



Short communication

The use of hydrogen-depleted coal syngas in solid oxide fuel cells

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ABSTRACT

Electrolyte-supported solid oxide fuel cells were operated using hydrogen, simulated coal syngas, and a hydrogen-depleted syngas as fuel. Open circuit voltages closely matched theoretical predictions, and carbon deposition was completely avoided. When 50% of the hydrogen flow rate was removed from the syngas mixture while increasing the overall flow rate to maintain the same fuel utilization, the drop in power density of the cell was less than 8%. Switching from syngas to hydrogen-depleted syngas caused an average increase in the area-specific resistance of $0.027 \Omega \text{ cm}^2$, or 4%. The results of this study suggest that solid oxide fuel cells could operate successfully using syngas that has been partially stripped of hydrogen for other purposes.

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1. Introduction

Solid oxide fuel cell (SOFC) systems have been demonstrated to produce electricity at greater efficiencies than conventional technologies and have the advantage of using a variety of fuels. SOFCs operated on natural gas are in commercial development, for example at Siemens-Westinghouse. Because the use of coal for power generation is expected to continue due to its availability and low cost, there is an interest in studying the use of coal syngas with solid oxide fuel cells [1–5].

Research has shown that SOFCs can operate using fuels containing hydrogen, carbon monoxide, and diluents found in a typical coal syngas mixture. However, anode polarization is known to increase when the carbon monoxide to hydrogen ratio is increased [6] due to the slower reaction rate of carbon monoxide oxidation [7]. Anode polarization further increases because of the slower overall diffusion to the reaction sites. These losses, termed concentration losses, are worsened by increasing diluents in the gas stream [8].

Since it is possible to vary the hydrogen content of the fuel in SOFCs and still continue operation, it stands to reason that some of the hydrogen in a syngas stream could be removed for other purposes. The remaining fuel, a hydrogen-depleted syngas (HDS) could then continue to be used in the cell. This process would create a high-value hydrogen source for other fuel cell types that might be

favored in some applications, such as PEM cells in transportation applications. The resulting diluted fuel gas would have a higher carbon monoxide to hydrogen ratio than the original syngas, leading to an increase in anode polarization.

When using mixed fuels, solid carbon will form on the SOFC anode at normal operating conditions, which can be near 1000°C [9]. Therefore, SOFCs must not be operated under such conditions. Carbon deposition can also be avoided by operating at high current densities, but this can result in higher concentration losses because the product gases dilute the incoming fuel. However, with anode-supported cells the anode polarization can actually be reduced at high current densities because the water–gas shift reaction promotes the exchange of carbon monoxide for hydrogen [5].

SOFCs are typically classified into two categories: electrode-supported and electrolyte-supported. Both types of SOFCs have unique advantages. Electrode-supported cells allow for a thinner electrolyte with less resistance. However, the thick electrode creates higher concentration losses since gas molecules have a longer diffusion path to reaction sites. Conversely, electrolyte-supported cells have shorter diffusion paths but rely on thicker, less conductive electrolytes for support.

Because anode polarization was expected to be the dominant inefficiency when using HDS, an electrolyte-supported cell was chosen for this study. Nextcells with an active area of $\sim 1.33 \text{ cm}^2$ were purchased from Nextech Materials. These cells contain an LSM/GDC cathode and three-layer, proprietary, scandia-stabilized zirconia (ScSZ) electrolyte. The gadolinium-doped ceria (GDC) anode is covered with a protective layer of yttria-stabilized zirconia

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Table 1
Experiment flow rates

Fuel	Component	Flow rate (mL/min)	Percentage (%)
Humidified hydrogen	H ₂	351.09	83.8
	H ₂ O	67.87	16.2
Syngas	H ₂	139.65	24.9
	H ₂ O	90.86	16.2
	CO	211.44	37.7
	CO ₂	86.37	15.4
	N ₂	32.53	5.8
HDS	H ₂	87.16	14.22
	H ₂ O	113.41	18.50
	CO	263.93	43.06
	CO ₂	107.81	17.59
	N ₂	40.60	6.63

that prevents reduction of the GDC layer while added nickel assures conductivity and encourages oxidation reactions.

The goal of this study was to determine the changes in SOFC performance when removing a significant portion of hydrogen from a chosen syngas mixture. If reasonable performance can be achieved using HDS while avoiding carbon deposition, then the technical challenges will be overcome and the economics of partial removal of hydrogen from syngas could be compared to direct use of the syngas.

2. Experimental

The testing methods used in this study were similar to prior fuel cell research conducted by the Ohio Coal Research Center (OCRC) [1]. However, in this case a new facility with new test stands was constructed to allow test parameters to be controlled from outside of the laboratory, thus improving safety by limiting exposure to areas containing hazardous gases. A description of the design of the facility and the safety system has been published previously [10].

Cells were operated at ambient pressure. A furnace was used to increase the cell temperature to 820 °C over a period of 8 h and to maintain that temperature for the duration of the tests. Heating the cell too quickly could cause it to crack or cause the different layers to separate so the manufacturer's recommended heat rate was used. Nitrogen and airflows were then provided to the anode and cathode, respectively, during startup and fuel was incrementally added to the anode side. Temperature and pressure were monitored remotely.

Each cell was tested using three fuel mixtures: humidified hydrogen, syngas, and HDS. Ideal reversible voltage for each fuel source was calculated using Eq. (1), assuming that the electrolyte is an ideal ionic conductor and electrons will not short across the cell [8]. In this equation, R is the gas constant, T is the cell temperature, F is Faraday's constant, p'' is the partial pressure of oxygen at the cathode, and p' is the partial pressure of oxygen at the anode.

$$V = \frac{RT}{4F} \ln \left[\frac{p''_{O_2}}{p'_{O_2}} \right] \quad (1)$$

The syngas mixture used in testing is given in Table 1. HDS was defined as removing 50% of the hydrogen flow in the syngas with a concurrent increase in the overall flow rate to maintain the same fuel utilization value. These fuel mixtures were created using bottled gas sources, mass flow controllers, and a water bubbler that was maintained at a constant temperature corresponding to the partial pressure of the desired water content. Since changes in the overall cell resistance can occur over time, hydrogen was provided to the cell with the equal humidity of syngas so that no time was spent

waiting for the bubbler temperature to rise from room temperature after the change from hydrogen to syngas. Because a constant bubbler temperature was maintained, the change in cell performance was seen immediately when switching to syngas. No gas cleanup methods were assumed for these tests, meaning that the other constituents were not altered. The high temperature of syngas would prevent water from condensing during a hydrogen removal process. This means that the molar flow rate of water would also not change while the overall flow would be reduced. The bubbler temperature was increased during HDS trials in order to replicate this.

Low fuel utilization (2%) was used in this study to simulate the inlet conditions of the fuel cell where carbon deposition would likely occur. If deposition was avoided at these conditions, then it certainly would not be expected when using a higher fuel utilization value. Following testing, cells were examined using scanning-electron microscopy (SEM). Electron dispersion spectroscopy (EDS) was used to determine if any carbon deposition had occurred.

Platinum wires were attached to platinum mesh current collectors secured to the anode and cathode by adding layers of nickel and LSM, respectively, to the cell. Ceramic flanges were used to hold the cell and direct the fuel appropriately. Once the operating temperature was reached, a Solartron 1470 potentiostat was used to draw a constant current through the cell. The current was increased and decreased to produce a VI plot every hour. In some trials, a Solartron 1252 Frequency Response Analyzer was used for electrochemical impedance spectroscopy (EIS). This data was taken at a potential offset near peak power density.

Since SOFCs often exhibit significant part-to-part variation, each cell was exposed to the three different fuel types during testing so that relative performance effects could be observed. No load was applied to the cell during fuel changes. Instead, the open circuit voltage (OCV) was monitored until it stabilized, indicating that the new gas composition had stabilized and the previous fuel was flushed from the test system. More details on the experimental procedures are available elsewhere [11].

3. Results and discussion

3.1. Open circuit voltage

The theoretical OCVs were calculated using Eq. (1), assuming that the fuel gas was at equilibrium. Since the flow rates and compositions were controlled, the measured open circuit potential was expected to have little variation from the theoretical values. However, poor sealing, inaccurate humidity levels and difficulties in testing caused the OCV to slightly deviate from the expected value. At one point, the automatic refilling mechanism on the bubbler malfunctioned and insufficient water was delivered to the syngas mixture, leading to a drastic increase in ASR towards the end of the test, implying that carbon deposition may have occurred. However, for all tests where proper sealing and humidification were achieved, the measured OCV value was within 10 mV of the calculated result. These values are shown below in Table 2.

Another factor which influenced the OCV was the pressure of the test stand. Different flow rates and variations in the water level of the bubbler caused the pressure within the system to change over time, often exceeding 5.5 kPa. In order to accommodate long test

Table 2
Reversible cell voltage at 820 °C

Fuel source	Calculated (V)	Measured
Hydrogen (16.2% water)	1.01	1.011
Syngas (Pittsburgh No. 8)	.969	.972
Hydrogen-depleted syngas (HDS)	.945	.946

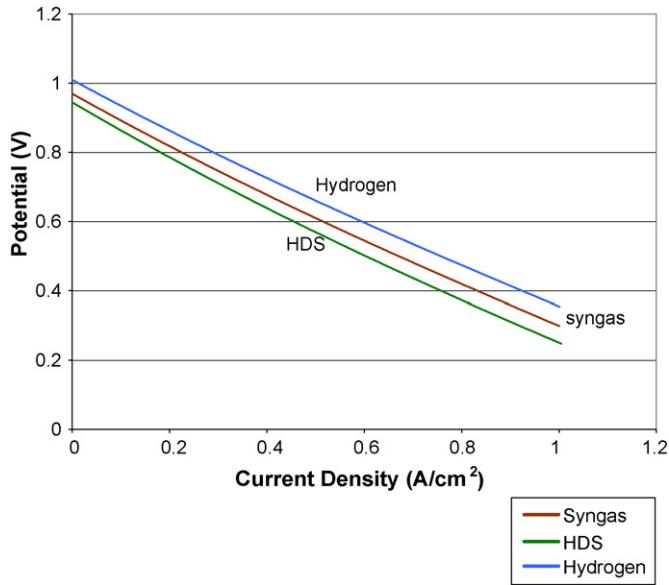


Fig. 1. Representative characteristic curves for various fuels at 820 °C.

times, a tall bubbler was used that could impart significant elevation head on the system. While this had little effect on the reactions taking place in the cell, it did significantly impact the humidity imposed on the fuel gas by the water bubbler. Therefore, future work should either adjust the bubbler temperature to compensate for backpressure seen during testing or use other methods of water delivery. As shown in Table 2, the slightly lower water content of the syngas caused a small increase in the predicted OCV compared to HDS. These values were nearly identical to the measured values.

As a result of this data, it was concluded that no significantly unforeseen losses in OCV occurred when using HDS in place of syngas. The drop in the theoretical potential due to the reduced hydrogen content of HDS means that even if increased activation and concentration losses are negligible, there would still be a drop in the performance of the cell when removing hydrogen for other purposes.

3.2. Area-specific resistance (ASR)

Fig. 1 shows representative VI scans for hydrogen, syngas and HDS. The ASR was taken as the average slope of these lines. Although there is a clear offset in the potentials of the fuels, the curves appear otherwise almost identical. However, there is small difference in the slopes. When switching from syngas to HDS, the mean increase in ASR was $0.027 \Omega \text{ cm}^2$, or 4%. Because only a small number of valid tests were completed, the statistical uncertainty associated with the mean ASR value was relatively large, but with 95% confidence the increase in the overall resistance for similar cells may be less than 9%.

Changes in the ASR were observed for some cells, particularly early during testing. Despite having the same startup conditions, the time required to achieve a stable operating condition varied for different cells. Therefore, EIS was used to provide additional information regarding cell performance. Representative impedance spectra for two different times of operation are shown in Fig. 2. Although the overall resistance showed a significant change, only the ohmic resistance (left-most x-intercept) actually increased. The contributions associated with electrode polarization remained mostly constant during these tests.

The increase in the polarization found from EIS near the peak power density deviated slightly from the change in the ASR. This

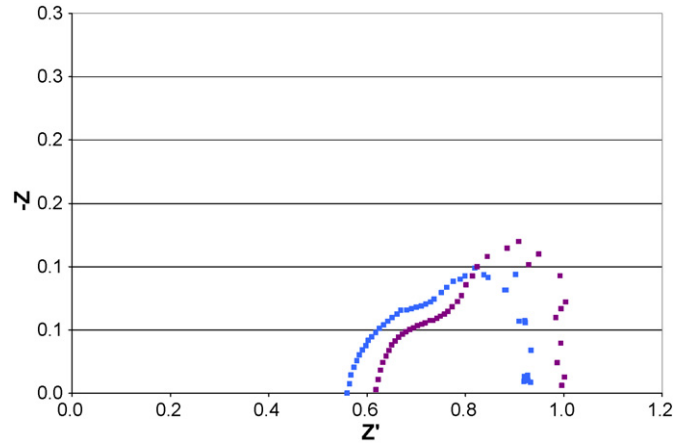


Fig. 2. Impedance spectra for a SOFC over time using hydrogen.

was likely due to EIS data being taken only at one point of the slightly nonlinear performance curve. Since EIS was used infrequently, no statistical claims could be made regarding this data. However, when switching from syngas to HDS the average change in the total resistance per EIS was $0.023 \Omega \text{ cm}^2$. Fig. 3 depicts impedance spectra for the same cell when using different fuels and operating at 0.5 V. When less water was present in the syngas, and therefore carbon monoxide oxidation occurred more readily, the impedance increased.

The changes in the OCV and ASR of the cell when switching from syngas to HDS both affect the power density of the cell. Assuming a linear performance curve, the loss in power density can be calculated using Eq. 2, where ΔV is the change in the OCV, i is the current density, and ΔASR is the change in the area-specific resistance of the cell. Using the mean changes in these values and assuming a constant overall cell resistance, the mean loss in maximum power density was 7.8%. Due to the statistical uncertainties mentioned above, it can only be stated with 95% confidence that the loss in power density is less than 13.8%.

$$\Delta P = \Delta V * i + \Delta ASR * i^2 \tag{2}$$

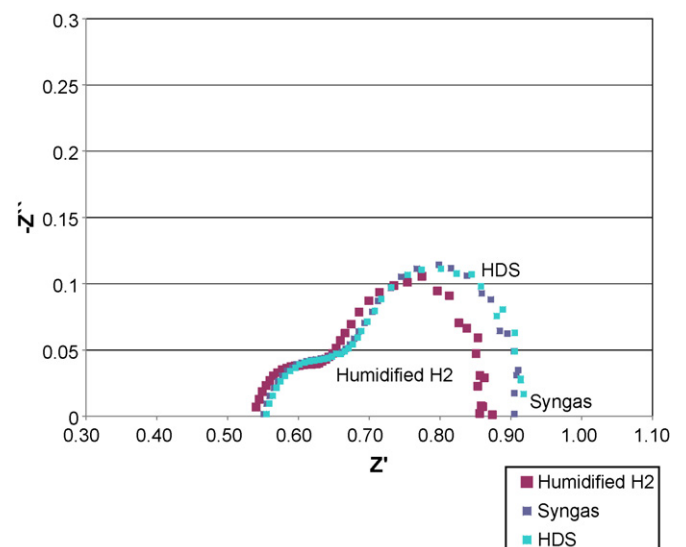


Fig. 3. Impedance spectra for SOFC using various fuels.

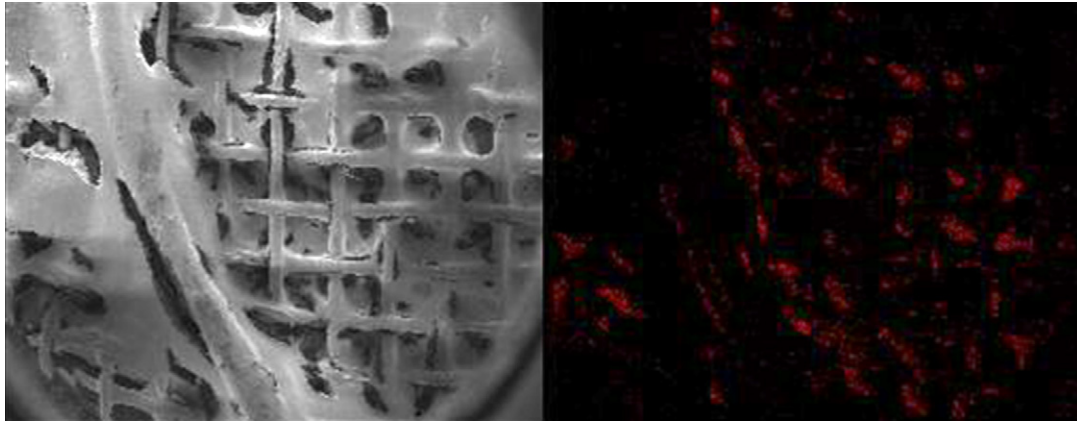


Fig. 4. SEM image (left) of SOFC tested with only hydrogen and EDS carbon concentration map (right) showing carbon present in platinum current collection material but not located on surface nickel layer.

3.3. Carbon deposition

SEM with an EDS was used to inspect the surfaces of the cells used in this study. Fig. 4 shows two images taken of a cell tested using only humidified hydrogen. In the first image, the platinum mesh, which was mostly covered with nickel paint, can be seen. The second image shows the location of carbon on the surface. Prior

modeling had shown that carbon deposition was not favored for coal syngas at ambient pressure in temperatures near 800 °C [2]. Therefore, the test conditions were such that no carbon deposition was expected. In this case, the carbon concentrations shown in this image mostly correspond to the grid shape of the platinum mesh. Further investigation showed that other small concentrations were present in pre-existing contaminant clusters. This conclusion was

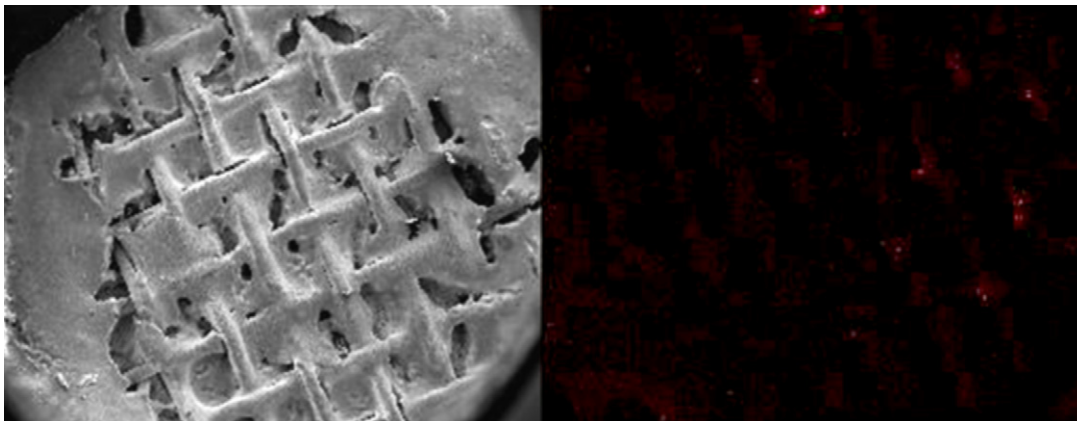


Fig. 5. SEM image (left) of cell tested with syngas and HDS and EDS carbon concentration map (right) showing very little carbon present on anode, none of which was the result of carbon deposition.

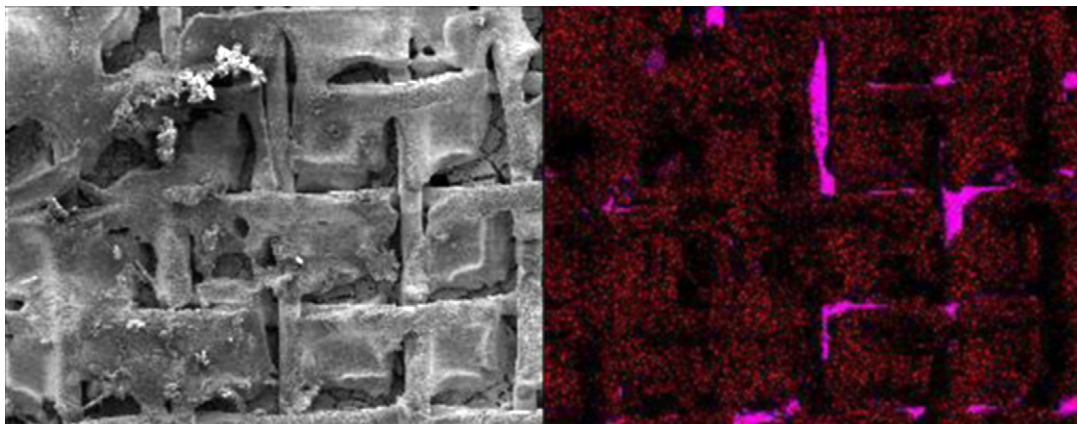


Fig. 6. SEM image (left) of cell tested with syngas containing only 6.7% water and EDS carbon concentration map (right) shows that carbon was not restricted to exposed platinum (pink) but rather was covering the entire anode. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

based on the fact that the small carbon-containing particles were also made up of elements not present in the fuel or test system.

Similar results, shown in Fig. 5, were found for cells exposed to syngas and HDS. Carbon was clearly present in the platinum mesh in large (~8 wt%) amounts. This was confirmed with measurements of the unused, bare platinum wire. Besides the mesh, the amount of carbon that could be found on the cell was no more than on the cell tested with only hydrogen. Again, these areas appeared to be small contaminants present before testing began, reinforced by the presence of elements such as selenium.

The trial using insufficient humidity for the syngas mixtures resulted in carbon deposition, which is shown in Fig. 6. The image suggests that the carbon was not restricted to the platinum mesh and actually covered a significant fraction of the surface area. The carbon deposition that occurred in this trial probably had a large impact on the performance of the cell. During this trial, the ASR increased over time, rising drastically near the end of the test. This would be expected as carbon deposits covered available oxidation sites.

When fuel gas conditions were maintained at the desired level, no carbon deposits were detected using EDS. It is possible that longer test times would be required before the carbon could accumulate to measurable levels. However, the extremely low fuel utilization (2%) used in this study would favor carbon deposition far more than when utilization is high. Therefore, carbon deposition as a failure mode is unlikely.

4. Summary and conclusions

Three different fuels were used during the testing of electrolyte-supported SOFCs. In each case, the open circuit potential was found to be nearly identical to the theoretical value. When 50% of the hydrogen content was removed from the syngas, the ASR of the cell increased by $0.027 \Omega \text{ cm}^2$, or 4%. The combined effect of the

OCV decrease and the increased losses resulted in a loss of peak power density of less than 10%. Further, when fuel conditions were accurately maintained, no carbon deposition was detected.

Future work could focus on reducing experimental uncertainty by increasing the number of replicated tests and repeating the tests for HDS with different levels of hydrogen removed. Since a method of hydrogen extraction was not identified in this study, it remains to be explored what changes extraction methods may have on the syngas stream and contaminant levels. If no additional failure modes were discovered related to extraction methods, removing hydrogen from syngas streams and allowing SOFCs to operate using HDS could be a question of economics rather than science.

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