td>
<td>151.5</td>
<td>151.5</td>
<td>151.5</td>
<td>151.5</td>
</tr>
<tr>
<td>N₂ (Nml/min)</td>
<td>386.4</td>
<td>386.4</td>
<td>386.4</td>
<td>386.4</td>
<td>386.4</td>
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</tr>
<tr>
<td>CH₄ (Nml/min)</td>
<td>15.2</td>
<td>15.2</td>
<td>15.2</td>
<td>15.2</td>
<td>15.2</td>
<td>15.2</td>
<td>15.2</td>
<td>15.2</td>
</tr>
<tr>
<td>CO₂ (Nml/min)</td>
<td>68.2</td>
<td>59.2</td>
<td>58.7</td>
<td>54.4</td>
<td>50.2</td>
<td>42.2</td>
<td>25.2</td>
<td>10.2</td>
</tr>
<tr>
<td>CO (Nml/min) CO₂dirty (Nml/min)</td>
<td>136.4</td>
<td>136.4</td>
<td>136.4</td>
<td>136.4</td>
<td>136.4</td>
<td>136.4</td>
<td>136.4</td>
<td>136.4</td>
</tr>
<tr>
<td>H₂S (ppm(v))</td>
<td>0.8</td>
<td>0.9</td>
<td>1.3</td>
<td>1.7</td>
<td>2.4</td>
<td>4.0</td>
<td>5.4</td>
<td>6.4</td>
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<tr>
<td>H₂O (g/h)</td>
<td>2.9</td>
<td>2.9</td>
<td>2.9</td>
<td>2.9</td>
<td>2.9</td>
<td>2.9</td>
<td>2.9</td>
<td>2.9</td>
</tr>
</tbody>
</table>

Table 2 - Gas mixture adopted for the sulfur adsorption test on H.C. Starck cell (ASC 4), DIR (Direct Internal Reforming).

<table>
<thead>
<tr>
<th>DIR 50% clean</th>
<th>H₂S 0.8 ppm(v)</th>
<th>H₂S 1.6 ppm(v)</th>
<th>H₂S 2.4 ppm(v)</th>
<th>H₂S 4 ppm(v)</th>
<th>H₂S 5.4 ppm(v)</th>
<th>H₂S 6.7 ppm(v)</th>
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<tbody>
<tr>
<td>H₂ (Nml/min)</td>
<td>250</td>
<td>250</td>
<td>250</td>
<td>250</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>N₂ (Nml/min)</td>
<td>62.5</td>
<td>62.5</td>
<td>62.5</td>
<td>62.5</td>
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<tr>
<td>CH₄ (Nml/min)</td>
<td>41.7</td>
<td>36.7</td>
<td>31.7</td>
<td>26.7</td>
<td>16.7</td>
<td>7.7</td>
</tr>
<tr>
<td>CO₂ (Nml/min)</td>
<td>5</td>
<td>10</td>
<td>15</td>
<td>25</td>
<td>34</td>
<td>41.7</td>
</tr>
<tr>
<td>CO₂dirty (Nml/min)</td>
<td>0.8</td>
<td>1.6</td>
<td>2.4</td>
<td>4.0</td>
<td>5.4</td>
<td>6.7</td>
</tr>
<tr>
<td>H₂S (ppm(v))</td>
<td>6.0</td>
<td>6.0</td>
<td>6.0</td>
<td>6.0</td>
<td>6.0</td>
<td>6.0</td>
</tr>
</tbody>
</table>
Results and discussion

The SOLIDpower ASC700 cell was fed with a representative gas mixture representative of a bio-
syngas or a biogas reformate. Likewise, the ASC4 was fed with a representative gas mixture of a
biogas produced during the anaerobic digestion of the organic fraction of municipal solid waste.
Equation (7) was used in order to evaluate the relationship between sulfur coverage and the

Figure 1 – N$_2$ adsorption-desorption isotherm at 77 K for the Ni-based anode. The filled square
symbols denote adsorption whereas the empty circle symbols denote desorption.
performance drop. The cell voltage drop was studied and results are reported in figure 2, that
describes the cell voltage profiles for ASC700 (a) and ASC4 (b) cells, respectively.
Figure 2 clearly shows how an increasing concentration of H$_2$S produces a significant performance drop. It is possible to observe a fast initial degradation followed by a quasi-stable voltage profile for each H$_2$S concentration value added to the mixture. When the H$_2$S concentration is increased, the first decreasing step is accelerated (which is more evident in figures 3 and 4). Zha et al., (2007) and Rostrup-Nielsen, (2006) found that this first voltage drop to a rapid adsorption of sulfur on the Ni surface, which blocked the active sites against hydrogen adsorption and oxidation. This drop is thus a result of a fast chemisorption that blocks the Ni sites which are most active for the electrochemical conversion of H$_2$. This first voltage decrease is predominant with respect to the continuous slow degradation rate.

The voltage of the ASC700 cell during the sulfur poisoning test is shown in figure 3. ASC700 shows a performance degradation of 0.8% when the H$_2$S is 0.8 ppm(v), and 5.2%, when the H$_2$S concentration is 6.4 ppm(v). Similar behavior was observed for the ASC4 cell (not reported here) where a performance drop that ranges from 0.05% to 5.1% is obtained by varying the H$_2$S concentration from 0.8 to 6.7 ppm(v).

As shown in figure 3a, sulfur poisoning of the Ni-anode is a phenomenon that is partially reversible. Once the H$_2$S flow is stopped, a voltage increase that suggests S desorption from Ni sites is observed. The desorption trends are quite similar to the corresponding adsorption trends. As reported by Rasmussen and Hagen, (2009), once the H$_2$S concentration of 2 ppm(v) is removed the cell performance is completely regenerated [8]. However, above 2 ppm(v) of H$_2$S, the performance recovery is not complete. It is likely that some sulfur remains trapped in the three-phase boundary (TPB), thus permanently increasing the anode polarization. This is supported by figures 3b and 3c, where it can be seen that increasing the H$_2$S concentration also leads to increases in the anode
polarization due to concentration polarization, associated with the transport of gaseous fuel through the anode. Electrochemical Impedance Spectroscopy was adopted to investigate the cell losses during the poisoning test with a sulfur compound. These measurements were carried out in galvanostatic mode, with a constant current at FU 30% and 0.32 Acm$^{-2}$. The H$_2$S concentration, as shown in figures 3b and 3c, does not cause any appreciable variation of the ohmic resistance. If the H$_2$S concentration is increased, the high frequency circle of the EIS spectra is affected. Ni is in fact deactivated by sulfur because fewer Ni active sites remain available, as the H$_2$S concentration increases due to an increase in the equilibrium sulfur coverage. The low frequency circle amplitude is also affected and this is possibly due to a slower gas conversion phenomenon. It was found that the low frequency semicircle was mainly affected by the presence of sulfur, a result which is consistent with the results of other studies [11,26]. The frequency range of this arc is consistent with the range that can be expected for diffusion-related processes [27]. An increase in the arc value is also registered when the H$_2$S concentration is raised. This is due to the three phase boundary (TPB) reduction from the nickel active sites blocked by the sulfur compound.
Starting Vcell

- H2S 0.8 ppmv - recovery
- H2S 0.9 ppmv - rec.
- H2S 1.3 ppmv - rec.
- H2S 1.7 ppmv - rec.
- H2S 2.4 ppmv - rec.
- H2S 4 ppmv - rec.
- H2S 5.4 ppmv - rec.
- H2S 6.4 ppmv - rec.
Figure 3a – SOLIDpower cell increasing and decreasing H$_2$S concentration impact on cell performance.

Figure 3b – The impact of H$_2$S concentration on a SOLIDpower single cell as observed through Electrochemical Impedance Spectroscopy (EIS) experiments.
Figure 3c – SOLIDpower cell increasing and decreasing H\(_2\)S concentration impact on cell performance – Electrochemical Impedance Spectroscopy (EIS) frequency diagram.

Figure 3a also shows how, the time at which the cell performance reaches a new stable value becomes shorter as the H\(_2\)S concentration is increase, while the performance drop is enhanced. For instance, after 4.6 h of the test, the cell voltage becomes stable around 740 mV, by adding H\(_2\)S to the fuel syngas 1.7 ppm(v), thus dropping 12 mV for the original voltage of 752 mV. Adding 2.4 ppm(v) of H\(_2\)S, after 2.9 h of the test, the cell voltage stabilizes around 734 mV (in the ASC700 cell). This is clearly due to the greater amount of sulfur that adsorbs on the active catalytic sites. Obviously, with a higher sulfur concentration in the gaseous stream the transient cell stabilization becomes shorter, as the catalytic sites are covered in a shorter time.

The reversible cell performance degradation investigated by feeding the cell with a given sulfur amount and then following this by a regeneration step in a clean gas mixture. However, when the
H$_2$S concentration value is increased, the regeneration phase requires more time to reach the initial voltage condition. As an example, when 0.8 ppm(v) of H$_2$S is removed from the fuel mix, the cell voltage reaches the starting value after 6 h, while when 0.9 ppm(v) of H$_2$S is removed, the starting conditions are reached after more than 10 h. This regeneration delay is a consequence of the higher H$_2$S concentration in the contaminated fuel mixture: more time is required to remove a larger number of sulfur atoms from the nickel sites with the clean fuel mixture. This phenomenon is linked to the number of particles that adsorb on the surface, which depends on adsorption kinetics [28].

The transition from reversible to irreversible cell degradation behavior could be described by the chemisorption of a higher sulfur concentration which is adsorbed on the Ni active surface sites. The transition from reversible to irreversible behavior was experimentally investigated for both ASC4 and ASC700. The experimental threshold concentration was observed in the cell voltage profile during the sulfur poisoning test. ASC4 and ASC700 showed irreversible behavior above 2 ppm(v). In fact, the regeneration step for the ASC700 cell after the 2.4 ppm(v) poisoning does not reach the starting condition of ~750 mV. Likewise, for the ASC4 cell, after the poisoning test with 2.4 ppm(v) the initial voltage condition of ~740 mV is no longer reached, as reported in figures 2 and 3.

Considering the results presented in table 3, it can be seen that the performance drop is slightly higher for same H$_2$S concentration for the ASC4. However, the performance recovery is always better for this cell. The performance drop starts from -1.16% and -0.04% at 0.8 ppm(v) – -5.6% and -5.02% at ≈6.5 ppm(v), respectively for ASC700 and ASC4.

In the voltage recovery phase, after the sulfur poisoning is stopped, the ASC4 cell shows a significant loss in performance. This is presumably related to the sulfur inhibition of the direct internal reforming of methane into CO and H$_2$, as reported by Rostrup-Nielsen, (2006) [25]. Syngas or biogas reformate adopted as fuel with the contemporary presence of sulfur contaminants affects the adsorption/desorption time. As reported by Rostrup-Nielsen, (2006) and Rasmussen and Hagen (2010), methane and carbon monoxide, that has to be reformed into equivalent hydrogen, are
affected to a great extent by the presence of H$_2$S [25], [29]. They observed that the main contribution to cell performance degradation was related to the blockage of methane conversion into available electrochemical fuel.

Table 3- Performance drop at different H$_2$S concentrations for ASC 700 and ASC 4.

<table>
<thead>
<tr>
<th>H$_2$S (ppm(v))</th>
<th>Performance drop (%)</th>
<th>H$_2$S (ppm(v))</th>
<th>Performance drop (%)</th>
</tr>
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<tr>
<td>0</td>
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<td>0</td>
<td>0.00</td>
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<td>0.8</td>
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<td>-0.04</td>
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<td>-1.60</td>
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<td>-4.71</td>
<td>4.0</td>
<td>-3.40</td>
</tr>
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<td>0</td>
<td>-1.24</td>
<td>0</td>
<td>-2.49</td>
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<td>-4.81</td>
<td>5.4</td>
<td>-4.13</td>
</tr>
<tr>
<td>0</td>
<td>-1.46</td>
<td>0</td>
<td>-2.33</td>
</tr>
<tr>
<td>6.4</td>
<td>-5.66</td>
<td>6.7</td>
<td>-5.02</td>
</tr>
<tr>
<td>0</td>
<td>-2.14</td>
<td>0</td>
<td>-4.32</td>
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In order to further extend the findings observed on the single cells, the effect of sulfur was also tested on a short-stack supplied by Topsoe Fuel Cell (Denmark). The short-stack was fed with a simulated gas mixture (CH$_4$ 0.3%, CO$_2$ 10%, CO 19.3%, H$_2$ 50.6% and H$_2$O 19.9%) in which the H$_2$S concentration was increased from 0.01 ppm(v) to 25 ppm(v). This test was carried out at a higher FU (60%) and 0.14 Acm$^{-2}$ (while the single cells were tested at FU 30% and 0.32 Acm$^{-2}$ at the same operating temperature). Figure 4 shows a comparison between the results of the single cells and the short-stack considering the loss in cell potential caused by the addition of H$_2$S. The short-stack already starts to deactivate at lower H$_2$S concentration values than those of single cells: for example, 1.5 ppm(v) causes an average voltage decrease of almost 63 mV per cell, while the degradation for the single cells was only about 20 mV. The higher performance of the stack cells towards sulfur poisoning suggests a reduction in the TPB length.
Figure 4 – The effect of sulfur poisoning on cell performance losses – single cells and stack.

Figure 5 plots the cell performance drop (%) versus sulfur coverage for the ASC4 and ASC700 single cells and for the short-stack. The sulfur coverage was evaluated with Eq. (7), while the performance drop was assessed on the basis of the experiments.

A very good correlation was found between the performance drop ($P$) and the sulfur coverage. The correlation can be expressed by Eq. (13).

$$P = k \cdot (\theta_S - \theta_{\text{min}}) \quad (13)$$

These results are in full agreement with those of Hansen (2008)[14]. The coefficient of determination ranges from 0.9826 and 0.9908 for single cells and 0.9971 for the short-stack. The
sulfur coverage versus performance drop trend between the stack and cells cannot be compared, due to the different operating conditions (FU, i).

The ASC700 cell shows a performance drop of 1.6% for single cells at 80% of sulfur coverage, while this value is around 2% for the ASC4 cell. As can be seen from this figure, the syngas test (ASC 700) is comparable with the partial direct internal reforming of biogas (ASC4). This result is evidenced even though the syngas test showed a better performance in the H$_2$S poisoning test.

A lower sulfur coverage is needed for the stack to reach a given performance drop. For instance, a performance drop of 4% is observed for a sulfur coverage of 69% for the stack, while the same performance drop is reached at about 85% of sulfur coverage for a single cell. Considering the same sulfur coverage, the SOFC stack shows a more remarkable performance drop. This is due to the different operating conditions, FU and current density. A lower fuel quantity with the same amount of sulfur available in the anode compartment causes the performance drop to increase.
As observed by Hansen (2008), the slopes are similar for each curve, while the x-axis intercept ($\theta_{min}$) increases as the current density rises [14]. In fact, it goes from 0.1905 (short-stack) at 0.14 Acm$^{-2}$ to 0.369 and 0.389 (ASC single cells) at 0.32 Acm$^{-2}$. As reported by Brightman et al., (2011) and Cheng et al., (2007), the degree of poisoning is lower for higher current density [9], [26]. A higher current density means a higher flux of O$^2-$ and hence a higher sulfur desorption rate.

$$S_{(ads)} + 2O^{2-} = SO_{2(g)} + 4e^-$$  \hspace{1cm} (14)

Figure 6 clearly shows the strong dependence of between the performance drop on the sulfur coverage for different H$_2$S concentration values. This figure shows that increasing the sulfur coverage produces a resulting potential.
The coverage time was experimentally derived from an analysis of the cell voltage performance in galvanostatic mode at a given H\textsubscript{2}S concentration. An example of two different H\textsubscript{2}S concentration values for ASC700 is given in figure 7. The coverage time is experimentally derived (a) at 1.7 ppm(v) and (b) at 6.4 ppm(v) of H\textsubscript{2}S. The stable voltage profile is achieved after 4.1 h and 1.32 h respectively. It can be assumed that all the catalytic sites are saturated by the sulfur at these conditions. This time was evaluated experimentally considering when the voltage level achieved a stable behavior. The time to coverage was also evaluated using the model described by Eqs. (8-12) considering the temperature, pH\textsubscript{2}S and pH\textsubscript{2}. The coverage time could be essential for an evaluation of the cell voltage performance, especially in order to determine the first degradation time. It is useful to know the coverage time of the cell, considering the situation in which the gas cleaning section starts to elute at dangerous, but still reversible H\textsubscript{2}S concentration values (from 0 to 1.5 ppm(v)). It is possible to foresee the behavior of the coverage time, from the cell materials and structure, the operating temperature, the biogas mixture and the H\textsubscript{2}S concentration, and thus to foresee the impact on cell performance. This impact could be reversible or irreversible depending on the time that elapses before a cleaning bed maintenance.
Cell Voltage (mV) vs Elapsed time (h)

- **t = 4.1 h**
  - H2S 1.689ppmv

- **t = 1.32 h**
  - H2S 6.401ppmv
Figure 7 – Coverage time experimentally derived for ASC 700 (a) at 1.7 ppm(v) and (b) at 6.4 ppm(v) of H$_2$S.

Figure 8 illustrates the time-to-coverage trend of sulfur on anode nickel sites for variations of the H$_2$S concentration. As expected, the trend shows a decrease in the coverage time as the H$_2$S concentration in the gas mixture is increased.

Tables 4 and 5 summarize the experimental and model data for the time-to-coverage evaluation of nickel sites at different H$_2$S concentration for ASC700 and ASC4.

The error between the values calculated with the model and from the experiments falls between 7% and 9% for ASC700, while it is around 4% to 16% for ASC4. The ASC700 data are in better agreement than the ASC4 results: this could be due to the greater amount of information achieved by the manufacturer. The model adopted for ASC4 still needs to be refined with additional information, especially concerning the amount of nickel contained in the cell.

**Table 4 – Experimental and model values of the coverage time (ASC 700) for different H$_2$S concentration.**

<table>
<thead>
<tr>
<th>H$_2$S (ppm(v))</th>
<th>0.8</th>
<th>0.9</th>
<th>1.3</th>
<th>1.7</th>
<th>2.4</th>
<th>4</th>
<th>5.4</th>
<th>6.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>t – experimental (h)</td>
<td>8.60</td>
<td>7.30</td>
<td>5.60</td>
<td>4.10</td>
<td>2.90</td>
<td>1.98</td>
<td>1.43</td>
<td>1.32</td>
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<tr>
<td>t – model (h)</td>
<td>8.22</td>
<td>7.79</td>
<td>5.50</td>
<td>4.26</td>
<td>3.01</td>
<td>1.86</td>
<td>1.40</td>
<td>1.20</td>
</tr>
<tr>
<td>Δ%</td>
<td>4.4</td>
<td>-6.7</td>
<td>1.8</td>
<td>-3.9</td>
<td>-3.7</td>
<td>5.9</td>
<td>1.9</td>
<td>8.9</td>
</tr>
</tbody>
</table>

**Table 5 – Experimental and model values of the coverage time (ASC 4) for different H$_2$S concentration.**

<table>
<thead>
<tr>
<th>H$_2$S (ppm(v))</th>
<th>0.8</th>
<th>0.9</th>
<th>1.3</th>
<th>1.7</th>
<th>2.4</th>
<th>4</th>
<th>5.4</th>
<th>6.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>t – experimental (h)</td>
<td>4.6</td>
<td>7.6</td>
<td>5.9</td>
<td>4.3</td>
<td>3.5</td>
<td>2.7</td>
<td>1.9</td>
<td>1.3</td>
</tr>
<tr>
<td>t – model (h)</td>
<td>4.22</td>
<td>7.79</td>
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<td>1.86</td>
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<tr>
<td>Δ%</td>
<td>4.4</td>
<td>-6.7</td>
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<td>-3.7</td>
<td>5.9</td>
<td>1.9</td>
<td>8.9</td>
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</table>
Figure 8 (a-b), gives the time to coverage versus the H$_2$S concentration, and a hyperbolic trend can be observed. A higher value of H$_2$S than 2 ppm(v) in the gas mixture yields a time to coverage of around 2 h. When more than 2 ppm(v) of H$_2$S is added to the fuel mixture, the coverage time does not decrease significantly. The profile derivative below 2 ppm(v), is very steep and it can be seen that even a small concentration variation has an important effect on the time-to-coverage.

It is possible to deduce, from figure 8, that there is a concentration above which the time-to-coverage does not change significantly. The loss in cell potential is linked directly to the time-to-coverage value. This concentration limit (around 2 ppm(v)) shows that sulfur saturation is achieved in 2 h, and the time to coverage value does not change when more of the H$_2$S concentration is added because the active sites are already saturated.
The graphs show the relationship between the time to coverage (h) and the H₂S concentration (ppm(v)) for two different models: ASC700 and ASC4. The graph for ASC700 demonstrates a rapid decrease in time to coverage as the H₂S concentration increases, indicating a strong correlation. Similarly, the graph for ASC4 also shows a significant decrease in time to coverage with increasing H₂S concentration, although the rate of decrease is slightly less compared to ASC700.
Conclusion

In this work the surface coverage of sulfur on nickel-based anodes has been correlated to real fuel feeding conditions to estimate the coverage time. The latter has been used to predict, with a known amount of H$_2$S, the time at which the cell voltage shows the strongest decrease related to the first detrimental sulfur mechanism. This first mechanism is described by the chemisorption theory of sulfur and it is predominant with respect to the continuous slow degradation rate, as reported in literature [25].

In order to feed an SOFC stack with biogenous fuel, a gas cleaning section is mandatory: before approaching the breakthrough time of volatile sulfur compounds, the sulfur concentration may be higher than 1 – 2 ppm(v) and this could affect the SOFC performance. The cell material properties of a cell, the operating temperature and the partial pressure ratio ($\text{p}_{\text{H}_2\text{S}}/\text{p}_{\text{H}_2\text{eq}}$) are all required to be known to establish the cell voltage performance with reversible H$_2$S concentration impact.

The time-to-coverage for equilibrium sulfur up-take on the Ni anode of an anode-supported type SOFC has been evaluated using the model described by Eqs. (8-12). Knowledge of the sulfur poisoning coverage time on nickel sites is essential to evaluate cell voltage performance, especially in order to determine the first degradation time. The sulfur surface coverage time has been evaluated for two different cells and a SOFC stack fed with a simulated biogas mixture with a variable concentration of H$_2$S.

In the voltage recovery phase, after sulfur poisoning was stopped, the biogas-fed cell with partially direct reforming (ASC4) shows a significant loss in cell performance. This is due to the sulfur inhibition of the direct internal reforming of methane into CO and H$_2$, as shown in different literature studies [25][29]. In fact, compared to the syngas case (ASC700 cell), the reactive mixture
content is higher in the partial direct biogas internal reformate case. This sulfur inhibition deteriorates as the fuel utilization value increases. In conclusion, sulfur poisoning is less detrimental in the case of a syngas mixture, due to the lower reactive gas mixture. In fact, if the methane content is increased, the sulfur action is more pronounced and reforming into H$_2$ and CO is blocked. This situation, as reported by Weber et al., (2013) [30], can also alter the thermal balance of the stack.

The ASC4 cell shows a poorer performance than the ASC700 cell, considering the sulfur coverage relationship with the performance drop. For single cells at 80% of sulfur coverage the ASC700 cell shows a performance drop of 1.6%, while this value is around 2% for the case of the ASC4 cell. The sulfur coverage versus performance drop trend between the stack and cells cannot be compared, due to their different operating conditions (FU, i).

Higher H$_2$S concentrations than 2 ppm(v) show irreversible behavior on cell performance, as can also be seen from the time to coverage profile. In fact, when more than 2 ppm(v) is added, the time to coverage value does not deteriorate in time. At this concentration level, the sulfur saturation is achieved in 2 h, with the active sites being saturated and the TPB irreversibly reduced. This irreversible degradation concentration limit is also the point from which the time to coverage does not change. An experimental model has been implemented with geometry, cell composition and operating working conditions to compare theoretical and experimental time to coverage values. The model has allowed the maximum difference ratio, which ranges from 16% to 9% for the ASC4 and ASC700 cells, respectively, to be obtained. Future refining of the model will have to be carried out considering the gas outlet composition.
Acknowledgments

This work has been partly funded by the European Union under the SOFCOM project (www.sofcom.eu, contract number 278798). In addition this research has also been a part of the national PRIN-2009 project “Analisi sperimentale ed energetico/strategica dell’utilizzo di syngas da carbone e biomassa per l’alimentazione di celle SOFC integrate con processo di separazione della CO₂”.
Nomenclature:

ASC 4 – anode supported cell from H.C. Starck GmbH;

ASC 700 – anode supported cell from SOLIDpower Spa;

$C_s$ – overall specific sulfur capacity of the anode catalyst (g cm$^{-2}$);

$FU$ – fuel utilization (%);

$H_2S_{ppmv}$ – hydrogen sulfide concentration;

$i$ – current density (A cm$^{-2}$);

$k$ – coefficient for the correlation of performance loss;

$m_s$ – mass sulfur flowrate (g s$^{-1}$);

$mS_{Ni}$ – specific sulfur mass adsorbed on nickel surface (g cm$^{-2}$Ni);

$MW_s$ – sulfur molecular weight (g mol$^{-1}$);

$N_A$ – avogadro number (mol$^{-1}$);

$Ni$ – nickel;

$Ni_{BET}$ – specific surface of nickel (m$^2$ g$^{-1}$);

$NiS$ - nickel sulfide;

$n_{\text{Fuel}_{in}}$ – total molar flow rate at the inlet(mol s$^{-1}$);

$n_{H_2_{eq}}$ – equivalent hydrogen flowrate (mol s$^{-1}$);
\( n_{H,S} \) – hydrogen sulfide molar flowrate (mol s\(^{-1}\));

\( P \) – correlation of the performance loss in percent;

\( p_{H_{2},eq} \) – partial pressure H\(_{2}\)eq (atm);

\( p_{H,S} \) – partial pressure H\(_{2}\)S (atm);

\( R \) – gas constant coefficient;

\( s \) – specific sulfur atoms (cm\(^{-2}\)Ni);

\( S_{ads} \) – sulfur adsorption;

\( S_{Ni} \) – anode catalytic (Ni) surface area (cm\(^{2}\));

\( \tau_{S} \) – time to coverage (h);

\( T \) – operating temperature (K);

\( TPB \) – Three Phase Boundary;

\( \varphi_{min} \) – minimum surface coverage (min);

\( \varphi_{S} \) – sulfur coverage (%);

\( \Gamma_{S} \) – sulfur atoms stuck onto a monolayer of Ni surface area (S atoms Ni cm\(^{-2}\));

\( \dot{V}_{S} \) – volumetric sulfur flow rate (mol s\(^{-1}\));

\( W_{Ni} \) – nickel weight (g);

\( \Lambda_{e} \) – equilibrium sulfur capacity (g).
References


[27] P. V. Aravind, J.P. Ouweltjes, J. Schoonman, Diffusion Impedance on Nickel/Gadolinia-
doi:10.1149/1.3231490.

exposed to H2 fuel containing H2S using Raman spectroscopy, J. Power Sources. 156 (2006)


Table captions

Table 1 – Gas mixture adopted for the sulfur adsorption test on the SOLIDpower cell (ASC 700).

Table 2 – Gas mixture adopted for the sulfur adsorption test on H.C. Starck cell (ASC 4), DIR (Direct Internal Reforming).

Table 3 – Performance drop at different H2S concentrations for ASC 700 and ASC 4.

Table 4 – Experimental and model values of the coverage time (ASC 700) for different H2S concentration.

Table 5 – Experimental and model values of the coverage time (ASC 4) for different H2S concentration.
Table 1

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<tr>
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<th>Syngas reformate clean</th>
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<th>H₂S 0.9 ppm(v)</th>
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<th>H₂S 1.69 ppm(v)</th>
<th>H₂S 2.4 ppm(v)</th>
<th>H₂S 4.04 ppm(v)</th>
<th>H₂S 5.4 ppm(v)</th>
<th>H₂S 6.4 ppm(v)</th>
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<td>H₂ (Nml/min)</td>
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<td>26.0</td>
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<tr>
<td>H₂S (ppm(v))</td>
<td>0.8</td>
<td>0.9</td>
<td>1.3</td>
<td>1.7</td>
<td>2.4</td>
<td>4.0</td>
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<tr>
<td>H₂O (g/h)</td>
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<td>2.9</td>
<td>2.9</td>
<td>2.9</td>
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Table 2

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<th>DIR 50% clean</th>
<th>H2S 0.8 ppm(v)</th>
<th>H2S 1.6 ppm(v)</th>
<th>H2S 2.4 ppm(v)</th>
<th>H2S 4 ppm(v)</th>
<th>H2S 5.4 ppm(v)</th>
<th>H2S 6.7 ppm(v)</th>
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<tr>
<td>H2 (Nml/min)</td>
<td>250</td>
<td>250</td>
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<td>N2 (Nml/min)</td>
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<tr>
<td>CH4 (Nml/min)</td>
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<td>62.5</td>
<td>62.5</td>
<td>62.5</td>
<td>62.5</td>
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<tr>
<td>CO2 (Nml/min)</td>
<td>41.7</td>
<td>36.7</td>
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<td>CO2dirty (Nml/min)</td>
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<td>4.0</td>
<td>5.4</td>
<td>6.7</td>
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Table 3

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<th>Performance drop (%)</th>
<th>H₂S (ppm(v))</th>
<th>Performance drop (%)</th>
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<td>H$_2$S (ppm(v))</td>
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<td>1.3</td>
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<td>t – experimental (h)</td>
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<td>7.30</td>
<td>5.60</td>
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<td>t – model (h)</td>
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<td>7.79</td>
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<td>∆%</td>
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<td>t – experimental (h)</td>
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<td>t – model (h)</td>
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<td>$\Delta%$</td>
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Figure captions

**Figure 1** – N2 adsorption-desorption isotherm at 77 K for the Ni-based anode. The filled square symbols denote adsorption whereas the empty circle symbols denote desorption.

**Figure 2** – Cell voltage for the ASC 700 – (a) SOLIDpower and the ASC 4 – (b) H.C. Starck cell fed by a syngas mixture and by a 50% vol. direct internal reforming (DIR) biogas mixture with the addition of a variable concentrations of H2S.

**Figure 3a** – SOLIDpower cell increasing and decreasing H2S concentration impact on cell performance.

**Figure 3b** – The impact of H2S concentration on a SOLIDpower single cell as observed through Electrochemical Impedance Spectroscopy (EIS) experiments.

**Figure 3c** – SOLIDpower cell increasing and decreasing H2S concentration impact on cell performance – Electrochemical Impedance Spectroscopy (EIS) frequency diagram.

**Figure 4** – The effect of sulfur poisoning on cell performance losses – single cells and stack.

**Figure 5** – Performance drop versus sulfur coverage – single cells and stack.

**Figure 6** – Losses in cell potential: versus sulfur coverage and sulfur concentration – single cells and stack.

**Figure 7** – Coverage time experimentally derived for ASC 700 (a) at 1.7 ppm(v) and (b) at 6.4 ppm(v) of H2S.

**Figure 8** – Coverage time evaluated experimentally and from the model for different H2S concentration (a) ASC 700 and (b) ASC 4.
Fig. 1: Adsorbed volume (cm$^3$ g$^{-1}$, STP) vs. relative pressure ($p/p_0$).
Figure 2 – a

Figure 2 – b
Figure 3 - a

![Graph showing cell voltage over time for different concentrations of H2S (0.8 ppmv to 6.4 ppmv).](image-url)
Figure 3 - b
Figure 3 - c

![Graph showing frequency response](image)

- Z Imag (Ω cm²)

Freq. (Hz)

0.0 0.05 0.10 0.15 0.20 0.25

-0.00 0.00 0.05 0.10 0.15 0.20 0.25

0.0 0.1 1.0 10.0 100.0 1,000.0 10,000.0 100,000.0
Figure 4

![Graph showing the relationship between H$_2$S concentration and loss in cell potential. The graph includes data points for TOFC - FU 60% - 0.14 A cm$^{-2}$, ASC 4 - FU 30% - 0.32 A cm$^{-2}$, and ASC 700 - FU 30% - 0.32 A cm$^{-2}$, indicating that loss in cell potential increases with H$_2$S concentration.]
Figure 5

- TOFC - FU 60% - 0.14 Acm-2
- ASC 4 - FU 30% - 0.32 Acm-2
- ASC 700 - FU 30% - 0.32 Acm-2

Performance drop (%) vs. Sulfur coverage ($\Theta_S$)

Equations:
- $y = 0.3357\Theta_S - 0.1905$
  $R^2 = 0.9971$
- $y = 0.5116\Theta_S - 0.3899$
  $R^2 = 0.9826$
- $y = 0.477\Theta_S - 0.3695$
  $R^2 = 0.9908$
Figure 6

\[ \Theta_s = 1.45 - 9.53 \cdot 10^{-5} T + 4.17 \cdot 10^{-5} T \ln \left( \frac{pH_2S}{pH_2} \right) \]
Figure 7 - a

Cell Voltage (mV) vs. Elapsed time (h)

- $t = 4.1 \text{ h}$
- $\text{H}_2\text{S} 1.689 \text{ppmv}$
Figure 7 - b

Cell Voltage (mV) vs. Elapsed time (h)

Cell Voltage

Elapsed time (h)

t = 1,32 h
H2S 6.401 ppmv
Figure 8 - a

- t - exp ASC700
- t - model ASC700
Figure 8 – b

- t - exp ASC4
- t - model ASC4

Time to coverage (h)

$H_2S$ concentration (ppm(v))