

Effects of coal syngas and H₂S on the performance of solid oxide fuel cells: Single-cell tests

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Abstract

The performance of single-cell planar solid oxide fuel cells using coal syngas, with and without hydrogen sulfide (H₂S), was studied. A state-of-the-art gas delivery system, data acquisition system, and test stand were designed and assembled for experimentation. All cells were tested at 850 °C with a constant current load of 14.3 A (current density of 0.20 A cm⁻²). The results from using syngas with no H₂S indicated no degradation after 290 h of operation. After immediately injecting CO (and water) in the H₂-N₂ mixture, there was a slight tendency of improving performance (power) and then the behavior remained steady. On the other hand, results for the test with syngas in the presence of H₂S (200–240 ppm) indicated good performance over 570 h (650 h total operation time) with 10–12.5% degradation. The results suggest these cells can be used for extended periods of time for syngas applications, and in the presence of H₂S the cells show no major degradation.

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1. Introduction

Solid oxide fuel cells (SOFC) have increasingly become more attractive due to their high efficiency and flexibility to handle contaminants, such as CO and CO₂, which are present in fuels for such as syngas derived from coal. However, coal syngas also contains hydrogen sulfide (H₂S) and its presence is one of the major obstacles to implementing a coal syngas SOFC, since an anode catalyst able to handle the presence of H₂S without deterioration over time has not been developed. Therefore, sulfur-tolerant anode materials for SOFCs need to be developed in order to improve the performance of these fuel cells to operate with fuels that contain high sulfur levels, such as coal-derived syngas. Because coal is expected to be the single largest fuel source for electricity generation in the foreseeable future [1,2], a SOFC operating on coal-derived syngas with high sulfur content can play an important role in the commercialization of SOFCs [2].

Several attempts have been made in order to develop an anode material that can withstand the hydrogen sulfide presence in some fuels [2–19], and the materials used and conditions are summarized in Table 1. Pujare et al. [3,4] studied the direct electrochemical oxidation of H₂S for solid oxide fuel cell applications. Their cell consisted of a thiospinel CuFe₂S₄ anode and a La_{0.89}Sr_{0.10}MnO₃ cathode. Ytria-stabilized Zirconia (ZrO₂ with 8 wt% of Y₂O₃) was used as the electrolyte. Their results indicate that the thiospinel CuFe₂S₄ anode seems to have a good stability under the H₂S environment; however, many issues remain unclear, such as the optimum operating conditions, an explanation of the observed results, time performance of the fuel cell was not evaluated, and the cell components were not analyzed and characterized after operation with H₂S. In other similar studies, researchers from the same group investigated the performance of different anode materials, such as WS₂ and the thiospinels CuNi₂S₄, CuCo₂S₄, CuFe₂S₄, NiCo₂S₄, and NiFe₂S₄, for the oxidation of H₂S at 900 °C [5]. The authors concluded that the thiospinels and metal sulfides were suitable electro-catalysts for the oxidation of H₂S, with the following trend in the kinetics (exchange current densities): NiFe₂S₄ > WS₂ > CuCo₂S₄ > CuFe₂S₄ ≈ NiCo₂S₄ > CuNi₂S₄. As in the previous work from the group, the same issues remained unclear [3].

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Table 1
Summary of the different anode materials and conditions tested for H₂S tolerance

Material	Conditions	Reference
La _{0.4} Sr _{0.6} BO ₃ /YSZ (where B = Mn, Ti, Cr)	Direct H ₂ S oxidation	[2]
Thiospinel CuFe ₂ S ₄	Direct H ₂ S oxidation	[3,4]
Tungsten sulfide WS ₂ and thiospinels: CuNi ₂ S ₄ , CuCo ₂ S ₄ , CuFe ₂ S ₄ , NiCo ₂ S ₄ , and NiFe ₂ S ₄	Direct H ₂ S oxidation at 900 °C	[5]
Platinum Pt	Direct H ₂ S oxidation at 650–850 °C	[6]
Platinum Pt	Direct H ₂ S oxidation at 650–750 °C	[7]
Platinum Pt	Direct H ₂ S oxidation, with a Samaria-doped ceria electrolyte	[8]
Tungsten sulfide WS ₂ , cobalt sulfide CoS ₂ , and lithium cobalt oxide LiCoO ₂	H ₂ /H ₂ S fuel	[9]
NiO-YSZ	H ₂ /H ₂ S fuel, using impedance spectroscopy and DC polarization methods	[10]
Platinum Pt	Direct H ₂ S oxidation	[11]
Platinum Pt + Titania TiO ₂	Direct H ₂ S oxidation	[12]
MoS ₂ , FeMoS, NiMoS, and CoMoS	Direct H ₂ S oxidation at 750–850 °C	[13]
MoS ₂ -NiS-Ag	Direct H ₂ S oxidation (variable flows) at 750–850 °C	[14]
NiMoS ₂ -Ag-YSZ	Direct H ₂ S oxidation at 750–850 °C	[15]
Oxides La _{0.9} Sr _{0.1} Ga _{0.8} Cr _{0.2} O ₃ , LaCr _{0.9} Ti _{0.1} O ₃ , Y _{0.9} Ca _{0.1} FeO ₃ , and Sr _{0.1} Co _{0.8} Fe _{0.2} O ₃	Direct H ₂ S oxidation at 900 °C	[16]
La _{0.7} Sr _{0.3} VO ₃ (LSV)	H ₂ /H ₂ S fuel	[17,18]
Ceria CeO ₂ -Cu-YSZ	<i>n</i> -Decane/H ₂ S fuel	[19]

Yentekakis and Vayenas investigated the electrochemical oxidation of H₂S in a cell using a platinum anode and cathode, and ZrO₂ (8 wt% Y₂O₃) electrolyte [6]. H₂S and air were oxidized and reduced at the anode and cathode electrodes, respectively, at ambient pressure and between 650 and 800 °C. They found production of both elemental S and SO₂. The authors do not report the effect of time on the performance of the cell. Of particular note to our study, Kirk and Winnick studied the performance of hydrogen sulfide/air solid oxide fuel cells using different ceria-based electrolytes with Pt as the anode and cathode material [7]. Their experimental tests were performed at intermediate temperatures, 650–750 °C. The authors did not reach a conclusion about the compounds and reactions that take place during the oxidation of H₂S. In addition, the operating times of the cell were very short (4 h). Researchers from the same group performed a more extensive study on the utilization of hydrogen sulfide in a SOFC using a ceria-based electrolyte [8]. The cell studied used platinum as the anode and cathode material, and a Samaria-doped ceria electrolyte ([CeO₂]_{0.8}[SmO_{1.5}]). They demonstrated that at high utilization of H₂S a total oxidation of H₂S to SO₂ is the preferred pathway for the reaction. Their results are in agreement with the results reported by Yentekakis and Vayenas [6]. The operating times of the fuel cell were not discussed by the authors. Yates and Winnick examined different sulfide anode materials for hydrogen SOFCs [9]. The anode materials evaluated included tungsten sulfide (WS₂), cobalt sulfide (CoS₂), and lithium cobalt oxide (LiCoO₂). The authors found that the CoS₂ electrode was unstable even at short times (1 h). Better electrochemical performance over time was achieved when using LiCoO₂ and WS₂ anodes. However, the maximum times were 36 h of operation. From the results obtained, it is still unclear what reactions take place at the anode. Matsuzaki and Yasuda investigated the effect of H₂S on the electrochemical performance of a hydrogen/H₂S solid oxide fuel cell using impedance spectroscopy and DC polarization methods [10]. Their cell con-

sisted of a NiO-YSZ anode, YSZ electrolyte, and a platinum paste cathode. The authors concluded that the electrochemical performance of the fuel cell decreases with time due to the presence of H₂S. Further, they concluded that the low concentrations of H₂S deteriorated the performance of the anode at 1273 K, the effect of H₂S on the performance of the fuel cell is worse at lower temperatures, and the degree of sulfur poisoning in the fuel cell depends on the total content of sulfur in the fuel and not on the partial pressure of S₂ [10].

Liu et al. studied the electrochemical performance of a hydrogen sulfide SOFC with a platinum anode and cathode and YSZ electrolyte ([ZrO₂]_{0.92}[Y₂O₃]_{0.08}) [11]. The authors concluded that Pt is not a suitable anode material for an H₂S stream due to the formation of PtS contaminants on the anode surface, increasing the resistance of the SOFC and ultimately leading to the detachment of the Pt anode from the YSZ electrolyte. Researchers from the same group tried different strategies to overcome this problem using traditional trial-and-error experimental methods [12–14]. An improvement was observed when a thin layer of Titania was placed between the platinum anode electrode and the YSZ electrolyte [12]. Liu et al. [13] evaluated the electrochemical performance of four different sulfide catalysts as anode electrodes for H₂S/air solid oxide fuel cells in the range 750–850 °C. The materials tested were: MoS₂, FeMoS, NiMoS, and CoMoS. MoS₂ has a better activity than Pt for oxidation of H₂S to sulfur; however, there was a loss of MoS₂ with time because the material is volatile above 450 °C. Authors from the same group evaluated the effect of gas flow rates on the anode and cathode streams on the performance of an H₂S/air SOFC in the range 750–850 °C [14]. The anode and cathode materials were MoS₂-NiS-Ag and Pt, respectively. YSZ was used as the electrolyte. The authors found that the open circuit voltage of the cell is independent of air flow rate but increased with increasing H₂S flow rate. Finally, Wei et al. [15] studied a new anode composite made of NiMoS (90%), Ag (5%), and YSZ

(5%) admixed together for an optimum composition and they applied three-phase boundary theory. They found an improvement in the performance of the anode over previous results but did not specify the time of operation. Wang et al. [16] studied the conductivity and chemical stability of different oxides, sulfides, and lithiated sulfides exposed to H_2S at $900^\circ C$. The oxide materials evaluated were $La_{0.9}Sr_{0.1}Ga_{0.8}Cr_{0.2}O_3$, $LaCr_{0.9}Ti_{0.1}O_3$, $Y_{0.9}Ca_{0.1}FeO_3$, and $Sr_{0.1}Co_{0.8}Fe_{0.2}O_3$. Their results suggest that the $Y_{0.9}Ca_{0.1}FeO_3$ group (oxides, sulfides, and lithiated sulfides) are promising materials to be used as electrodes for SOFCs handling fuels containing H_2S . However, a more complete study as well as long-term stability tests of electrodes needs to be made. In a different study, Kim et al. [19] showed that a SOFC with an anode made of 10% ceria, 20% copper, and YSZ exhibited a good performance when *n*-decane with two levels of sulfur content was introduced to the cell for as long as 18 and 100 h. Even though they showed that the anode could be regenerated after sulfur exposure by passing steam, they did not have the same feed composition for both tests, where they first introduced 50% *n*-decane with 5000 ppm of sulfur (given by thiophene) in N_2 for 18 h, and the other test had only 5% *n*-decane with 100 ppm sulfur in N_2 for up to 100 h, which helped to obtain a more stable performance which they found after those 100 h tests [19].

More recently, Aguilar et al. at Georgia Tech studied the SOFC operation with H_2S to investigate the performance of a new anode material $La_{0.7}Sr_{0.3}VO_3$ (LSV) [17,18]. They operated at different temperatures and $H_2:H_2S$ ratios and found that the new material had good performance but over very short periods of time (up to 48 h) and that it had preferential oxidation towards H_2S . No thorough before-and-after analysis of the material was presented. Mukundan et al. [2] also studied H_2S performance for a similar material $La_{0.4}Sr_{0.6}BO_3/YSZ$ (where B = Mn, Ti, Cr). They found that for the material $La_{0.4}Sr_{0.6}TiO_3$ (LST)/YSZ there was no degradation (up to only 8–24 h) in the presence of $H_2:H_2S$, and no characterization studies before and after testing were presented. On the other hand, Weber et al. [20] studied the operation of a single cell with conventional Ni-YSZ-cermet anodes running with mixtures of H_2/CO and CH_4/H_2O , centering their investigation on the direct methane oxidation at the anode and the influence of the steam to carbon ratio effect on the cell performance. They found that the CO content decreases the performance, while they could operate the cell for up to 1000 h on pure methane without serious degradation [20].

In summary, the literature review indicates that many issues still remain unclear regarding the screening of some materials for the oxidation of H_2S and for the coal-derived syngas operation of SOFCs. Specifically, the screening of the sulfur-tolerant materials has been performed at different conditions and under different comparison criteria (e.g., chemical stability, electrochemical stability, operating times, etc.). Also, the stability of the materials during time has not been studied in depth or has not been performed for long periods of time when using H_2S and/or syngas. Finally, and what we feel to be the most significant, *the effect of H_2S when present in a H_2 and CO stream (as the case of coal syngas) has not been defined.*

In this work, we report the outstanding long-term performance of single-cell experiments of planar solid oxide fuel cells

operating with coal-derived syngas (H_2 , CO, and H_2O) with and without hydrogen sulfide (H_2S).

2. Experimental

2.1. Cells description

The electrolyte-supported planar solid oxide fuel cells used in these studies were provided by SOFCo, and complete details about their description have been previously described in the literature [21]. Briefly, the cells are made of a three-layered anode which consists of a layer of nickel and gadolinium doped ceria (Ni-GDC), a layer of GDC and a layer of Ni for a total anode thickness of $40\ \mu m$; a tape cast 3 mol% yttria doped stabilized zirconia (3YSZ) $120\ \mu m$ thick electrolyte; and a cathode with a total thickness of $50\ \mu m$ consisting of two layers: one of $La_{0.75}Sr_{0.2}MnO_3$ (LSM) and 3YSZ and on top of that a layer of LSM only [21].

2.2. Single-cell test setup

The experimental setup for the single-cell tests is illustrated in Figs. 1–4. The gas delivery system (GDS) and data acquisition system (DAS) were designed at Ohio University (Figs. 1 and 2), and coupled to the test stand provided by SOFCo (Fig. 4). Note that the active area for the cell is $68.1\ cm^2$ (Fig. 3). For all the experiments, the temperature was kept constant at $850^\circ C$. The fuel stream consisted of a combination of H_2 , N_2 , CO, H_2O , and H_2S in order to simulate coal-derived syngas fuels. The total fuel flow (injected at the bottom) was kept at 0.430 slpm while the air flow (top) was 2.5 slpm (Figs. 3 and 4). Water was added to the mixture by passing the fuel through a bubbler full of water located at the test stand, in which the temperature was varied from room temperature up to $70^\circ C$ to increase H_2O content. The H_2S injection (Fig. 1) was completed using a gas cylinder with a CO– H_2S mixture for a final composition of 200–240 ppm of H_2S . Thus, this being our first study we focus on differentiating the CO–water and CO–water– H_2S effects on the cells, which allows the analysis of the coal-derived syngas effects on SOFCs.

2.3. Experimental testing

At first, air and fuel (a mixture of 48.8% H_2 –48.8% N_2 and 2.4% H_2O) were injected to the cell while the temperature was increased (ramped) for 24 h until the operating value of $850^\circ C$ was reached at which point the operating current load (14.3 A, or a current density $0.20\ A\ cm^{-2}$ for the $68.1\ cm^2$ cells) was initiated and was kept constant in order to monitor the cell performance by looking at the voltage (or power) produced and at the area-specific resistance (ASR) [22,23] variation.

After achieving stable conditions, CO was added to the mixture and the bubbler temperature was raised in order to increase the steam to carbon ratio (S/C) [20] and to minimize the carbon deposition in the heatup zone. Thus, a typical composition of a syngas mixture in a cell was: 24.8% H_2 –35.7% N_2 –40% CO (dry basis); or 20% H_2 –33% CO–29% N_2 –18% H_2O (wet basis; S/C = 0.55–0.60). The electrochemical experiments were carried

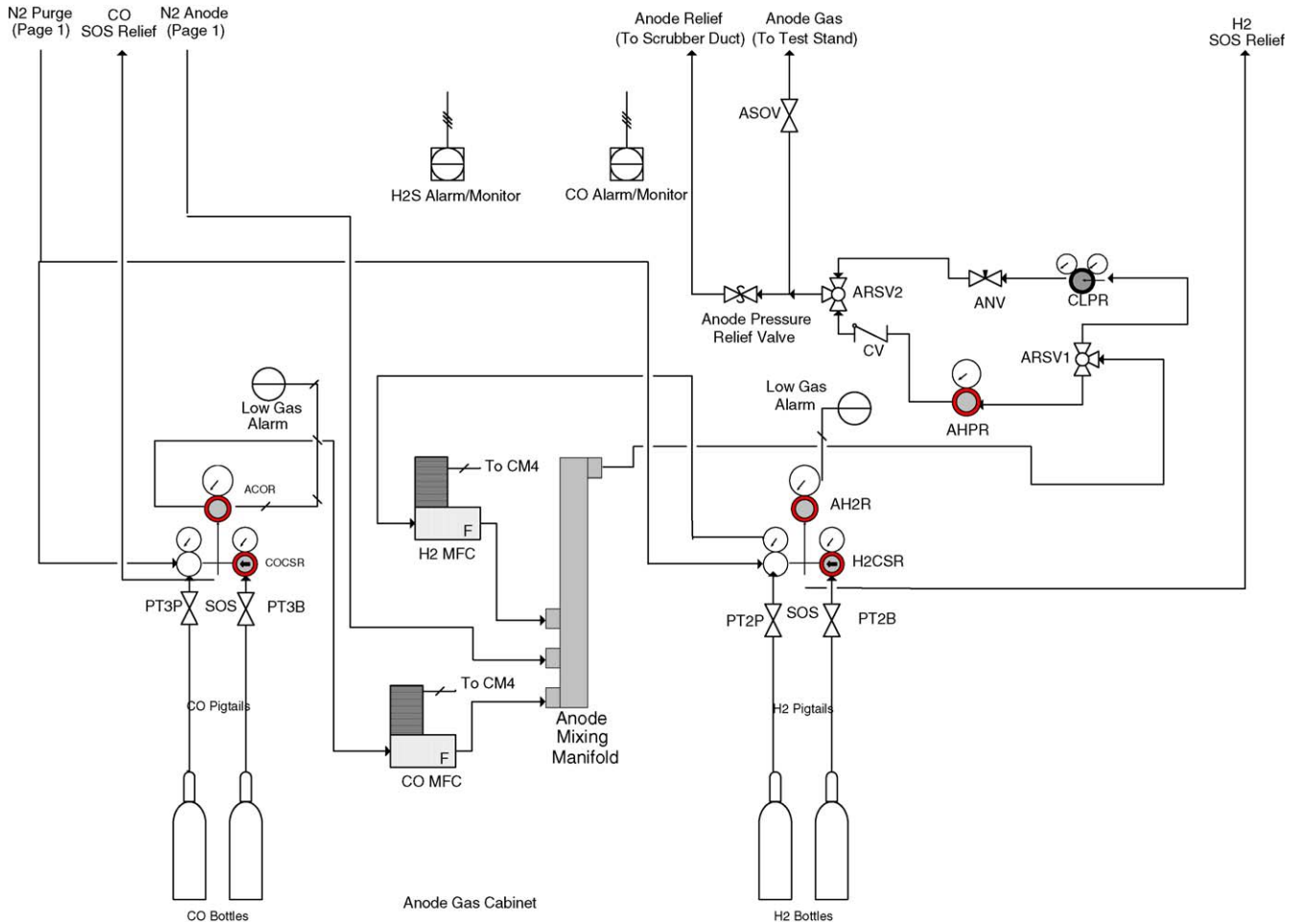


Fig. 1. Gas delivery system (GDS) PID, anode side.

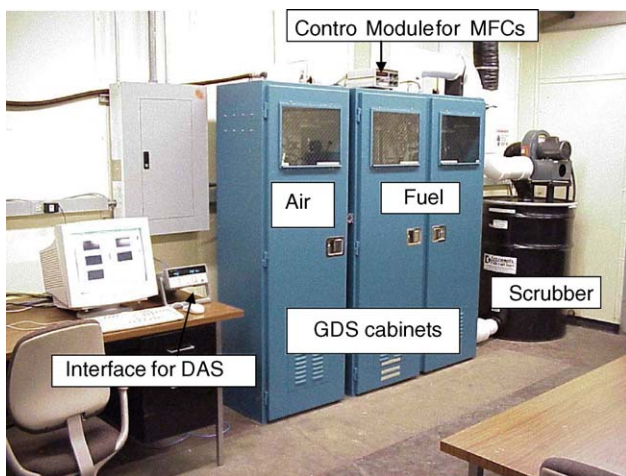


Fig. 2. Picture of the GDS with scrubber and DAS with interface and PC inside the room (SOFCo). The GDS cabinets (with venting system plus activated-coal filled scrubber in case of H_2S escape events) contain the mass flow controllers for the different gases and sensors for H_2S and CO, as well as the gas cylinders. The control module for the different MFCs is located above GDS cabinets. The DAS system (which uses National Instrument's LabView software) is formed by the interface and PC, and records the data from the GDS and the tests stand's (voltage temperature).

out using an Agilent N33006A DC electronic load (Fig. 4), while all the data were acquired using National Instrument's software (LabView) and hardware (Fig. 2). All the experiments were carried out at the SOFCo-Alliance facilities. SEM and EDXS material analysis were done by using a JOEL-2300 scanning electron microscope with a Link Systems energy dispersive X-ray spectroscopy (provided by the Physics Department at Ohio University [OU]), and a Cambridge S240 SEM with better resolution (OU Biosciences Department). Also, for the material analysis X-ray photoelectron spectroscopy (XPS) tests were done by using an AXIS His 165 and Ultra System (OU Physics Department).

3. Results and discussion

3.1. Test with syngas mixture $CO-H_2-N_2-H_2O$

Single-cell tests were operated on a syngas mixture as described in Section 2. The power traces of four representative tests are shown in Fig. 5. In the first three tests (Tests #3–5) the power is fairly constant for the 300 h shown.

The voltage–current scan curve and power degradation (after 90 h) for Test #5 are illustrated in Fig. 6. For the operating cur-

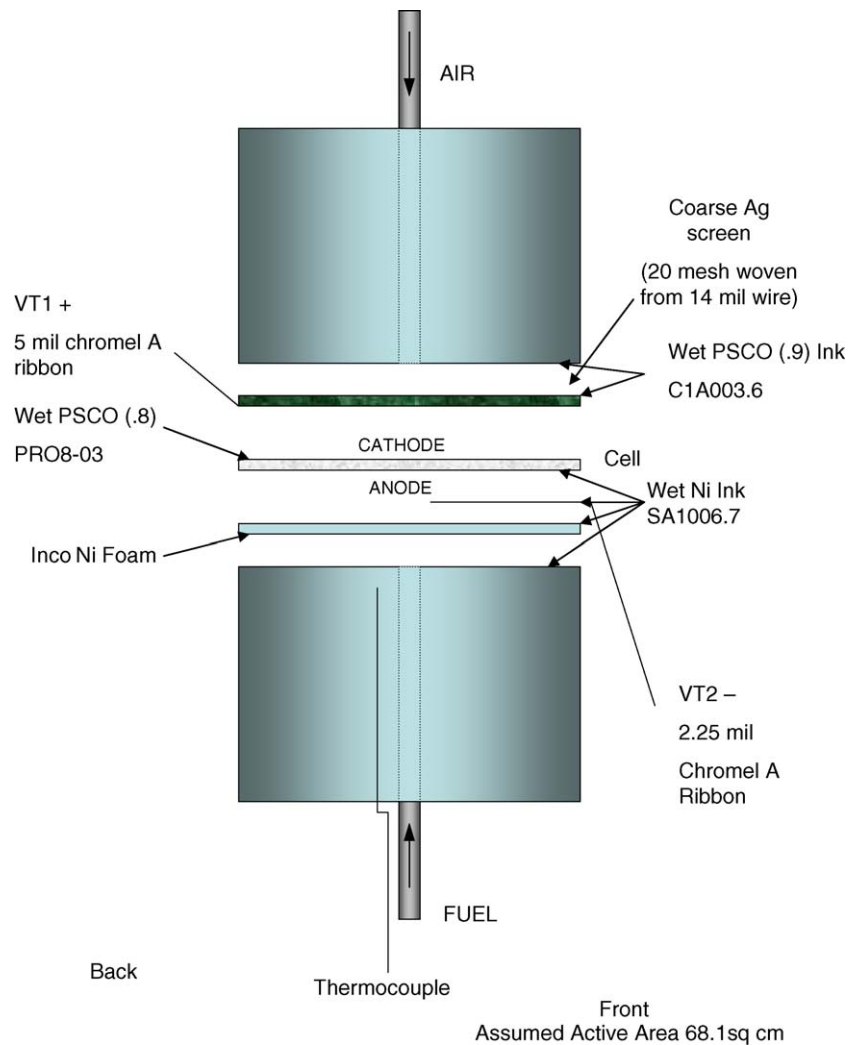


Fig. 3. Single-cell test details. The approximate active area was 68.1 cm^2 (10.6 in.^2).

rent ($\approx 0.20 \text{ A cm}^{-2}$) the cell showed a potential of 0.76 V (less than the initial at OCV, 0.96 V) after 90 h (with 20 h of CO introduced in the mixture) and a power of 10.1 W (slightly less than the initial, 11.0 W). The maximum power density obtained at 850°C at that time (90 h) was 15.3 W with a current density of 0.46 A cm^{-2} and a potential of 0.50 V . This indicates that the performance of the cell was improved to some extent over this period of time.

Fig. 7 shows the potential variation in time for this cell (Test #5). The cell starts with a potential of 0.76 V and then decreases. After 20 h , the cell potential sparingly increases to 0.77 V . After CO is introduced (together with H_2O), at 70 h , the potential continues to slowly increase and then decreases until a constant voltage was reached for the rest of the 290 h of operation time. This behavior suggests a tendency of the CO to react with the water to form H_2 and CO_2 (water-gas shift reaction), which in turn improves the yield of H_2 . Moreover, the performance for the first 70 h ($\text{H}_2\text{-N}_2$ mixture with $\approx 2\text{--}3\%$ water) is comparable to that of previous works done with SOFCo's materials [22,23], and to other works [24,25]. Jiang et al. [24] studied the cell behavior for the conventional Ni-YSZ anode material prepared by ion

impregnation and operating with H_2 and $3\% \text{ H}_2\text{O}$, and Ishihara et al. [25] used Ni-Ce_{0.8}Gd_{0.2}O₂ (GDC) anode material (10% NiO mixed with GDC) for cells operating on H_2 humidified with 3% water.

Fig. 8 shows the history (for Test #5) of the area-specific resistance [22,23], which value comes from the slope of V versus I of the V/I scan. The cell starts with an ASR of $0.96 \Omega \text{ cm}^2$ and after 290 h increases to $1.03 \Omega \text{ cm}^2$, which indicates only a 7% increase (degradation). At first, the ASR increases (see Fig. 8) until 70 h when CO is introduced, and at this point the ASR begins to slowly decrease (no degradation, but enhancing voltage–power production), which is in agreement with the voltage behavior observed after CO was introduced.

This test illustrates the excellent long-term performance of the cell with syngas conditions. Nevertheless, longer tests ($>500 \text{ h}$) need to be performed in order to ensure more realistic long-term performance. In addition, the S/C ratio of 0.55 was sufficient to prevent coking at the anode (which tends to reduce the available sites for fuel oxidation at the surface of the anode), thus enhancing the performance of the cell during the long operation time. Therefore, the Ni-GDC anode material of the cells

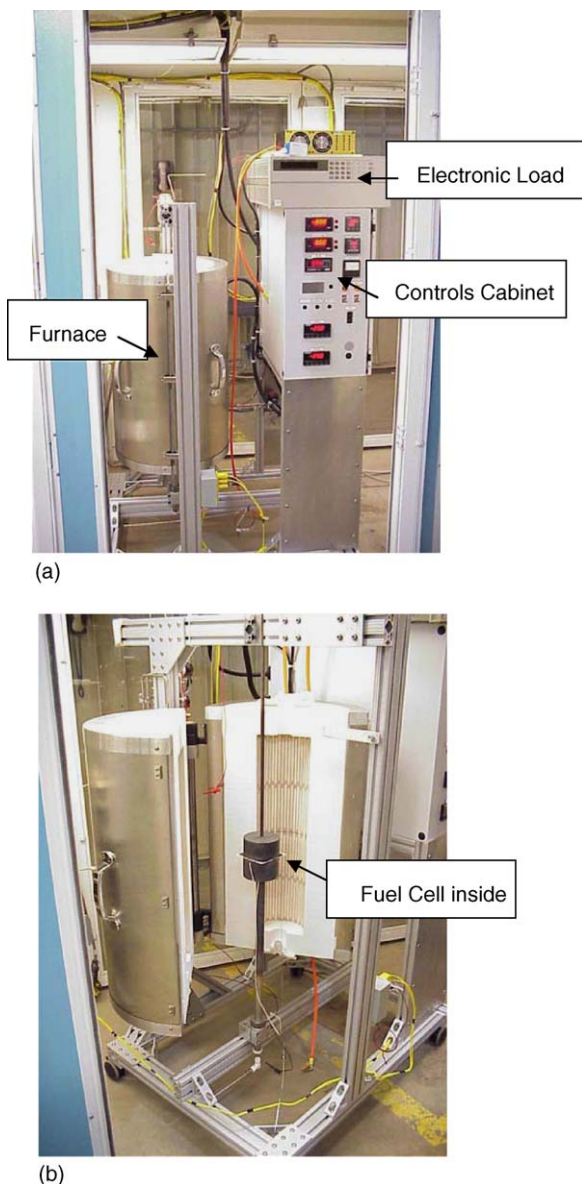


Fig. 4. Test stand pictures. (a) The basic components of the test stand are a furnace, an electronic load (simple potentiostat) and the controls cabinet. (b) The position of the single-cell assembly is centered vertically within the clam shell furnace to provide equal preheat energy to the anode and cathode feed gases.

shows excellent results when the cells are operated under syngas conditions, in agreement with the work by Chen et al. [26] in which they found that the addition of ceria to the Ni-YSZ anode material enhanced the performance of the cell operated only for few hours with methane with no more than 10% H₂O content. In contrast, Weber et al. [20] found that CO decreases the performance of the cell, and even though the anode material was the conventional Ni-YSZ, they only capable of operating for short periods of time with dry methane.

3.2. Test with syngas mixture and H₂S (200–240 ppm)

In a fourth test (Test #6, Fig. 5), H₂S was introduced at a concentration of 200–240 ppm after 50 h which immediately caused

the fuel cell power to drop 6%. The power then slowly declined before stabilizing at a 10–12.5% total degradation after 500 h with H₂S which held constant up to 570–600 h when operation was discontinued.

Fig. 9 displays the final *V/I* scan for the H₂S Test #6 (after 650 h of operation). At the end of the trial for the operating current (0.20 A cm⁻²) the cell showed a voltage of 0.64 V (less than the initial 0.73 V) and a power of 8.9 W (less than the initial, 10.4 W). The maximum power density obtained after 650 h was 9.1 W with a current density of 0.18 A cm⁻² and a voltage 0.67 V, thus the cell performance had decreased over time. These values are similar to those of the final *V/I* scan, suggesting that the degradation was tending to stabilize and perhaps more time needed to be allowed in order to check if the cell could stabilize. The *V/I* scan (comparing Figs. 6 and 9) confirms that the H₂S causes the voltage to drop.

Fig. 10 shows the potential variation for this Test #6 during the 650 h of operation. Here, the potential starts, as it was before, increasing (enhancing performance) immediately after CO is introduced (0 h) from 0.73 V to up to 0.74 V until 72 h. At that time, 200–240 ppm of H₂S was introduced in the mixture and the potential began to decrease until a final value of 0.64 V was reached after 650 h, for a potential (power-produced)-based degradation [21] of 10–12.5%, which shows as it was previously described that the cell performed reasonably when H₂S is present in the syngas mixture. Nevertheless, as it was mentioned before having the H₂S mixed with CO limits the analysis since the performance involves combined effects of CO–water–H₂S, but the results showed that when the cells are operated with combined CO–water–H₂S in the syngas mixture their performance is acceptable.

Also, it may be noticed that the cell was tending to stabilize toward the termination of the trial (after more than 500 h with H₂S) and perhaps more time was needed to corroborate that tendency. This behavior suggests that a surface reaction was taking place, involving S (from the H₂S) and some of the components of the anode material (Ni, Ce, and Gd), thus the anode material was tending to compensate the presence of H₂S. If this was taking place the cell tends to stabilize once the possible surface reaction slows or stops (no more surfaces sites are active for that reaction to take place). Also, this suggests that the addition of GDC to the Ni-YSZ anode material compensates for the loss of active sites, which possibly implies that only Ni sites were affected (reacting with S to form NiS) according to previous works [2,10,15,17,23].

Fig. 11 shows the ASR history H₂S Test #6. Also here, the ASR begins to slightly decrease after CO is injected (0 h) and then after H₂S is injected (72 h) starts increasing for an ASR-based degradation rate of 24% after injection of H₂S. This test shows that the cell behaves reasonably after injecting H₂S for 570 h. Comparing to the former test, the degradation (ASR) is higher (expected) even though there is a slight tendency of stabilization (ASR starts slightly to decrease) after 500 h, but more time would have been necessary to draw stronger conclusions.

The recovery of the cell was also examined in an additional test (Test #8, Fig. 12) by returning to a clean gas stream after the cell was exposed to H₂S for 24 h. The cell responded similarly

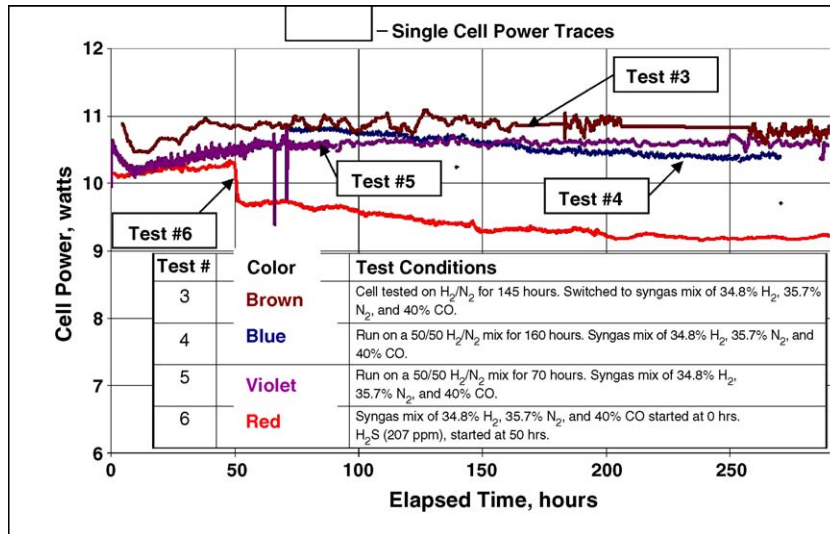


Fig. 5. Single-cell power traces. For Test #6 (color red, includes H₂S) the power drops immediately after H₂S injection (at 50 h of operation), and its decay is more pronounced from 50 to 100 h than for all the other tests (syngas only) which indicates an appreciable H₂S effect on the cell performance (see Section 3). (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)

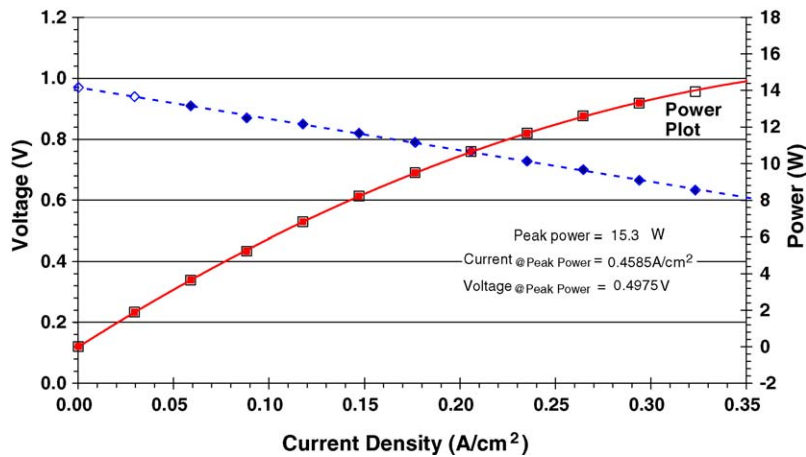


Fig. 6. V/I scan after 90 h for the cell running with syngas mixture (no H₂S), Test #5.

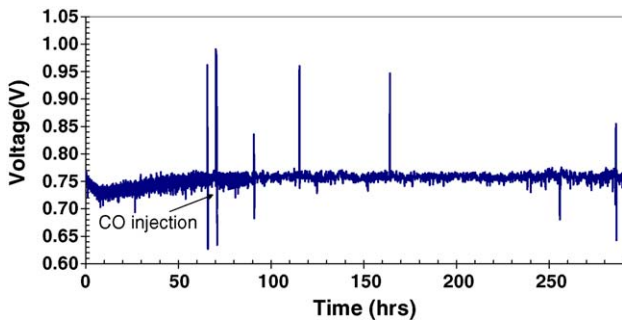


Fig. 7. Voltage variation of Test #5 running with syngas mixture with no H₂S. The cell performs exceptionally well after 290 h when the voltage produced (0.76 V) is slightly less than the initial OCV (0.77 V). Total running time was 290 h with no degradation.

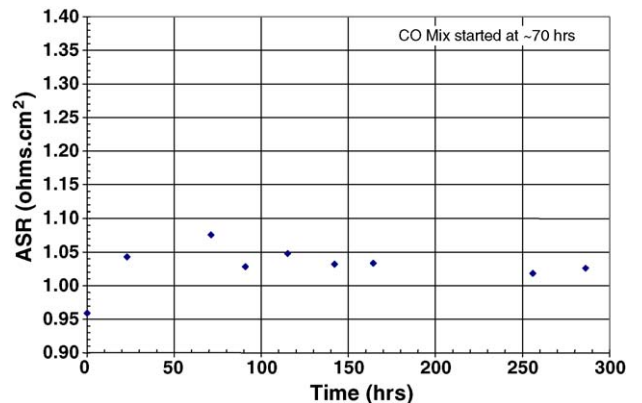


Fig. 8. Area-specific resistance (ASR) history for syngas mixture Test #5 with no H₂S. The cell shows no degradation after 290 h.

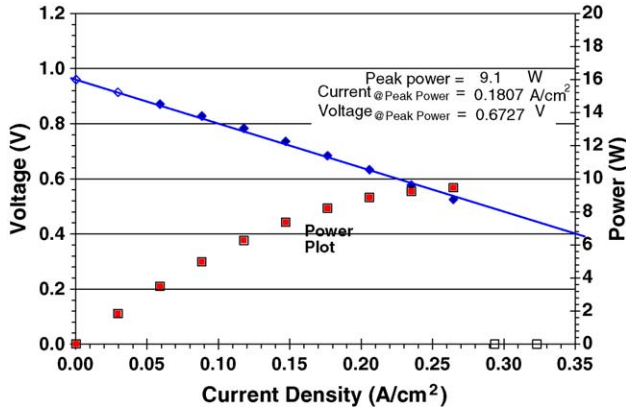


Fig. 9. Final *V/I* scan after 650 h for Test #6 with H₂S.

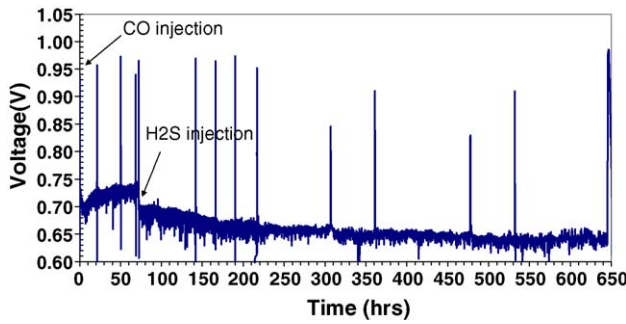


Fig. 10. Voltage variation of Test #6. The cell performs reasonably well after 650 h when the voltage produced (0.637 V) is approximately 10–12.5% less than the initial OCV (0.728 V).

to Test #6 previously shown (Figs. 5, 10 and 11), demonstrating a 6% decrease in power immediately after H₂S was introduced. When clean gas was reintroduced the power recovered, but not completely, remaining 3% below the initial power level.

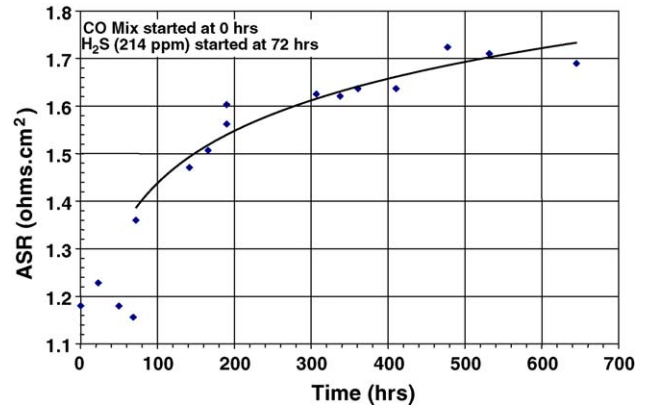


Fig. 11. Area-specific resistance (ASR) history for syngas with H₂S test. The cell behaves similarly than the test with no H₂S the first 72 h, and then starts degrading due to the H₂S presence for 570 h (up to 24% degradation, ASR-based).

3.3. Material analysis

The anode materials were analyzed before and after each trial using SEM, EDXS, and XPS. The anode cross-sectional structure of the fresh cell before testing and its components EDXS analysis are shown in Figs. 13 and 14, respectively. The main components of the cross-sectional anode region are depicted in each peak, namely Ni, Ce, Gd, and Zr.

After operating the cells with syngas with no H₂S, the components are essentially unchanged (Fig. 15), indicating the structure remains the same. EDXS analysis showed no C on the surface, confirming that there was no coking on the anode surface, and corroborating the outstanding performance of this cell with no degradation after 290 h.

The results for material analysis after the addition of H₂S are shown in Figs. 16 and 17. After Test #6 with H₂S and a total duration of 650 h, the SEM picture (Fig. 16) shows different morphology at the surface than the fresh anode (see Fig. 13). Also,

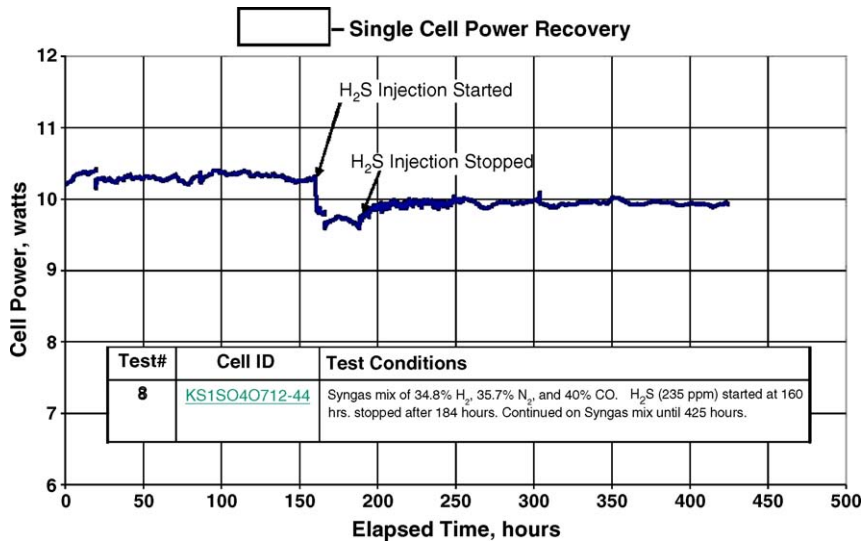


Fig. 12. Single-cell power recovery (Test #8).

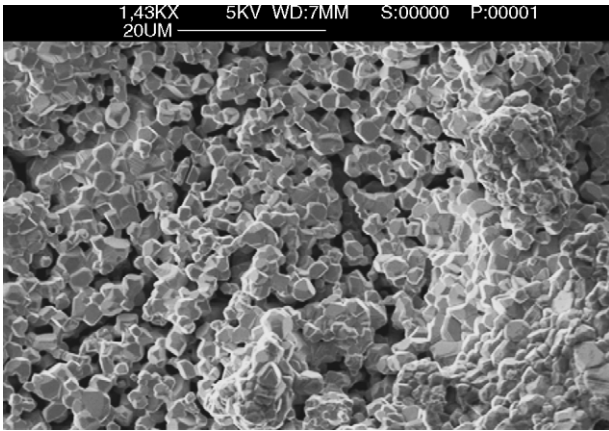


Fig. 13. SEM surface area structure of a portion of the anode-SOFC fresh cell (before testing).

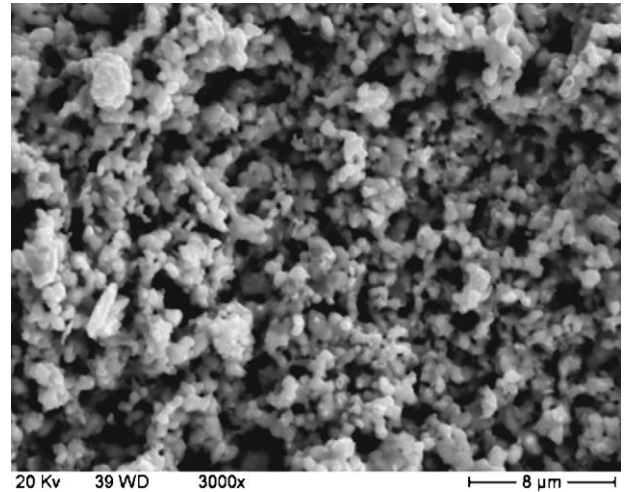


Fig. 16. SEM surface area structure of a portion of the anode after 650 h for Test #6 with H₂S.

the structure shows sulfur incorporated at the surface, while the Ni, Ce, and Gd presence is essentially the same (Fig. 17). This verifies that the H₂S had an effect, if not the primary cause for the loss of performance in the cell. This suggests that the expected mechanism for degradation was covering of part of the active surface of the anode due to the possible formation sulfur com-

pounds, such as NiS and/or CeS₂. From the results of the EDXS analysis, having essentially the same anodic structural components before and after testing (Ce, Ni, and Gd) indicates no serious delamination. Also, these results suggest that after 570 h

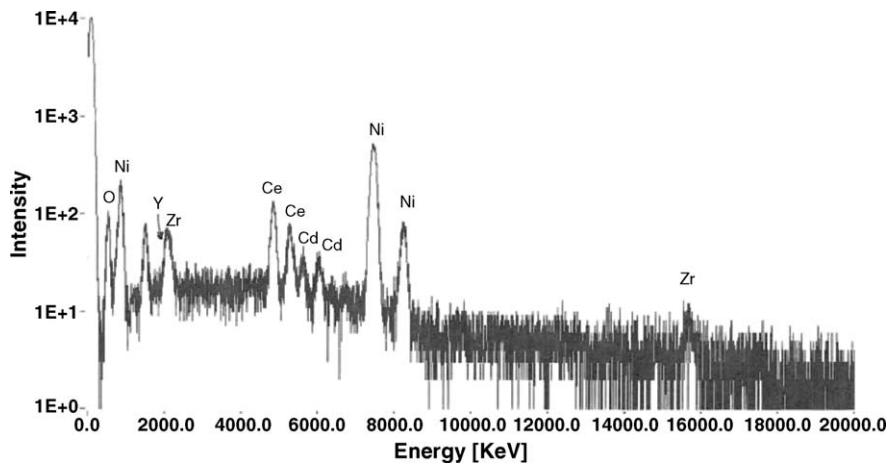


Fig. 14. EDXS analysis of a cross-sectional area of the anode structure (fresh cell before testing). Main components are: Ni, Gd, Ce, and Zr.

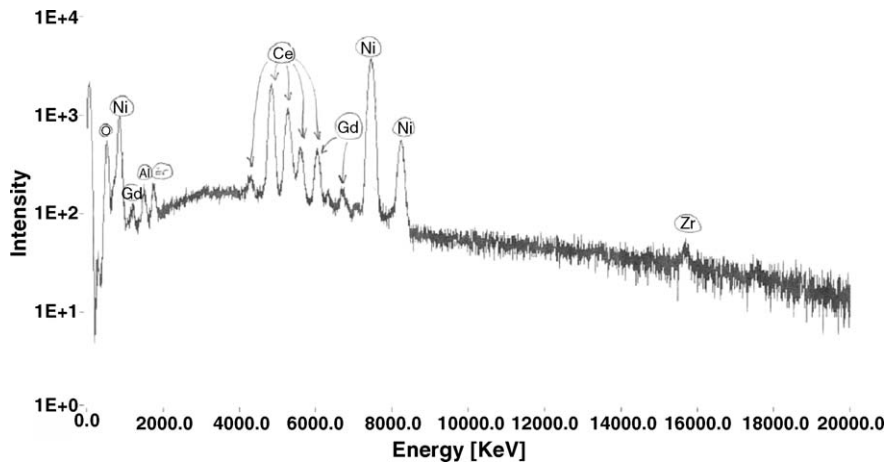


Fig. 15. EDXS analysis of a cross-sectional area of the anode structure after 290 h on the tests with syngas with no H₂S.

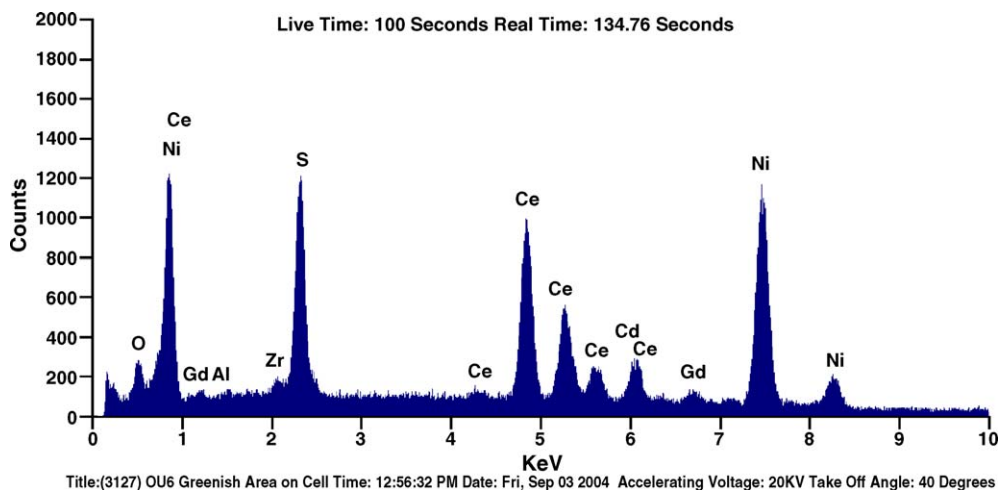


Fig. 17. EDXS analysis of a cross-sectional area of the anode structure after 650 h for the test with H₂S.

of operation with H₂S the Gd doped ceria (GDC) presence in the cell enhanced its performance and makes it a suitable sulfur-tolerant material. It was found for other applications [27] that a Pt-Ni catalyst supported on doped ceria allowed the reforming of isooctane containing 50 ppm of S (given by benzothiophene) for 1700 h with only a 5% loss of activity.

The XPS analysis performed on the anode materials before and after testing corroborates these results. The concentration at the surface of the anode of the Ni, Gd, and Ce elements remained unchanged for the Test #5 after syngas conditions with no H₂S compared to the fresh anode material composition, while for

Test #6 after H₂S exposure there was a 5–7% loss in the Ni composition and a 1–2% gain of sulfur (Fig. 18) at the anode surface (Ce and Gd composition remained essentially unchanged). This suggests that the proposed mechanism for degradation may include NiS formation for these tests. Other metals, such as Fe, Cr, and Mo, were also noticeable after both tests, syngas with and without H₂S, but their presence was due to the piping material (Inconel) used for the anode line and were introduced by the fuel which contained water, but they did not seem to affect the cells behavior.

Thus, the Ni-GDC cell seems to be a good candidate for operating with syngas in the presence of H₂S, in contrast to many studies that show Ni-YSZ degrades significantly in the presence of sulfur [2,10,15,17,19,23].

4. Conclusions

The effects of coal syngas with and without hydrogen sulfide (H₂S) on the performance of single-cell planar solid oxide fuel cell setups were studied. The results indicate that the coal syngas does not have a significantly deleterious effect on the long-term cell performance, although longer tests (>500 h) under syngas conditions need to be completed. The introduction of 200–240 ppm of H₂S appears to have an immediate impact on cell performance on the order of 6–8% power loss, being the total degradation only 10–12.5%. However, after more than 600 h the cell tends to stabilize (potential and ASR) which indicates that perhaps longer experiments need to be performed to verify this tendency. Some of the power loss caused by the H₂S presence may be recoverable when H₂S is removed. The fact of having H₂S mixed with CO limited the analysis since the performance involves combined effects of CO–water–H₂S, but the results showed that when the cells are tested with combined CO–water–H₂S in the syngas mixture their performance is acceptable. Further tests are being carried out with H₂S mixed with N₂, thus the separate effects of CO, H₂O, and H₂S are being studied and will be published in the near future.

The results on the material analysis suggest that the presence of GDC enhanced the sulfur tolerance of the cell. It was found in

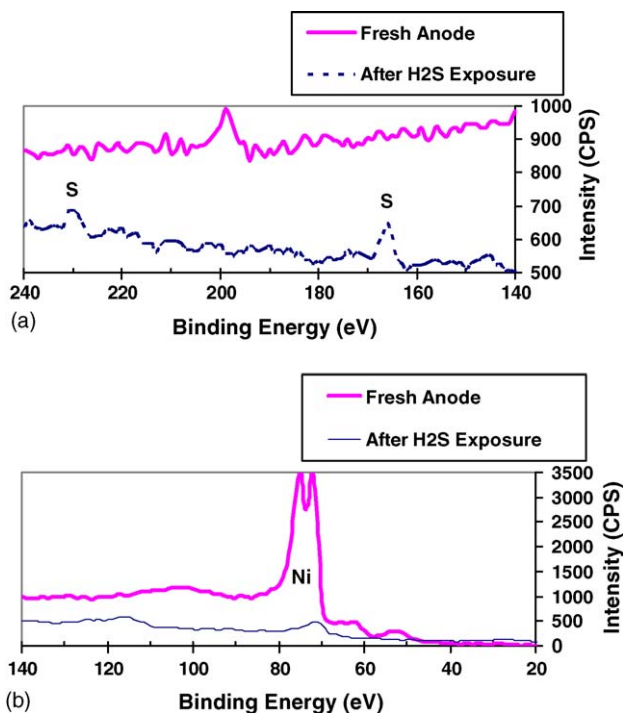


Fig. 18. XPS analysis for the anode surface before testing (fresh cell) and after H₂S exposure (Test #6). (a) In Test #6, the two peaks corresponding to sulfur (2s and 2p levels) are clearly identified in contrast to the scan for the fresh anode. (b) The fresh anode shows a larger peak for one of the Ni levels than the test after exposure with H₂S.

other applications [27] that a Pt-Ni catalyst supported on GDC had provided sulfur tolerance in reforming processes. Thus, the Ni-GDC cell seems to be a reasonable candidate for operating with syngas in the presence of H₂S, in contrast with other studies which show that Ni-YSZ degrades significantly in the presence of sulfur.

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