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# Review Effects of coal syngas impurities on anodes of solid oxide fuel cells

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## ABSTRACT

A literature review is conducted to summarize the studies on the identification of impurities in coal syngas and their effects on the performance of Ni-yttria stabilized zirconia (Ni-YSZ) anode of solid oxide fuel cells (SOFCs). Coal syngas typically contains major species, CO, H<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub>, N<sub>2</sub>, and H<sub>2</sub>S as well as trace impurities. Thermodynamic equilibrium calculations have indicated that trace impurities species such as Be, Cr, K, Na, and V in the coal syngas form condensed phases under warm gas cleanup conditions and can be effectively removed by the cleanup processes. For meaningful data comparison, a practical parameter is formulated to quantify the level of degradation normalized with respect to the relevant experimental parameters. Experimental results show that the existence of Hg, Si, Zn and NH<sub>3</sub> in the coal syngas impacts the SOFC anode performance to some extent. Impurity species such as Cl, Sb, As, and P cause severe cell voltage degradation due to attack on the Ni-YSZ anode. Sb, As and P have the potential to react with Ni to form secondary phases in the Ni-YSZ anode, which deteriorate the catalytic activity of the anode.

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#### Contents

1. 2.	Background Thermodynamic equilibrium calculations			
3.	Effects of coal syngas impurities on SOFC performance			
	3.1. Data con	nparisons	597	
	3.1.1.	Arsenic (As)	598	
	3.1.2.	Phosphorus (P)	598	
	3.1.3.	Antimony (Sb)	598	
	3.1.4.	Ammonia (NH3)	599	
	3.1.5.	Zinc (Zn)	599	
	3.1.6.	Chlorine (Cl)	600	
	3.1.7.	Mercury (Hg)	600	
	3.1.8.	Cadmium (Cd)	600	
	3.1.9.	Selenium (Se)	601	
	3.1.10.	Silicon (Si)	601	
4.	Summary and	remarks	601	
	Acknowledgements			
	References		601	

### 1. Background

\* Corresponding author. Tel.: +1 304 293 3111x2335; fax: +1 304 293 6689. *E-mail address:* fcayan@mix.wvu.edu (F.N. Cayan). Solid oxide fuel cells have become one of the most viable candidates for future power plants due to their high efficiency and fuel flexibility. Coal is the most abundant fuel source for electricity generation. The combination of a coal gasifier with a SOFC not only

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#### Table 1

Syngas compositions generated by different gasifiers (vol.%) [4]

Gasifier type	Moving-bed	Fluidized-bed	Fluidized-bed		Entrained-bed			
	Lurgi <sup>a</sup> Illinois no. 6 <sup>b</sup>	Winkler <sup>a</sup> Texas lignite <sup>b</sup>	Destec <sup>a</sup> Appalachian Bit. <sup>b</sup>	Koppers-Totzek <sup>a</sup> Illinois no. 6 <sup>b</sup>	Texaco <sup>a</sup> Illinois no. 6 <sup>b</sup>	Shell <sup>a</sup> Illinois no. 6 <sup>b</sup>	Siemens <sup>a</sup>	
Mol percent								
Ar	Trace	0.7	0.8	0.9	0.9	1.1		
CH4	3.3	4.6	0.6	-	0.1	-	0.002	
C2H4	0.1	-	-	-	-	-	-	
C2H6	0.2	-	-	-	-	-	-	
CO	5.8	33.1	45.2	43.8	39.6	63.1	27.001	
CO2	11.8	15.5	8.0	4.6	10.8	1.5	1.770	
COS	Trace	-	-	0.1	-	0.1	0.037	
H2	16.1	28.3	33.9	21.1	30.3	26.7	13.211	
H2O	61.8	16.8	9.8	27.5	16.5	2.0	53.165	
H2S	0.5	0.2	0.9	1.1	1.0	1.3	0.421	
N2	0.1	0.6	0.6	0.9	0.7	4.1	4.375	
NH3+HCN	0.3	0.1	0.2	-	-	-	0.006	

<sup>a</sup> Manufacturer.

<sup>b</sup> Coal.

provides clean energy by reducing the emissions but also may help reduce plant costs because high efficiency electrochemical systems should result in smaller physical plant size for a given electric power output as compared to conventional electricity generation techniques.

Coal gasification is a process in which coal is mixed with an oxidant  $(O_2 \text{ or air})$  and steam in a reactor operating under the pressure of 24–70 atm at 500–1800 °C to produce syngas-containing CO, H<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub> and N<sub>2</sub> and also trace amounts of nearly all of the naturally occurring elements depending on the rank and geographical origin of the coal [1,2]. oxygen-blown gasification is often used since less combustion of coal is needed to heat the reactants and less work is needed to compress the gases entering the reactor [2]. Moreover, oxygen-blown gasification will help enable future CO<sub>2</sub> sequestration techniques [3]. Three types of coal gasification systems have been used throughout industry; namely, moving-bed, fluid-bed, and entrained flow. Table 1 shows the compositions of the raw syngas derived from these three major gasification systems [4]. The product syngas composition is extremely dependent on the coal as well as the gasification process. Coal syngas is typically a "dirty" fuel that contains a lot of impurities. Table 2 shows trace impurities and their concentrations in the coal syngas generated by the gasification stream of Eastman Chemical Company's complex at Kingsport Tennessee and an estimate from Univer-

#### Table 2

Trace impurities and their concentration in coal syngas [5]

Contaminant	Concentration at the Kingsport facility (ppmv)	UND-EERC estimat
Arsine (AsH <sub>3</sub> )	0.15-0.58	0.2
Thiophene		1.6
Chlorine (Cl)		120
Methyl Fluoride (CH₃F)	2.6	
Methyl Chloride (CH <sub>3</sub> Cl)	2.01	
Hydrogen Chloride (HCl)	<1	
Fe(CO) <sub>5</sub>	0.05-5.6	
Ni(CO) <sub>5</sub>	0.001-0.025	
CH <sub>3</sub> SCN	2.1	
Phosphene (PH₃)	1.9	
Antimony (Sb)	0.025	0.07
Cadmium (Cd)		0.01
Chromium (Cr)	<0.025	6.0
Mercury (Hg)	<0.025	0.002
Selenium (Se)	<0.15	0.17
Vanadium (V)	<0.025	
Lead (Pb)		0.26
Zinc (Zn)	9.0	

sity of North Dakota Energy and Environmental Research Center [5].

Although recent studies have shown the feasibility of fueling SOFC systems with coal syngas [6–8], the performance and the durability of SOFCs are affected by the presence of the impurity species in coal syngas. Therefore, cleanup techniques like absorption, adsorption, diffusion through a membrane, chemical conversion and filtering have been employed to remove some of the species like H<sub>2</sub>S, halides and fly ash particles [1]. Although these present cleanup processes are capable of removing H<sub>2</sub>S, halide and particulate matter to very low levels, these processes are carried out at ambient temperature, thereby removing a significant portion of the syngas thermal energy [3]. The US DOE is currently working on the development of warm gas cleanup systems that will allow the removal of H<sub>2</sub>S, HCN, HCl, particulate matter and alkali species from coal syngas at temperatures of 250–500 °C [1,3,9]

The impact of major impurities, such as sulfur and carbon on the Ni-YSZ anode has been studied by researchers and the results are available in the literature [10–12]. However, the shortterm and long-term effects of trace impurities (As and P) on the SOFC performance are still unclear. In order to formulate remedies for the undesirable effects of the impurities, it is imperative to understand the underlying mechanisms through which the cell performance has deteriorated. In this paper, a literature review is presented to summarize the studies on the identification of various impurities in coal syngas and their effects on performance of SOFCs.

# 2. Thermodynamic equilibrium calculations

Thermodynamic equilibrium calculations have been performed by several researchers to predict the chemical nature and abundance of relevant trace impurity species as a function of temperature range expected in a coal gasification system [2,3,13–16]. The exact identity of the species proceeding from the gasifier to the fuel cell depends on the starting coal composition, the gasifier design and the syngas cleanup technology used. Trembly et al. [3] have performed these calculations under warm gas cleanup conditions and concluded that trace species like Be, Cr, K, Na, and V in coal syngas form condensed phases and can be removed efficiently before reaching SOFC anode. They also concluded that Sb, As, Cd, Pb, Hg, P, Zn and Se form vapor phase species. In addition, Sb, As and P have the potential to form secondary phases with Ni in the SOFC. Krishnan et al. [14] also made thermodynamic equilibrium calculations using gas streams representative of an oxygen-blown slugging

Table 3		
Status of trace impurity species in a coal gas stream	[14]	

Component	>1000 °C	400-800°C	100-400°C	<100 °C
As	AsO, As <sub>2</sub>	AsO, As <sub>4</sub>	As <sub>2</sub>	AsH <sub>3</sub>
Ве	Be(OH) <sub>2</sub>	Condensed species	Condensed Species	Condensed Species
Hg	Hg	Hg	Hg, HgCl <sub>2</sub>	Hg, HgCl <sub>2</sub>
В	HBO	HBO	HBO	_
V	VO <sub>2</sub>	Condensed species	Condensed species	Condensed species
Se	H <sub>2</sub> Se, Se, SeO	H <sub>2</sub> Se	H <sub>2</sub> Se	H <sub>2</sub> Se
Ni	NiCl, NiCl <sub>2</sub>	Condensed species	Ni(CO) <sub>4</sub>	Ni(CO) <sub>4</sub>
Со	CoCl <sub>2</sub> , CoCl	Condensed species	Condensed species	Condensed species
Sb	SbO, Sb <sub>2</sub>	SbO, Sb <sub>2</sub>	Sb <sub>4</sub>	Condensed species
Cd	Cd	Cd	CdCl <sub>2</sub>	Condensed species
Pb	Pb, PbCl <sub>2</sub>	PbS, Pb, PbCl <sub>2</sub>	Condensed species	Condensed species
Zn	Zn	Zn, ZnCl <sub>2</sub>	Condensed species	Condensed species

gasifier. Table 3 displays the chemical forms and partitioning of the trace species at different temperature ranges [14].

As can be seen from Table 3, although the results may vary with the coal and operating conditions of the gasifier, under cold gas cleanup conditions (<100 °C) some impurity species like Be, V, Co, Sb, Cd, Pb and Zn will form condensed phases and can be removed efficiently. However, under warm/hot gas cleanup conditions (>250 °C), trace species like Sb, Cd, Pb and Zn will form vapor phase species and may not be captured by the filters. These impurities have a potential to interact with the SOFC anode.

## 3. Effects of coal syngas impurities on SOFC performance

So far, commonly used anode material for YSZ electrolyte based SOFCs is Ni-YSZ in which nickel metal particles and YSZ particles are intermixed. Ni is known to be a good catalyst for hydrogen oxidation as well as an electron conductor. YSZ provides ionic conductivity to allow oxygen ions to diffuse farther into the anode. When using Ni-YSZ anode fueled with H<sub>2</sub> at 800 °C, the maximum power density that can be achieved is ~1 W cm<sup>-2</sup> [17]. The Ni-YSZ anode allows the reaction between the H<sub>2</sub> and CO in the fuel gas and the oxygen ions transported through YSZ electrolyte to generate electrons and CO<sub>2</sub> and H<sub>2</sub>O gases. When a Ni-YSZ anode is operated in the impurity-containing syngas, the impurities may affect:

- the mass transport of fuel gas molecules due to adsorption of the impurities on the anode surface and consequent blockage of gas diffusion channels,
- the catalytic ability of Ni toward chemical and electrochemical reactions since impurity atoms on the surface poison (deactivate) triple phase boundaries,
- the ability of YSZ to transport the oxygen ions by forming other phases (zirconium silicate or phosphate are theoretically possible),
- the electrical conductivity of Ni by forming Ni alloys,
- the conductivity of interconnect-anode interface, and
- the structural integrity of the Ni-YSZ anode and seal materials.

The above material interactions may also affect other material properties, such as thermal conductivity, porosity and modulus of elasticity which, in turn, may lead to performance degradation. The effect of trace impurity species on the performance of SOFC anodes must be measured in order to (i) determine the required level for removal of these species from coal syngas before reaching the anode and (ii) to develop new anode materials that resist the attack of these undesired poisoning effects.

Sulfur-containing compounds, which are primarily, present as  $H_2S$  in the coal syngas have received most attention [10–12,18–20] since they are known to have a significant impact on SOFC anode performance [10]. Several possible mechanisms may account for

the performance degradation of the Ni-YSZ anode due to presence of H<sub>2</sub>S in the fuel. However, the exact mechanism is not clearly defined because of the lack of detailed experimental data [10]. The performance degradation due to the presence of H<sub>2</sub>S is usually attributed to physical adsorption of H<sub>2</sub>S at the surface of the Ni-YSZ anode thereby reducing the effective region for electrochemical reactions. Depending on sulfur concentrations levels, further reaction of the absorbed H<sub>2</sub>S with Ni can result in nickel sulfide (NiS) which also reduces available reaction sites and causes a steady loss of performance [21]. Again, depending on operating conditions, some studies indicate that this process is reversible when the contaminant is removed [10]. Raw coal syngas contains 100-300 ppm of H<sub>2</sub>S and higher while other impurities are present in the syngas at much lower levels, typically lower than 20 ppm. So far, a few investigations have been performed on the effects of the trace impurities other than sulfur.

## 3.1. Data comparisons

The effects of trace impurities (As, P, Sb, Zn, Cl, Hg, Cd and Se) on the performance of SOFCs have been investigated in previous literature. These results have given general insight to the mechanisms by which the trace species may interact with the Ni-YSZ anode. In this paper we seek to determine how well prior work can be compared given the variety of test methods and conditions that may be employed. To obtain a first-order comparison between the experimental results from various researches, we use a plot of the modified cell power density versus the operating time. The modified cell power density, *P*\*, is defined by

$$P_* = P_{\text{ref}} - \left(\frac{P_0 - P}{P_0}\right) \tag{1}$$

where  $P_{ref}$  is the reference power density taken as 1,  $P_0$  is the power density at the time when the trace specie is introduced and P is the power density at any time. Since the purpose of this review is to study general trends of degradation, the experimental data from the literature is smoothed by curve fitting and then presented as functions of concentration and temperature (see Fig. 1). With this we anticipate that when data from different researchers are compared in the normalized sense  $(P^* vs. time)$  the influence due to operating at different fuel gas concentrations (H<sub>2</sub> and CO) and in the narrow range of current density ( $\sim$ 0.2–0.5 A cm<sup>-2</sup>) will be at least reduced. The only way to avoid such an approach as used here would be to impose detailed and strict test standards, but such has not vet been accepted by the research communittee. In short, while the experimental data reviewed in this paper are all for a Ni-YSZ anode based cell, there may be some variation in the experimental conditions and measurement techniques. That is why different experiments conducted by different investigators at seemingly similar or the same conditions may not yield the same results.



**Fig. 1.** Modified power density as a function of operating time upon exposure to 10 ppm  $As_2$  at 750 °C (inset figure: original experimental data from Ref. [23]).

## 3.1.1. Arsenic (As)

Arsenic is present in the coal syngas in the form of AsH<sub>3</sub> in the reducing environment of gasification and in the form of As<sub>2</sub> or As<sub>4</sub> molecule at warm gas cleanup system conditions [22]. Fig. 1 shows the modified cell power density as a function of operating time upon exposure of 10 ppm As<sub>2</sub> at 750 °C using the smoothed experimental data of Krishnan et al. [23]. It can be seen that a significant degradation occurs during first 10 h followed by a period of relatively slower but steady degradation. It was also reported that area specific resistance (ASR) increases from 1.40 to  $1.75 \Omega \text{ cm}^2$  after 60 h.

The effects of AsH<sub>3</sub> at 0.1 and 1 ppm level at 750 °C [22,23] and 1 ppm level at 800 °C [22,24] are shown in Fig. 2. The smoothed experimental data obtained from different researchers agree well at different temperatures. However, at 750 °C, the cell seems to be stable for 600 h and then it experiences a sudden decrease in the power density, which cannot be captured with the short-term experiments. At elevated operating temperature of the cell, the power density of the cell decreases more rapidly and then reaches a plateau.

Krishnan et al. [25] has also examined the As distribution on the Ni-YSZ anode surface and have found that it mainly reacts with Ni and appears at the Ni site. This is consistent with the results of Trembly et al. [3], which has shown that the conversion ratio of Ni



**Fig. 2.** Modified power density as a function of operating time upon exposure to 0.1 and 1 ppm AsH<sub>3</sub> at 750 and 800  $^{\circ}$ C (smoothed experimental data from Refs. [22–24]).



**Fig. 3.** Modified power density as a function of operating time upon exposure to 2, 5, 10 and 20 ppm levels of PH<sub>3</sub> at 750, 800 and 900  $^{\circ}$ C (smoothed experimental data from Refs. [24,26–28]).

to NiAs is very high. Ten percent Ni will convert to NiAs at 1 atm and 700 °C after 3000 h. Arsenic reacts with Ni to form NiAs, which indicates that the presence of AsH<sub>3</sub> affects the SOFC performance through the formation of a less electrically conductive phase. Hence AsH<sub>3</sub> should not pose as great a threat to the SOFC performance as the other trace species such as HCl and H<sub>2</sub>S which have been shown to attack the critical reaction zone near the electrolyte [22].

#### 3.1.2. Phosphorus (P)

The nature of phosphorous compounds in the coal syngas is not known accurately. However equilibrium calculations [3,25] indicated that P may exist as  $(P_2O_3)_2$  (g) and  $PH_3$ (g) depending on the temperature and pressure of the gas cleanup system. Under the SOFC operating conditions (typically at 700–900 °C and atmospheric pressure), PH<sub>3</sub> (g) is hydrolyzed to form HPO<sub>2</sub> vapor [25].

Marina et al. [24] have studied the effects of 2 ppm PH<sub>3</sub> at 800 °C for 600 h. The tests have showed that that exposure to PH<sub>3</sub> leads to the anode degradation and this degradation is irreversible. It was also reported that ASR of the cell increased from 0.19 to  $0.27 \Omega \text{ cm}^2$  after 280 h. The degradation is due to the formation of a new phase between phosphorous and YSZ as opposed to the fact that As attacks Ni [25]. However, there is also other evidence showing that PH<sub>3</sub> in coal syngas forms Ni<sub>5</sub>P<sub>2</sub> [3]. On the other hand, in the presence of oxygen, PH<sub>3</sub> can also be oxidized to be P<sub>2</sub>O<sub>5</sub>, so the amount of Ni<sub>5</sub>P<sub>2</sub> can be reduced [3]. Fig. 3 shows the smoothed results from experiments of [24,26–28].

Researchers at West Virginia University have also studied the effect of PH<sub>3</sub> on the performance of Ni-YSZ anode. Zhi et al. [28] have employed electrochemical impedance spectroscopy (EIS) to examine the charge transfer and the mass transfer processes in the Ni-YSZ anode during operation in the PH<sub>3</sub>-containing syngas. Their results have shown that the charge-transfer resistance and the mass transfer resistance significantly increase upon exposure to the PH<sub>3</sub>-containing syngas while the performance of the Ni-YSZ is stable in the clean syngas. After exposure to the PH<sub>3</sub>-containing syngas, the morphology of the Ni-YSZ anode surface significantly changed as shown in Fig. 4. The anode surface has become smoothed (at a local level), and the porosity of the anode is reduced. Further XRD analysis has revealed that P has reacted with Ni and Zr, leading to the formation of Ni<sub>3</sub>(PO)<sub>4</sub> and ZrP<sub>2</sub>O<sub>7</sub> (Fig. 5).

### 3.1.3. Antimony (Sb)

Under the warm gas cleanup conditions, antimony is mainly present in the form of  $SbO_2H_2$  [3]. Thermodynamic equilibrium



Fig. 4. SEM images: (a) a Ni-YSZ anode operated in the clean syngas and (b) a Ni-YSZ anode operated in the PH<sub>3</sub>-containing syngas.



**Fig. 5.** XRD patterns: (a) a Ni-YSZ anode operated in the clean syngas and (b) a Ni-YSZ anode operated in the PH<sub>3</sub>-containing syngas.

calculations have shown that it is possible for Sb to react with Ni to form a NiSb alloy. However, the conversion ratio is not high ( $\sim$ 3.5%) [3]. Krishnan et al. [29] have studied the effect of SbO, which is claimed to be the stable species under the anode operating condition. The presence of 8 ppm level of SbO in the fuel stream does not result in any significant decline ( $\sim$ 1%) of the power density at 800 and 850 °C after 100 h (Fig. 6). Interestingly at 750 °C a slight improvement is observed in performance at the same condition. Given the lack of detailed data before the injection of the SbO, it is



**Fig. 6.** Modified power density as a function of the operating time upon exposure to 8 ppm SbO at 750, 800 and 850 °C (smoothed experimental data from Ref. [29]).

unclear if the improvement is due to a "burn-in" effect, or due to SbO interacting with the cell materials.

#### 3.1.4. Ammonia (NH<sub>3</sub>)

The concentration of ammonia in coal syngas can be as high as 0.5 volume percent depending on the gasifier design and operating condition [30]. The tolerance limit of NH<sub>3</sub> for the SOFC is reported to be 5000 ppm. After 6500 h testing with simulated coal syngas at 1000 °C, the fuel cell did not show any measurable degradation [31]. Such a result will eventually need to be confirmed for present SOFC technology which operates at much lower temperatures.

## 3.1.5. Zinc (Zn)

According to thermodynamic predictions, zinc is expected to form a condensed metal-oxide at warm gas conditions [25]. Hence, zinc should not exist in significant concentrations within the gas that reaches the anode. Further, it is reported that Zn vapor (whatever may reach the cell) may be carried over the electrode surface without deposition [25]. If it coexists with HCl in the coal syngas, the carryover effect will be enhanced. Therefore the effect of Zn poisoning should be smaller than that of As and P. Fig. 7 shows the modified cell power density as a function of the operating time upon exposure to a high concentration of zinc (10 ppm Zn vapor) at 750 and 800 °C [25]. During 100 h of testing, the cell degrades slowly and the degradation is less than 1% at 750 and 800 °C. This is well within the normal decay rate for current SOFC technology. However, increasing the operation temperature accelerates the degradation.



**Fig. 7.** Modified power density as a function of the operating time upon exposure to 10 ppm Zn at 750 and 800 °C (smoothed experimental data from Ref. [25]).



**Fig. 8.** Modified power density as a function of the operating time upon exposure to  $40 \text{ ppm CH}_3\text{Cl}$  at 800 and 850 °C (smoothed experimental data from Ref. [5]).

## 3.1.6. Chlorine (Cl)

Chlorine is typically present in the forms of HCl and CH<sub>3</sub>Cl in the coal syngas. Krishnan et al. [5] studied the effect of CH<sub>3</sub>Cl and found no significant degradation of the performance after 140 h of exposure to 40 ppm CH<sub>3</sub>Cl at 800 °C (Fig. 8). However, when the temperature is increased from 800 to 850 °C, degradation also increases (~6%).

Recently, Trembly et al. [32] have investigated the effect of HCl on the SOFC at 800 and 900 °C. The results have indicated that introduction of 20–160 ppm HCl leads to a performance loss of circa 13–52% (Fig. 9). It was also shown that the cell performance loss at 800 °C is mostly associated with the increase in charge-transfer resistance whereas at 900 °C the performance losses are affected by increases in the ohmic resistance and charge-transfer resistance across the SOFC [32]. Fig. 9 also shows the smoothed results from experiments of [25] conducted by introducing 40 ppm HCl at 750 and 800 °C. Although the experimental conditions are similar, observed degradation is different. This may be due to different measurement techniques.

# 3.1.7. Mercury (Hg)

Mercury appears in the form of vapor in the coal syngas due to its high vapor pressure. When a cell is exposed to 7 ppm Hg vapor, the



**Fig. 9.** Modified power density as a function of the operating time upon exposure to 20, 40 and 160 ppm levels of HCl at 750, 800 and 900 °C (smoothed experimental data from Refs. [25,32]).



**Fig. 10.** Modified power density as a function of the operating time upon exposure to 7 ppm and 180 ppb levels of Hg at 750, 800 and 850 °C (smoothed experimental data from Ref. [29]).

performance of the cell shows no significant degradation at 750 °C after 150 h [29] (Fig. 10). However, the cell performance declines more rapidly at 800 °C ( $\sim$ 2% of degradation). After the introduction of 180 ppb Hg vapor to the system, the performance of the cell shows no significant degradation after 120 h of testing [23,29] (Fig. 10). However, at 750 °C, an improvement is observed in performance at the same condition.

It was thought that HgO could be condensed and deposited on the surface of anode, leading to the blockage of the diffusion of  $H_2$ into the triple phase boundary. However, further work has revealed that Hg shows no tendency to form oxides [3].

### 3.1.8. Cadmium (Cd)

Under the warm gas cleanup condition, the Cd vapor is found to be the only equilibrium form [3]. Krishnan et al. [29] has tested the SOFC anode in 5 ppm Cd vapor at 800 and 850 °C for 120 h. No significant degradation is observed at 800 °C. However, 25% of power density is lost at 850 °C (Fig. 11). The degraded performance may be due to formation of secondary Cd phases since Ni and Cd were found to form compounds at the Ni rich regions at 800 °C [33].



**Fig. 11.** Modified power density as a function of the operating time upon exposure to 5 ppm Cd vapor at 800 and 850 °C (smoothed experimental data from Ref. [29]).



**Fig. 12.** Modified power density as a function of the operating time upon exposure to 0.5 and 5 ppm levels of  $H_2Se$  at 800 °C (smoothed experimental data from Ref. [33]).

#### 3.1.9. Selenium (Se)

Selenium could be present in the forms of  $H_2Se$ , AsSe and PbSe under the warm gas cleanup condition [3]. Fig. 12 shows the variation of the modified power density with time after introduction of 0.5 and 5 ppm levels of  $H_2Se$  [34]. The introduction of 0.5 ppm  $H_2Se$  causes the power density to be degraded steadily. Increasing the  $H_2Se$  concentration to 5 ppm leads to a significant loss of the power density at the initial stage; about 20–25% of power density is lost after 75 h of exposure. It was also reported that the observed degradation is partially reversible upon re-exposure of the anode to pure  $H_2$  [34]. The rapid, reversible part of degradation indicates a surface adsorption mechanism while the permanent part implies either formation of a secondary phase inhibiting the cell transport and reaction processes or partial mechanical degradation of the current collection materials [34].

### 3.1.10. Silicon (Si)

Silicon is found to be present in the form of  $Si(OH)_4$  in the coal syngas.  $Si(OH)_4$  may decompose into  $SiO_2$  and  $H_2O$ .  $SiO_2$  could be depositing on the anode surface to form a silica rich region [17]. Although  $SiO_2$  is expected to have no severe impact on the performance, it may form a glass like layer with Na<sub>2</sub>O at the electrode and electrolyte interface.

#### 4. Summary and remarks

From a review of available literature, several conclusions can be reached regarding the effect of trace coal species on SOFC operation. Trace impurity species including As, Be, Cl, Cd, Cr, Hg, Na, K, P, Pb, Sb, Se, V, and Zn have been observed in the coal syngas exiting a gasifier. Thermodynamic equilibrium calculations predict the stable chemical forms of these species and their partitioning behavior between gas and solid phases in post cleanup gas streams. The impurity species that are present in the solid state are not considered to be problematic since they can be removed via filtration to satisfactory levels. Impurities such as Sb, As, Cd, Pb, Hg, P, and Se usually form vapor phases under warm gas cleanup conditions, which poses a potential threat. In addition, As, Hg and Se can also form vapor phase species under cold gas cleanup conditions (<100 °C), thus are likely to degrade the SOFC anode.

For meaningful data comparison, a practical parameter was formulated to quantify the level of degradation normalized with respect to the relevant experimental parameters. Experimental results show that the presence of Hg, Si, Zn and NH<sub>3</sub> in the coal syngas does not strongly affect the performance of the SOFCs. Cd and Se lead to the deterioration of SOFC anodes to some extent. Cl, As, Sb and P species cause severe degradation of SOFC anodes. As, Sb and P can react with Ni to form secondary phases. Impurity species degrade SOFC performance by poisoning the catalytic activity of Ni and by preventing the mass transport due to clogging of pores inside the anode.

Thus far, most literature shows tests performed within a short period (<300 h). However, tests longer than at least 10,000 h are required to ascertain the threat of impurities for commercial application. This is important because low levels of impurities may gradually accumulate during long-term operation. Within a short period, they may react only with the outer layer of the anode, possibly without significant effect on the SOFC performance until the impurities reach the triple phase boundary (electrolyte-anodefuel gas). In addition, thus far most tests are performed on single impurity species. However, the synergistic effects of simultaneous multiple impurities could alter both the degradation rate and mechanisms.

Finally, the experimental results from various researchers show different levels of degradation even for the same impurity level. Some of the differences noted may be the result of different operating conditions and different test methods used in the studies. However, it could also be due to a variety of other test hardware issues, which is why performing comparisons such as provided by the present paper can be valuable to help ensure meaningful conclusions are reached.

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