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# The effect of coal syngas containing AsH<sub>3</sub> on the performance of SOFCs: Investigations into the effect of operational temperature, current density and AsH<sub>3</sub> concentration

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#### Abstract

The performance of solid oxide fuel cells (SOFCs) using simulated coal-derived syngas, with and without arsine (AsH<sub>3</sub>), was studied. Anodesupported SOFCs were tested galvanostatically at 0.25 and 0.5 A cm<sup>-2</sup> at 750 and 800 °C with simulated coal syngas containing 0.1, 1, and 2 ppm AsH<sub>3</sub>. The tests with simulated coal syngas containing 1 ppm AsH<sub>3</sub> show little degradation over 100 h of operation. The tests with simulated coal syngas containing 2 ppm AsH<sub>3</sub> show some signs of degradation, however no secondary arsenide phases were found. Extended trial testing with 0.1 ppm AsH<sub>3</sub> showed degradation as well as the formation of a secondary nickel arsenide phase in the anode of the SOFC. Published by Elsevier B.V.

Keywords: Solid oxide fuel cell; Coal syngas; Experimental performance; Hydrogen chloride

# 1. Introduction

Although many studies in the past have taken into account the effect of major coal syngas constituents such as  $H_2S$  and HCl on SOFC performance degradation, little attention has been given to trace species contained in coal syngas with concentrations below 10 ppm. Previous research has shown that many trace species contained in coal have the ability (thermodynamic potential) to form volatile compounds under the gasification and warm/hot gas cleanup conditions proposed for use in integrated gasification and fuel cell (IGFC) power plants, and that these species also have the possibility (thermodynamic potential) of interacting with the SOFC anode [1]. The results from this work show that the elements (As, Cd, Hg, P, Pb, and Sb) all have the ability to form volatile compounds under warm/hot gas cleanup conditions (250–500 °C, 1–15 atm) and reach the SOFC anode where each may interact with SOFC anode materials Ni and YSZ.

Arsenic (As) is of particular interest because it is contained in most U.S. coals, is volatile under gasification and warm/hot gas cleanup conditions, and is toxic. Arsenic is readily found in coal with concentrations ranging 0.5–2090 ppmw [2]. Nearly all arsenic is converted to AsH<sub>3</sub> in the reducing environment of gasification. However, over warm/hot gas cleanup system conditions arsenic may be found in several volatile formations: As<sub>4</sub>, AsH<sub>3</sub>, and As<sub>3</sub>Pb [2]. Measurements completed to determine the concentration of arsenic in a coal-derived syngas after going through cleanup has shown a concentration range of 0.15–0.60 ppm AsH<sub>3</sub> [2]. Previous industrial research has shown only very low levels of arsenic are needed to form nickel arsenide phases in water gas shift catalysts [2–4]. Past thermodynamic calculations have shown that at concentrations of 0.15–0.60 ppm AsH<sub>3</sub> may react with Ni contained in the SOFC anode to form a secondary nickel arsenide phase [5,6].

Arsenic has been shown to cause problems in systems similar to the SOFC anode. Previously, industrial steam shift catalysts containing nickel (Ni) were poisoned by arsenic, with the compound Ni<sub>5</sub>As<sub>2</sub> found on the catalyst [7–9]. Testing has shown that concentrations of 1 to 5 ppm As<sub>2</sub>O<sub>3</sub> in steam will reduce catalytic activity of Ni-based steam reforming catalyst within four days of operation—concentrations as little as 1% As in Ni were found to have the same effect as chemisorbed sulfur [10]. Other research has shown that very low levels of arsenic are needed

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to form nickel arsenide phases in water gas shift catalysts [10]. In fact some research has shown that arsenic has a greater effect than sulfur on reactions concerning hydrogen [10]. Also poisoning of methanol synthesis catalyst by arsenic contained in coal-derived syngas used as the feed source to the process has also been reported [10].

However it must be noted that the temperatures of the above mentioned investigations (25–500 °C) are well below the operational temperature range of SOFCs (750–900 °C). Experimental investigations must be completed in order to determine if arsenic contained in coal-derived syngas poses any threat to SOFC operation. This paper presents results obtained from research investigating the effect of a simulated coal syngas containing AsH<sub>3</sub> on the performance of a SOFC.

## 2. Experimental

#### 2.1. Button cell description

Anode-supported SOFCs manufactured by Materials and Systems Research Inc. were used in this study. Each button SOFC consisted of a 3.00-cm diameter anode composed of a 1 mm Ni-8YSZ support structure and a 25-µm thick interlayer composed of a highly catalytic Ni–8YSZ mixture. The SOFC contained a 20 µm 8YSZ electrolyte, and a cathode composed of a 25-µm thick La<sub>0.8</sub>Sm<sub>0.2</sub>MnO<sub>3</sub>(LSM)-8YSZ interlayer and a 25-µm thick current-collection layer made of LSM.

## 2.2. Button cell test setup

A nickel current collection mesh was attached to the anode of each SOFC using nickel contact paste. A platinum current collection mesh was attached to the cathode of each SOFC using a platinum paint. Silver current cables and voltage taps were spot welded onto opposite sides of each current collection mesh. The button SOFCs were mounted between two alumina flanges and ceramic o-rings using mica as the sealing material.

For all tests, the button cell assembly was mounted in a furnace operated at 750 or 800 °C. Alicat<sup>TM</sup> mass flow controllers (MFCs) were used to control the fuel and air stream flow rates and compositions. Separate MFCs were used to control the flow rates of H<sub>2</sub>, CO, CO<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>/AsH<sub>3</sub> to the anode and air to the cathode. A temperature-controlled humidifier was used to control the water content of the simulated coal syngas provided to the anode and likewise for the air provided to the cathode. The total fuel flow rate was kept at approximately  $550 \pm 12.5$  sccm and the air-flow rate was kept at approximately  $2000 \pm 10$  sccm. The anode flow lines were heat traced to ensure no condensation would take place between the humidifier and furnace. AsH<sub>3</sub> was injected downstream of the stream reached the anode of the SOFC.

#### 2.3. Experimental testing

The SOFCs were heated from room temperature to 750 or 800 °C over 2 h. During the heating period the anode was pro-

vided 200 sccm of N<sub>2</sub> and the cathode was provided 500 sccm of air. Once the SOFC reached its operational temperature, the anode of the button cell was reduced by providing fuel flow containing 10% H<sub>2</sub> and balance N<sub>2</sub> for approximately 2h. After this time the fuel flow rate was switched to a pure H<sub>2</sub> feed for another 2 h. Upon reduction of the anode, which was indicated by a steady-open-circuit potential typically within 5% of the theoretical open-cell potential, the cathode-air-flow rate was increased to 2000 sccm, and the open cell voltage (OCV) was monitored for its expected Nernst value to ensure negligible leakage around the cell. The anode was then provided 400 sccm of H<sub>2</sub> and an Area Specific Resistance (ASR) measurement was completed over a potential range of 0.40-1.05 V at 0.05 V increments. If the ASR of the button cell was found to be within 10% of its design value (ca.  $0.5 \Omega \text{ cm}^2$ ), the cell was considered acceptable.

After the button cell was accepted for testing, it was operated galvanostatically at 0.25 or  $0.50 \,\mathrm{A}\,\mathrm{cm}^{-2}$  while the water bubbler was brought to its operational temperature. For reasons explained below, given that two primary streams of gas mixtures were used to provide the flow to the anode (the 'syngas stream' which passed through the humidifier and the 'trace specie gas stream' which did not pass through the humidifier), water-bubbler temperatures of 77 and 83 °C were used for the 1and 2-ppm AsH<sub>3</sub> trials, respectively. These two different waterbubbler temperatures were used in the testing to ensure a fuel gas with a constant composition was supplied to the fuel cell with AsH<sub>3</sub> concentration as the only variable. The AsH<sub>3</sub> was provided using a certified gas mixture of H<sub>2</sub> containing  $10.1 \pm 0.5$  ppm AsH<sub>3</sub>, and the total anode fuel-flow rate was fixed at 550 sccm. Because less H<sub>2</sub>/AsH<sub>3</sub> gas mixture was needed to achieve 1 ppm AsH<sub>3</sub>, more gas was humidified through the water bubbler, resulting in a lower operating temperature to achieve the same water content as in the 2 ppm  $AsH_3$  trial (none of the  $H_2/AsH_3$ ) gas was passed through the water bubbler because water acts as a scrubbing agent). Once the water bubbler stabilized at its operational temperature, a simulated coal syngas based on an entrained-flow gasifier was introduced to the anode [11]. Table 1 presents the simulated coal-syngas compositions used for both AsH<sub>3</sub> investigations.

Although typical entrained-flow-coal-gasification compositions only contain 15–17 vol.%  $H_2O$ , additional water was added to the system to ensure that coking did not take place at the anode (*note*: specific strategies for dealing with potential coking of the anode under coal-syngas operation remain to be identified). Fig. 1 presents the ternary (C–H–O) diagram for the system and the location of the compositions used in the testing.

Table 1 Simulated coal-derived syngas compositions used in testing

Component	1 ppm AsH <sub>3</sub> trials (vol.%)	2 ppm AsH <sub>3</sub> trials (vol.%)
H <sub>2</sub>	$29.1 \pm 0.7$	$29.1 \pm 0.8$
CO	$28.6 \pm 0.7$	$28.6 \pm 0.8$
$CO_2$	$12.0 \pm 0.3$	$12.0 \pm 0.3$
$N_2$	$3.2 \pm 0.1$	$3.2 \pm 0.1$
H <sub>2</sub> O	$27.1 \pm 0.6$	$27.1 \pm 0.7$
HC1	$1.0\pm0.1\mathrm{ppm}$	$2.0\pm0.1\mathrm{ppm}$



Fig. 1. C–H–O ternary diagram with a typical entrained-flow-syngas composition (red) and the composition used in the investigations (blue). Constant-temperature lines demarcate the regions with carbon deposition and without carbon deposition.

The button cell was operated galvanostatically for at least 24 h with the simulated coal-syngas mixtures before AsH<sub>3</sub> was introduced. Based on the flow rates presented in Table 1 and the certified gas mixture, approximately  $1.0 \pm 0.1$  and  $2.0 \pm 0.1$  ppm of AsH<sub>3</sub> were introduced to the anode of the SOFC during testing. ASR and electrochemical-impedance-spectroscopy measurements were made using an Agilent electronic load (N3301A), a Solartron impedance analyzer (SI 1260), and Solartron electrochemical interface (1287). The voltage and current of the SOFC were also monitored over time. After the trials, SEM and EDS analyses were completed using a JEOL JSM 6300FV SEM and Thermo Electron Noran System Six EDS. XRD analyses were also completed using an X-pert Pro PANlytical XRD.

# 3. Results and discussion

## 3.1. $750 \circ C \ 1 \ ppm \ AsH_3 \ trials$

The tests were completed as described in the experimental description. Fig. 2 presents the power-density–time-history profiles of the SOFCs operating with  $1.0 \pm 0.1$  ppm AsH<sub>3</sub> at 750 °C and 0.25 and 0.50 A cm<sup>-2</sup>.

From Fig. 2 it may be seen that  $1.0 \pm 0.1$  ppm AsH<sub>3</sub> had little effect on the power density of the SOFC over the 100 h time period. Fig. 2 shows that after approximately 24 h of operation with a simulated coal syngas, the injection of approximately 1 ppm AsH<sub>3</sub> did not cause any immediate changes in the operation of the SOFC. At the beginning of the trials, the SOFCs had operational potentials of  $0.756 \pm 0.004$  and  $0.550 \pm 0.007$  V for the 0.25 and 0.50 A cm<sup>-2</sup> trials, respectively. After 100 h of operation the SOFCs were operating at  $0.759 \pm 0.004$  and  $0.549 \pm 0.005$  V for the 0.25 and 0.50 A cm<sup>-2</sup> trials, respectively.



Fig. 2. SOFC power density operating at 750 °C, 0.25, and 0.50 A cm<sup>-2</sup> over time with  $1.0 \pm 0.1$  ppm AsH<sub>3</sub>.

tively. The operating voltages reported above were calculated using the average and standard deviation of 1 h of operational potentials leading up to 24 and 125 h of operation, respectively. The injection of  $AsH_3$  had not caused any appreciable change to the operation of the SOFCs. EIS data was collected at the beginning and the end of the trials. As can be seen from Fig. 4 only a small amount of degradation can be seen in the performance of the SOFC over the 100 h time period. Because there was only a slight amount of degradation that took place during the trial, and the fact that the signal-to-noise ratio of the EIS measurements was too low, the EIS data was unable to show the cause of the degradation (ohmic resistance or charge transfer resistance).

# 3.2. $750 \degree C 2 ppm AsH_3$ trial

A button cell test was completed at 750 °C containing  $2.0 \pm 0.1$  ppm AsH<sub>3</sub> at 0.25 Acm<sup>-2</sup>, and the results are shown in Fig. 3. Only the lower operational current density was chosen at the higher AsH<sub>3</sub> loading since the lower loading will allow for more AsH<sub>3</sub> to diffuse into the anode of the SOFC and interact with the anodic system (the reasoning for this choice is explained in more detail in Section 3.6).



Fig. 3. SOFC power density operating at  $750 \,^{\circ}$ C and  $0.25 \,\text{A} \,\text{cm}^{-2}$  with  $2.0 \pm 0.1 \,\text{ppm} \,\text{AsH}_3$ .



Fig. 4. SOFC power density operating at 800  $^\circ C$ , 0.25, and 0.50 A cm $^{-2}$  over time with 1.0  $\pm$  0.1 ppm AsH\_3.

From Fig. 3 it may be seen that upon the injection of approximately 2 ppm AsH<sub>3</sub>, a very small drop in the performance of the SOFC took place. As time progressed, the performance of the cell slightly degraded. The operational potential of the SOFC before the injection of AsH<sub>3</sub> was  $0.770 \pm 0.002$  V, and after 100 h of operation with the trace specie it was found to be  $0.720 \pm 0.014$  V. Also, it is noted that the operating potential of the SOFC became increasingly noisy over time. From prior experience with our test fixture, this leads us to the speculation that the AsH<sub>3</sub> may be affecting the anode current collection mesh more than the cell itself.

## 3.3. $800 \degree C 1 ppm AsH_3 trial$

The tests were completed as described in Section 2. Fig. 4 presents the power-density versus time-history profiles of the SOFCs operating with  $1.0 \pm 0.1$  ppm AsH<sub>3</sub> at 800 °C, 0.25 and 0.50 A cm<sup>-2</sup>.

Fig. 4 shows that after approximately 24 h of operation with a simulated coal syngas, the injection of 1 ppm AsH<sub>3</sub> did not cause any immediate changes in the operation of the SOFC. However, the AsH<sub>3</sub> did have a small effect on the performance of the SOFC over the 100 h time period. At the beginning of the trials, the SOFCs had operational potentials of  $0.690 \pm 0.002$ and  $0.600 \pm 0.010$  V for the 0.25 and 0.50 A cm<sup>-2</sup> trials, respectively. After 100 h of operation, the SOFCs were operating at  $0.600 \pm 0.004$  and  $0.590 \pm 0.010$  V for the 0.25 and 0.50 A cm<sup>-2</sup> trials, respectively. EIS data was also collected, and no changes could be seen in the EIS profiles at 24 and 125 h of operation taking into account the error associated with the measurements. While the data in Fig. 4 suggests that AsH<sub>3</sub> may be interacting with the SOFC cell, its effects are not as detrimental as other coal syngas species such as HCl and H<sub>2</sub>S whose effects on SOFC performance are more acute [12–14].

# 3.4. $800 \circ C 2 ppm AsH_3 trial$

Fig. 5 presents the data from an SOFC operated on a simulated coal syngas at 800 °C containing  $2.0 \pm 0.1$  ppm AsH<sub>3</sub> at 0.25 A cm<sup>-2</sup>.



Fig. 5. SOFC power density operating at  $800\,^\circ\text{C}$  and  $0.25\,\text{A}\,\text{cm}^{-2}$  with  $2.0\pm0.1\,\text{ppm}\,\text{AsH}_3$ .

From Fig. 5 it may be seen that shortly after the injection of approximately 2 ppm AsH<sub>3</sub> the performance of the cell abruptly improved and then decreased, following which it stabilized with a slight second drop towards the end of the trial. The cause for this particular behavior could not be identified. The operational potential of the SOFC before the injection of AsH<sub>3</sub> was  $0.809 \pm 0.004$  V and after 100 h of operation with the trace specie was found to be  $0.790 \pm 0.005$  V. This reveals that only a small degradation took place over the length of AsH<sub>3</sub> injection. Again due to the noise associated with the EIS measurements, no real change in the performance of the SOFC could be detected with the data obtained from the trial.

## 3.5. Extended trial testing

Although the trials presented above do give some indication of the effect of AsH<sub>3</sub> over time, an extended operation trial was also completed; however, this time the supply of AsH<sub>3</sub> was provided via a permeation tube from VICI Metronics. The AsH<sub>3</sub> permeation tube was calibrated to determine its permeation rate by bubbling the gas flowing past the permeation tube into an aqueous solution containing hydrochloric acid and hydrogen peroxide for 8 h. The concentration of AsH<sub>3</sub> was then determined by a digestion method. The results from this calibration testing showed that the permeation tube was able to produce approximately  $175.0 \pm 8.5$  ng min<sup>-1</sup> of AsH<sub>3</sub>. This permeation rate yields an AsH<sub>3</sub> concentration of approximately  $0.10 \pm 0.02$  ppm in the syngas delivered to the fuel cell, taking into account the error associated with the permeation tube and the mass flow controllers. The SOFC was operated at 800 °C and  $0.25 \text{ A cm}^{-2}$ . Fig. 6 presents the performance data for these tests in which the AsH<sub>3</sub> was injected after approximately 24 h of operation.

From Fig. 6 it may be seen that some degradation in fuel cell performance takes place over time. Just before injection, the SOFC had an operational potential of  $0.870 \pm 0.001$  V and after 800 h of operation it had an operational potential of  $0.807 \pm 0.001$  V. This data shows that even at 0.1 ppm, AsH<sub>3</sub> is possibly interacting with the SOFC materials.



Fig. 6. SOFC performance at  $800 \,^{\circ}$ C and  $0.25 \,\text{A cm}^{-2}$  with simulated coal syngas containing 0.1 ppm AsH<sub>3</sub> (not shown is the 24 h pre-AsH<sub>3</sub> conditioning period).

## 3.6. Post-trial analyses

To determine how the AsH<sub>3</sub> may have affected the SOFC anode materials, post-trial material analyses along with thermodynamic and anode transport simulations were performed. This section will highlight the results from these studies and their use in interpreting the results obtained from the experimental trials. Post-trial XRD analyses were completed on each SOFC used in this investigation to determine if the AsH<sub>3</sub> interacted with any of the anode components to form a secondary phase. Fig. 7 presents the XRD results.

From Fig. 7 it may be seen that the two main components (Ni and 8YSZ) of the SOFC anode were identified. In addition, a small amount of formation of the secondary phase NiAs(s) was detected for the extended 0.1 ppm trial. However, the results from the other short-term SOFC trials show no formation of a secondary nickel arsenide phase. (These results support the understanding that difficulties exist in attempting short-term high concentration studies to "speed" material degradation studies of lower concentrations. Specifically, one might expect that the 0.1 ppm trial would have had less of an effect on the per-



Fig. 7. SOFC anode XRD profiles after operation with CSG containing  $AsH_3$ . Phases identified are Ni (1), 8YSZ (2), and NiAs (3).



Fig. 8. Representative SOFC anode cross-section at 200×.

formance given that less total arsenic was passed over the cell; however, the opposite is evident from the data.)

SEM and EDS analyses were also completed on all of the SOFCs used in this study. Fig. 8 shows a typical cross-section of the SOFC.

In Fig. 8, the porous anode of the SOFC may be seen at the left of the figure and the interlayer of the anode of the SOFC may be seen at the right. EDS analyses were completed on each SOFC at the surface of the anode and throughout the SOFC cross-section. Nearly all of the trials showed no signs of As within the anode of the SOFCs tested. However, as was found in the XRD analyses, As was found in the anode of the cell operated for 800 h. The As was found at the surface of the SOFC anode, but not within the anode of the SOFC. Fig. 9 presents three EDS spectrums obtained from the points labeled 1, 2, and 3, respectively, in Fig. 8.

The formation of nickel arsenide as shown in Fig. 9 is probable based upon the thermodynamics associated with the formation of NiAs(s). Fig. 10 presents the equilibrium partial pressures of AsH<sub>3</sub> for Eq. (1):

$$AsH_3(g) + Ni(s) \rightarrow NiAs(s) + 1.5H_2(g)$$
(1)

From Fig. 10 it may be seen that the equilibrium partial pressure associated with  $AsH_3$  for the formation of NiAs(s) is much lower than the concentration found in actual coal syngas compositions. This information validates the formation of the nickel arsenide phase found in the SOFC operated for 800 h.

## 3.7. Transport model analyses

In order to estimate the possible transport behavior and concentration profiles of  $AsH_3$  through the anode under different cell current densities, an anode diffusion model, employing a



Fig. 9. EDS spectrums from points 1, 2, and 3 shown in Figs. 7 and 8 from SOFC operated for 800 h with simulated coal syngas containing 0.1 ppm AsH<sub>3</sub>.

mean transport pore model [15,16], was used assuming negligible reaction with the anode materials (such an analysis will give the maximum likely concentration of AsH<sub>3</sub> through the anode layer). The results for the trials containing 1 and 2 ppm AsH<sub>3</sub> are presented in Fig. 11.

From Fig. 11 it may be seen that the operational current density of the SOFC does affect the concentration of  $AsH_3$  throughout the anode of the SOFC. At lower current densities more  $AsH_3$  is able to transport into the anode of the SOFC inferring that the formation of the nickel arsenide phase should be easier at this lower operational current density. The Gibb's free energy of reaction for Eq. (1) was calculated at both the surface and interlayer interfaces based upon the  $H_2$  and  $AsH_3$ 



Fig. 10. AsH<sub>3</sub> equilibrium partial pressures for Eq. (1) over SOFC operational temperature range and  $0.29 \text{ atm H}_2$ .

partial pressures found from the modeling over the experimental conditions that were used in the testing described above. These calculations showed Gibb's free energy values in the range of -138.3 to -144.9 kJ mol<sup>-1</sup> at the anode surface and -138.8 to -145.5 kJ mol<sup>-1</sup> at the interlayer interface. These values show that the formation of nickel arsenide is only slightly favored at the anode–electrolyte interface.



Fig. 11. AsH<sub>3</sub> concentration profiles through the SOFC anode with a simulated coal syngas containing 1 ppm (a) and 2 ppm (b)  $AsH_3$ .

## 4. Discussion of the results

In summary, the results presented in this paper show that  $AsH_3$  does show some interaction with the SOFC anode. Specifically, in the 0.1 ppm AsH\_3 extended test trial (800 h), a small rate of degradation was shown to take place. For this test condition, the formation of NiAs(s) at the SOFC anode was found through XRD analysis. Further, the results showed that this secondary nickel phase only occurred at the outer anode surface.

In the other shorter trials where  $AsH_3$  concentrations of approximately 1 and 2 ppm were used, some degradation was shown to take place, although no secondary nickel arsenide phase formation was found to take place. This result occurred in spite of the fact that the total amount of  $AsH_3$  passed over the cell was greater for this case than for the extended trial.

The thermodynamic calculations that were completed verified that the formation of NiAs(s) at the SOFC anode can take place at the operational conditions an SOFC would encounter when operating with coal syngas as fuel. Finally, the diffusion modeling results showed (assuming inert AsH<sub>3</sub> behavior) that only a small decrease (4–9%) in the concentration of AsH<sub>3</sub> takes place between the anode surface and the anode interface at operational current densities of 0.25–0.50 A cm<sup>-2</sup>.

Altogether, the above results suggest that there is a strong adsorption of AsH<sub>3</sub> onto nickel which therefore limited the secondary nickel phase formation to the outer anode surface. This strong adsorption would hinder the transport of AsH<sub>3</sub> into the depth of the SOFC anode until either local adsorption equilibrium is reached or all of the nickel contained at the surface was converted into a secondary nickel arsenide phase. A first-order analysis for the depth of the anode that is likely to be affected by the AsH<sub>3</sub> transported to the anode surface shows that even when assuming 100% adsorption only a thin outer region of the anode surface is likely to be affected for any of the conditions tested. That is, for the tests completed, the amount of surface adsorption sites on nickel is far greater than the amount of AsH<sub>3</sub> that is expected to reach the outer surface of the anode due to convection/diffusion from the gas delivery stream. This result supports the finding that only the outer portion of the anode surface will be affected if fast adsorption of AsH<sub>3</sub> occurs.

Given the above finding that only the outer surface of the anode is affected, and the finding that secondary nickel phases form only after lengthy operation, the results from this work further suggest that the kinetics associated with the formation of NiAs(s) is slow. The SOFCs subjected to short-term AsH<sub>3</sub> injection showed no formation of a secondary nickel phase, while the SOFC subjected to extended testing showed such a secondary phase even though the extended test occurred at much lower AsH<sub>3</sub> concentration (0.1 ppm versus 1 and 2 ppm) and much less total AsH<sub>3</sub> delivery.

Finally, the results also indicate that the concentration of  $AsH_3$  in the coal syngas does not greatly affect the rate of reaction for the formation of the secondary nickel phase. That is, in spite of having a greater concentration and total amount of arsenic, the short-term high concentration tests (100 h @ 1 and 2 ppm) did not show any secondary nickel phase as evidenced by the extended low concentration test (800 h @ 0.1 ppm).

The fact that the As reacts mainly at the surface of the anode to form NiAs indicates that AsH<sub>3</sub> will primarily impact the performance of the cell through the formation of a less electrically conductive phase. Hence, AsH<sub>3</sub> should not pose as great a threat to cell performance as other trace coal syngas species such as HCl or H<sub>2</sub>S, which have been shown to as well attack the critical reaction zone near the electrolyte. In addition to these ideas, the formation of nickel arsenide within the anode of the SOFC may also be suppressed by the high H<sub>2</sub>O content of the gas inside the SOFC due to the electrochemical conversion of H<sub>2</sub> at the anode-electrolyte interface. Previous research has shown that steam may be used to remove arsenic from Ni-based steam shift catalyst pellets at temperatures between 700 and 800 °C [2]. Due to the large amount of steam found in the anode of the SOFC, this may be a reason for the suppression of the formation of nickel arsenide towards the anode-electrolyte interface.

Finally, given that extended testing shows a second nickel phase formation, and given that commercial SOFCs are intended to operate up to 40,000 h, it is concluded that the formation of secondary nickel arsenide phases will take place under existing SOFC coal syngas conditions, and that cleanup methods that ensure low concentrations of As ( $\ll$ 0.1 ppm) will be needed.

## 5. Conclusions

The effect of coal syngas containing AsH<sub>3</sub> on the performance of SOFCs at various operational temperatures, current densities, and AsH<sub>3</sub> concentrations were studied. The results indicate that secondary nickel arsenide phases are able to form in an SOFC anode in the presence of AsH<sub>3</sub>. The injection of 1 and 2 ppm AsH<sub>3</sub> was shown to cause a minor amount of degradation. The addition of the trace species also causes an increase the cell voltage fluctuation for reasons not yet clear. Although AsH3 has been shown to affect the anode of the SOFC, its effects are not nearly as acute or detrimental as those of other trace species such as HCl or H<sub>2</sub>S. Rather than attacking the electrochemically active sites (as by HCl and H<sub>2</sub>S), it instead forms a stable secondary nickel phase, first in the outer regions of anode of the SOFC due to fast adsorption. Because the cell degradation is relatively minor, it is apparent that the form of NiAs(s) created is not purely resistive to SOFC operation thereby allowing for the continued transport of electrons. While this work has shown that NiAs(s) forms at AsH<sub>3</sub> concentrations possibly expected in coal-based SOFC systems, it is recommended that longer-term tests be completed to better understand the rate and propagation behavior of the formation of secondary nickel arsenide phases in the SOFC anode. Since SOFCs are intended to operate for up to 40,000 h, the longer-term tests will help indicate if the propagation of NiAs(s) will further degrade the performance of the SOFC anode through eventual reaction of As with nickel at the more critical electrochemical interface.

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