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Analysis of gas phase composition in fuel and exhaust gas in Solid Oxide Fuel Cells

Wei Zhang
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Analysis of gas phase composition in fuel and exhaust gas in Solid Oxide Fuel Cells

Wei Zhang

Dissertation submitted
to the Eberly College of Arts and Sciences
at West Virginia University
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy in
Chemistry

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Morgantown, West Virginia
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Key words: Solid Oxide Fuel Cell, Mass Spectrometry, In-situ Methods,
Coal Syn-gas, phosphine, degradation.

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ABSTRACT

Analysis of gas phase composition in fuel and exhaust gas in Solid Oxide Fuel Cells

Wei Zhang

Direct utilization of coal syngas in Solid Oxide Fuel Cell faces a number of challenges. One of the impediments to the implementation of SOFCs is their degradation in the presence of impurities in the fuel. Phosphine (PH_3) is present in coal syngas at ppm levels, and a number of reports have shown that the nickel anode is damaged by long term exposure to ppm levels of phosphine in various fuels. Because phosphine is exposed to high temperatures ($\sim 800^\circ\text{C}$) and varying amounts of water and oxygen in the fuel, the exact nature of the phosphorus species reaching the anode is unknown. Thermodynamic calculations vary in the predicted species at equilibrium, some of which are HPO (mass 48), HPO_2 (mass 64), HPO_3 (mass 80), and P_4O_{10} (mass 288). Mass spectroscopic analyses of exhaust gases from SOFC test systems are provided, with and without Ni/YSZ anodes in the path of the gas flow. The mass spectrometer, a MKS Cirrus system, has a mass range of 1 – 100 amu and a detection limit of ~ 0.001 torr. The mass spectrometry is applied to full-cell tests. The cell is operated in H_2 as fuel. The cell is tested with and without 10-20 torr water added, with and without 20 ppm PH_3 added, and with different current applied to the cell. Degradation in cell performance is observed over short times during PH_3 exposure but not over the entire course of experiment. The water generated by the electrochemical oxidation of H_2 is detected. Leaks are assessed in the tests and air impurities such as N_2 , O_2 , Ar and CO_2 signals are also detected. No new mass signals appear in all conditions, suggesting that the possible phosphine reaction products have a mass outside the 100 amu range of the mass spectrometer. Post-mortem analysis of the cell using SEM, EDX and XRD was performed. After PH_3 exposure, a new layer of crystalline nickel phosphide material was found on the anode surface similar to the previous studies.

*Dedicated to my mother Fengying Bian, father Mingjiu Zhang
and my great wife Lu Luo*

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Chapter 1. Introduction

1.1 Background.

Solid Oxide Fuel Cells (SOFC) are devices that convert chemical energy in a gaseous fuel directly to useful electrical energy and high quality heat. SOFCs offer several advantages over heat engines. The SOFC does not need combustion, so it is highly efficient and environment friendly, and it does not contain moving parts that requires periodic maintenance. The most suited applications of SOFC will be for stationary power generation, especially power plants, where the cost of fuel and fuel delivery is high for the customers, and where it is much easier to deliver electricity to end customers. SOFC can utilize a wide variety of fuels, such as H_2 , natural gas (methane), coal syngas, biogas and diesel.[1-6] For most power plants, coal is the most economic and abundant fuel source.

In a solid oxide fuel cell, the fuel, such as hydrogen, is fed to the anode, and oxidized by oxygen ions, releasing electrons to the anode current lead. Then the electrons pass through the outer circuit and load, and return to the cathode of the solid oxide fuel cell. At the cathode, oxygen reacts with the electrons to form oxygen ions (O^{2-}). The oxygen ions pass through the electrolyte, which is ion-conductive, to the anode to complete the circuit. Figure 1.1 shows a complete circuit of a working solid oxide fuel cell, with the oxygen ion-conductive electrolyte.

Figure 1.1 Complete circuit of a Solid Oxide Fuel Cell © www.fctec.com

1.2 Significance

One of the major advantages of SOFC is the flexibility of fuel. Many types of fuel can be utilized directly by a solid oxide fuel cell. Coal is the most abundant fossil fuel in the earth. The United States of America has over one quarter of the coal reserves in the world. Currently, coal is mined in 26 of the 50 states. Primarily, coal is used to generate electricity. Over 40% of the electricity in the United States comes from burning coal.[7-9]

Solid oxide fuel cells offer great energy conversion efficiency over other power sources, while producing fewer emissions. Gasification of the coal is a relatively clean method compared to direct burning. Coal reacts with steam at high temperatures, producing syngas, a mixture of H_2 , CO , CO_2 and H_2O . Then most of the impurities in the gas, such as ash, are removed by gas cleanup. This “Clean Coal Technology” is used in

some power plants in the states of Florida and Indiana, such as the Tampa Electric's Polk Power Station in Florida. [10]

However, after the gasification and filtering, there are still trace levels of impurities. They are not harmful to the gas turbines in the existing power plants, and they are within the health limits in the exhaust gas. However, some of them are poisons to SOFCs. Research has been performed to investigate effects of these impurities on the Ni/YSZ anode of SOFCs. [11-12] Evidence of anode degradation was found because of the exposure to ppm level of impurities including PH_3 , H_2S , AsH_3 , etc. A great amount of work was done at West Virginia University to determine the possible mechanism of degradation, to develop new materials that will tolerate specific levels of impurities, and to improve the long term performance of SOFCs. [11, 13-16]

In the previous studies, little is known about the actual gas-phase composition near the anode of SOFC. Impurities such as PH_3 in the fuel are blended into the stream to simulate the actual syn-gas before it enters the heated operation zone. Reaction and possible products of PH_3 , H_2 and H_2O are not clear. There are no existing experimental data supporting the thermodynamically predicted products. What species of phosphorus is actually getting to the anode is also unknown. A detailed and accurate measurement of gas species around the anode is necessary.

1.3 Objectives

The major objectives of this work are the studies of reactions between impurities in coal syngas and other species at SOFC operation conditions, in-situ determination of

gas-phase composition of fuel and exhaust gases, electrochemical characterization of the SOFC performance and degradation, and post-mortem analysis of the cells.

In this study, a new method is developed using a special type of quadruple mass spectrometer called a Residual Gas Analyzer (RGA) to determine the partial pressures of gases. The RGA continuously samples the gas phase using a one meter-long heated capillary. The RGA is connected to one of the four sampling points, inlets and exhausts of the anode and cathode, respectively. It has the capability to provide on-line data and analysis while the SOFC is operating.

Electrochemical characterizations are carried out periodically during the testing of the SOFC, including open circuit voltage (OCV), cyclic voltammetry (CV) to obtain the power curve and polarization curve, and electrochemical impedance spectrometry (EIS). The degradation of the anode caused by the poisoning effects of PH_3 is evaluated by its electrochemical performance.

The micro-structural and material phase changes of the anode are determined by Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), X-Ray Photoelectron Spectroscopy (XPS) and Energy-dispersive X-ray Spectroscopy (EDX). These post tests are done after the operation of the SOFCs on a variety of fuel compositions.

1.4 Dissertation Organization

This dissertation consists of 7 chapters including the introduction.

Chapter 2 is a detailed literature review of the past and current studies of impurities in the coal-derived syngas and their effects on the anode of Solid Oxide Fuel

cells. The review emphasizes the degradation of the anode, including changes in electrochemical performance and microstructures. A brief introduction to the use of in-situ analytical methods in the solid oxide fuel cell studies is also provided.

The work in this dissertation started in a fuel cell test stand in WVU Chemical Engineering with air tests and leak checks of the system. After a few cell tests, the sealing of the cell was found to be loose and difficult to improve. Then the work was moved to WVU Mechanical Engineering (WVU MAE) to use the Probostat apparatus as the testing platform. In the year 2012, due to safety reasons, the work was moved to the WVU Chemistry Research Lab (CRL).

In Chapter 3 the work done in WVU Chemical Engineering is discussed. This test stand has gas supplies of H_2 , N_2 , H_2S and PH_3 . Leak checks of the gas handling system, humidifier and furnace were conducted. Whole cell tests with different levels of H_2S and current change were performed despite the leaks in the system. The leak to the air was very hard to eliminate completely. The work on this test stand was terminated.

In Chapter 4, the work carried out in the MAE with the use of the Probostat is described. The Probostat is introduced as a new cell test platform. The results of the cell test with PH_3 are provided.

In Chapter 5 the gas phase reactions of impurities in coal syngas at high temperatures (no cell) are addressed. The heart of this chapter is focused on the gas composition and reaction tests done in the CRL with a tube furnace configuration and the Probostat. Several testing conditions including dry and wet H_2 , with and without PH_3 , and

with and without a Ni/YSZ sample piece were investigated in detail with the mass spectrometer.

In Chapter 6, the discussion focuses on the whole cell tests with a glass tape seal in the CRL. The results of different gas compositions and different current densities are provided.

Chapter 7 summarizes the major observation of the work, and provides conclusions and a plan for the future research.

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Chapter 2. Literature review

2.1 Introduction to Solid Oxide Fuel Cells (SOFC).

Fuel Cells produce electrical energy directly by oxidizing a fuel. The origin of fuel cells can be tracked back to the early 19th century. In the year of 1838, William R. Grove developed a new type of wet cell, using hydrogen as fuel and oxygen as oxidizer, called “gas batteries”. [1] Currently there are numerous types of fuel cells being developed and intensively investigated. Fuel cells are usually classified and named by the type of electrolytes used. The current major types of fuel cells include Alkaline Fuel Cell (AFC), Direct Methanol Fuel Cell (DMFC), Phosphoric Acid Fuel Cell (PAFC), Polymer Electrolyte Membrane Fuel Cell (PEMFC), Molten Carbonate Fuel Cell (MCFC) and Solid Oxide Fuel Cell (SOFC). The technical specifications of these types of fuel cells are listed in Table 2.1. [2]

Solid Oxide Fuel Cells operate at relative high temperature ranging from 600 °C to 1000 °C. While generating electricity, SOFC also produce a gas stream at high temperature. In a large-scale stack, after it has been successfully started up, the SOFC system itself can produce enough heat to remain at operational conditions, and the by-product heat is also very useful. [3-4]

The energy conversion efficiency of fuel cells is excellent, ranging from 40%-70%, much better than most heat engines. Internal combustion engines retain an average efficiency of 18% - 20%, while there is a theoretical thermodynamic limit of 37%. Large

electricity-generating steam turbines have an efficiency of up to 40%. Gas turbines offer a range of efficiencies from 20% - 60%, depending on the specific working model and mode. [5] Among the different types of fuel cells, the SOFC gives the highest efficiency, up to 70% - 80%. The hot exhaust gas can be used to operate a gas turbine, making it a combined cycle, thus further increasing the overall system efficiency. [6-7]

Table 2.1 Comparison of different types of fuel cells. [2]

Types of fuel cell	Electrolyte	Operation temperature	Fuel	Efficiency
Alkaline fuel cell (AFC)	Potassium hydroxide (KOH)	50 – 200 ⁰ C	Hydrogen/ hydrazine	50 - 55%
Direct methanol fuel cell (DMFC)	Polymer	60 – 200 ⁰ C	Methanol	40 - 55%
Phosphoric acid fuel cell (PAFC)	Phosphoric acid	160 – 210 ⁰ C	Hydrocarbons	~40 %
Proton-exchange membrane fuel cell (PEMFC)	Proton-exchange membrane (polymer)	50 – 80 ⁰ C	Hydrogen	40 - 50%
Molten carbonate fuel cell (MCFC)	Molten carbonate salt	~650 ⁰ C	Hydrogen, CO, natural gas	45 - 55%
Solid oxide fuel cell (SOFC)	Ytria stabilized zirconia (YSZ)	600 – 1000 ⁰ C	Hydrogen, CO, natural gas, coal syngas, oil, etc.	70 - 80%

SOFCs have three major components, the anode, the cathode and the electrolyte. The three parts are sandwiched together and the anode and cathode are separated by the electrolyte. Materials used in SOFCs must be carefully selected to meet the special needs (high temperature, oxidation/reduction atmosphere) of functions and operating conditions.

The anode has multiple functions and must meet several requirements. The anode material is usually made very porous to allow diffusion of the fuel to the active layer near the electrolyte. The material in the anode is often nickel mixed with yttria stabilized zirconia (YSZ, ZrO_2 doped with Y_2O_3). Most of the oxidation reactions occur within 20 μm from the electrolyte, a region called the active layer. [47] In some studies and in commercially available SOFCs, the anode is made of two layers: the active layer next to the electrolyte, and the supporting Ni/YSZ structure. Ni is a good electron conductor. At the same time, Ni serves as a catalyst for the oxidation of hydrogen. YSZ is an oxygen ion conductor above 500°C. It transfers the oxygen ions from the electrolyte to the oxidized fuel, and upon reaction, water and CO_2 are formed. [8] With hydrogen fuel, for example, the anode reaction is:

The electrolyte is a dense layer that separates gases from the anode and cathode sides. Yttria stabilized zirconia (YSZ), which is dense and hard, is widely used as a major electrolyte material in SOFCs. It is purely ion conductive in operation, and only allows oxygen ions to pass from the cathode through the electrolyte to the anode, but not the electrons. Yttrium in the YSZ creates vacancies for the oxygen ions to flow, and the yttrium stabilizes the cubic crystal structure of zirconia. Gadolinium-doped ceria (GDC) and samarium-doped ceria (SDC) are also used in some studies to promote oxygen ion conductivity and lower the working temperature. [9-12]

The cathode material is often lanthanum strontium manganate (LSM, $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$). It is electron-conductive at high temperatures. Furthermore, in this

perovskite structure, missing oxygen ions in the face-center position can create oxygen vacancies, thus making it ionically conductive as well. [13] As in the anode, the LSM is blended with YSZ in the cathode structure. The cathode is also made porous. A site where the cathode, electrolyte and oxygen gas meet together is called triple-phase boundary (TPB). Oxygen molecules are reduced at the TPB. [14] The cathode half reaction is:

Kröger-Vink notation (V_o^{oo} is oxygen vacancy, O_o^x is oxygen ion in the lattice) of the cathode half reaction (consuming oxygen vacancies) is:

Kröger-Vink notation of the anode half reaction (generating oxygen vacancies) is:

The overall cell reaction is:

The application of the SOFC is often focused on power generation, from large-scale power plants to small generators (less than 100kW) such as residential, transportation and auxiliary power units. Currently, research is directed at reducing the cost – both initial and operational. The U.S. Department of Energy's (DOE) Solid State Energy Conversion Alliance (SECA) program has proposed to develop SOFC systems that cost no more than \$700 per kilowatt. [15] In the year 2010, a 25kW, 120 cell stack was tested at FuelCell Energy Inc. with a claimed cost of \$400/kW. [16] Power plants

using SOFC together with on-site coal gasifiers are proposed to be a good substitute for conventional coal burning plants, with their ability to remove most of the impurities and to capture the CO₂. This type of power plant is often called integrated gasification fuel cell (IGFC). With the SOFC's ability to reform methane internally, natural gas fuel cell (NGFC) systems are also a promising clean power source. [17-18] Figure 2.1 is an illustration of SOFC system integrated with either coal gasification or a natural gas system.

Future work on SOFC will focus on increasing the life span, lowering cost, developing large stack systems and capturing the CO₂. The DOE is planning to initiate 250 kW modules in 2017, and this size of modules is to be used as bricks to build multi-megawatts power plants. By 2020, these systems are expected to have a life span of about 10,000 hours. This will allow, by 2025, the commercialization of 1-5 MW coal and natural gas-based power plants, with no less than 99% CO₂ captured and nearly zero NO_x emission. [17]

Figure 2.1 IGFC/NGFC power generation system block diagram. [17]

2.2 Electrochemical characteristics of Solid Oxide Fuel Cell

Electrochemical characterization of a SOFC is done as a routine tool to judge the performance of the fuel cell. The redox reactions on the electrodes are intensively investigated in experiments and theoretical calculations. [23] There are two types of electrochemical methods often used in characterization. [24] The DC methods include open circuit voltage (OCV), polarization curve (I-V curve) and galvanostatic tests. The common AC method used is electrochemical impedance spectroscopy (EIS).

Theoretically, the reversible open circuit voltage of a solid oxide fuel cell under standard conditions can be calculated by the change of Gibbs free energy. Taking

hydrogen as fuel for example, the overall reaction is shown in Equation 2-3. The reversible OCV in theory is:

$$\Delta E^0 = \frac{-\Delta G^0}{4F} \quad (2-4)$$

Then the OCV at another given temperature T is:

$$\Delta E_T = \Delta E^0 + \frac{\Delta S}{4F} (T - T^0) \quad (2-5)$$

The OCV with a given gas composition can be calculated using the Nernst equation, (α is the activity for the gases.)

$$\Delta E = \Delta E^0 + \frac{RT}{4F} \ln\left(\frac{\alpha_{H_2}^2 \cdot \alpha_{O_2}}{\alpha_{H_2O}^2}\right) \quad (2-6)$$

For a hydrogen cell working at 800°C, with 3% water vapor present in the fuel stream and pressure at 1 atm, the calculated OCV is 1.103V. However, due to possible gas leaks between the anode side and the cathode side, the theoretical OCV is difficult to reach in actual fuel cell tests. Usually the OCV is around 1.06-1.08 V depending on the fuel type in practice. The OCV is an important factor for the evaluation of SOFC performance.

The efficiency of SOFC can be calculated by the ratio of the electrical energy (Gibbs free energy) to the total change of enthalpy of the reaction.

$$\eta = \frac{\Delta G}{\Delta H} \times 100\% \quad (2-7)$$

For hydrogen fuel cells, the enthalpy change $\Delta H = -243.83$ kJ per mole of gas phase water formed. This is called the Lower Heating Value (LHV), as the production water will not condense under SOFC working temperatures. The LHV acknowledges the true total heat that could theoretically be recovered from the hydrogen combustion reaction. Then the enthalpy change can be expressed by the voltage E_h :

$$E_h = \frac{-\Delta H}{zF} = 1.26V \quad (2-8)$$

So the efficiency becomes:

$$\eta = \frac{\Delta G}{\Delta H} = \frac{E}{E_h} = \frac{V}{1.26V} \times 100\% \quad (2-9)$$

For a typical hydrogen cell at 1.103V, the theoretical efficiency is about 85%.

The polarization of a SOFC is the sum of several voltage losses. The various polarizations reduce the performance, so efforts are made to minimize the voltage loss, although it is impossible to eliminate them completely. The three major types of polarization are reaction rate loss, ohmic resistance loss and concentration loss. An example of calculated polarizations and their effective ranges in a SOFC model are shown in the I-V curve in Figure 2.2. [25]

Figure 2.2 Typical polarization curve for a SOFC model. [25]

The actual output voltage is given by:

$$V_{FC} = E - V_{act} - V_{ohmic} - V_{conc} \quad (2-10)$$

Here in the equation, V_{FC} is the output voltage of the fuel cell at any current. E is the Nernst reversible voltage. V_{act} is the activation voltage loss. This loss is due to the activation energy that the redox reaction needs to overcome to proceed. V_{ohmic} is the ohmic voltage loss, including the ion resistance in the electrolyte, which is dominant, and electron resistance within the electrodes. V_{conc} is the concentration voltage loss. This occurs mainly at high current because of the mass transfer rate limitation of reactant to the active zone of each electrode.

Electrochemical impedance spectroscopy is another useful characterization method. In EIS measurements, an AC voltage is applied to the cell, while the amplitude and phase of the AC current are monitored.

The AC voltage is:

$$E_{ac} = |E_{ac}| \sin(\omega t) \quad (2-11)$$

The AC current is:

$$I_{ac} = |I_{ac}| \sin(\omega t + \varphi) \quad (2-12)$$

φ is the phase shift of current relative to the AC voltage.

By definition from Ohm's law, the impedance is expressed as:

$$Z(\omega) = \frac{E_{ac}}{I_{ac}} = \frac{|E_{ac}| \sin(\omega t)}{|I_{ac}| \sin(\omega t + \varphi)} = |Z| \frac{\sin(\omega t)}{\sin(\omega t + \varphi)} \quad (2-13)$$

The impedance is often expressed using complex numbers, to reveal its real part (Z') and imaginary part (Z''): (j is the square root of -1) [26]

$$Z(\omega) = \frac{E_{ac}}{I_{ac}} = |Z|(\cos\varphi + j\sin\varphi) = Z' + Z'' \quad (2-14)$$

The two parts are often plotted on the Nyquist plot. The real part is on the horizontal axis and the negative value of the imaginary part is on the vertical axis. Figure 2.3 is an example of Nyquist plot. The higher frequency is on the left (smaller Z') side and the lower frequency is on the right (larger Z') side. The high frequency intercept on the horizontal axis represents the ohmic (or series) resistance R_s . The low frequency intercept represents the sum of ohmic and all polarization resistances $R_s + R_p$.

Figure 2.3 Example of a Nyquist plot from electrochemical impedance spectroscopy.

2.3 Trace amount impurities in coal syngas.

The cleanest way to utilize coal is through gasification. Coal gasification not only generates combustible syngas, but also produces useful materials for the chemical industry, without the necessity of burning the coal. For example, syngas can be used in the Fischer–Tropsch process to produce diesel, or converted into methane, methanol, and dimethyl ether in catalytic processes. [48] In a coal gasification reactor, the coal is heated to high temperature (600-1000°C), and is reacted with steam and oxygen at high pressure (up to 70 atm). [19] The reaction includes the partial oxidation of carbon, steam-carbon oxidation and the water-gas shift reaction:

The major components of coal syngas are H₂, CO, CO₂ and H₂O, with some trace amount of impurities. The composition of syngas products varies from different gasification plants. Table 2.2 shows an example of product gas from a typical gasification plant product gas. [20, 22]

Table 2.2 Typical major gas composition in coal syngas. [20, 22]

Component	Concentration (vol. %)
H ₂	29.3
CO	28.7
CO ₂	11.8
H ₂ O	27.2
N ₂	3.0

The trace impurities also differ by plant and the geographical origin of the coal. SOFCs can use the H₂ and CO in syngas as fuel. CO is a fuel and not a poison for SOFC anodes. However, some trace amount of impurities will harm the anode in many ways. There are methods of gas clean-up treatment for syngas to remove H₂S, halides and ash particles at ambient temperature. But for a more energy efficient process, future power plant design is expected to include removal of H₂S, HCN, HCl, ash and alkali at 250-

500°C in modern syngas plants, which is also being studied as a warm gas clean-up system. [21-22]

Table 2.3 Trace impurities and their concentrations in coal syngas [21]

Contaminant	Concentration at the Kingsport facility (ppm)
Arsine (AsH₃)	0.15-0.58
Thiophene	
Chlorine (Cl)	
Methyl Fluoride (CH₃F)	2.6
Methyl Chloride (CH₃Cl)	2.01
Hydrogen Chloride (HCl)	<1
Fe(CO)₅	0.05-5.6
Ni(CO)₅	0.001-0.025
CH₃SCN	2.1
Phosphine (PH₃)	1.9
Antimony (Sb)	0.025
Cadmium (Cd)	
Chromium (Cr)	<0.025
Mercury (Hg)	<0.025
Selenium (Se)	<0.15
Vanadium (V)	<0.025
Lead (Pb)	
Zinc (Zn)	9.0

Although coal syngas is cleaned, it still carries trace impurities such as arsine, hydrogen sulfide, phosphine and hydrogen chloride. Table 2.3 lists some of the impurities found in a Kingsport, TN syngas facility. These volatile species are detected after the warm gas clean-up process where the syngas has been cooled. However, while the SOFC is under

operating conditions with temperature up to 800⁰C, it is still not clear what species actually get to the anode, and, how these species affect the anode performance. More specific information is needed in addition to the components and the elemental analyses.

2.4 Gas phase species under SOFC working conditions.

The form and reactions of the phosphorus compounds in coal syngas under SOFC working conditions are still not clearly known. Calculations and experimental approaches have generated various results. Phosphorus may exist as phosphine (PH₃) at ambient temperature. However, Trembly et al. have done thermodynamic modeling at equilibrium and under warm gas clean up conditions (200-500⁰C, 1-15 atm). The initial gas composition was assumed as literature values described previously in Table 2.2 and the initial amount of PH₃ was set to 1.9 ppm. The thermodynamic modeling package is the FACTSAGE software with databases from GTI-Technologies. This calculation suggests that two trace vapor-phase forms of phosphorus found in the coal syngas after warm gas clean up were (P₂O₃)₂ and PH₃, while various trace amounts of HPO_x are also found to form depending on the temperatures and pressures. [28] Of these two species, PH₃ exhibits the possibility of reacting with the Ni/YSZ anode by thermodynamic calculations with a negative change of Gibbs free energy. One of the reactions is:

The PH₃ concentration is also found to depend on the partial pressure of oxygen (P_{O2}). A larger P_{O2} corresponds to more oxidized phosphorus, thus a lower PH₃. [28]

C. Xu et al. have calculated a thermodynamic phase diagram of the nickel/phosphorous system by using FACTSAGE software [33]. The phase diagram in Figure 2.4 shows that PH_3 can react with Ni to form nickel phosphide via reaction (2-18, 2-19 and 2-20). At 800°C , the most thermodynamically stable phases are Ni_2P and Ni_6P_5 . Ni_5P_2 may exist as a secondary phase while the local cell temperature increases due to current flow.

Figure 2.4 Thermodynamic phase diagram of potential Ni products with 10 ppm of PH_3 present in reducing atmosphere. [33]

Bao et al. performed thermodynamic equilibrium calculations to predict the chemical nature and abundance of relevant trace impurity species as a function of the temperature range expected in a coal gasification system. [27-29, 46] For these

calculations, the system pressure was assumed to be 10 atm and the impurities level was at 10 ppm initially. Phosphorus may exist as gas phase PH_3 when the gas is cooled to low temperature at high pressures after it exists the coal gasifier. However, under SOFC operation temperatures ranging from 700°C to 900°C and at 1 atm, PH_3 may be hydrolyzed to form mainly HPO_2 and HPO_3 as shown in Table 2.4.

Table 2.4 Thermodynamically calculated partial pressures of phosphorus compounds under anode gas conditions.(1 atm) [27]

Gaseous Species	Partial pressure (atm)				
	727 °C	777 °C	827 °C	877 °C	877 °C
CO	0.23	0.24	0.25	0.26	0.27
CO ₂	0.19	0.17	0.16	0.15	0.15
H ₂	0.37	0.36	0.35	0.34	0.33
H ₂ O	0.21	0.22	0.23	0.24	0.25
HPO	6.75×10^{-8}	9.33×10^{-8}	1.24×10^{-7}	1.61×10^{-7}	2.04×10^{-7}
HPO ₂	2.85×10^{-5}	2.83×10^{-5}	2.83×10^{-5}	2.82×10^{-5}	2.81×10^{-5}
HPO ₃	1.64×10^{-7}	1.82×10^{-7}	2.02×10^{-7}	2.23×10^{-7}	2.44×10^{-7}
PH ₃	1.00×10^{-9}	7.72×10^{-10}	5.96×10^{-10}	4.68×10^{-10}	3.75×10^{-10}

In another experimental study, Bao et al. from SRI International suggest that at 995K (772°C), in the presence of water vapor, PH_3 will undergo a hydrolysis reaction to form HPO_2 and HPO_3 . [29]

Also, in a technical report prepared by SRI Intl., a high-temperature Knudsen cell mass spectrometry is used to identify the chemistry of PH_3 , AsH_3 , etc, at a temperature range 750 ° to 850 °C, and the data are compared with the available calculated thermodynamic data. [27] The observed and calculated data are listed in Table 2.5. The calculations assume that all species are in equilibrium.

Table 2.5 Comparison of the measured and calculated partial pressures of the observed vapor species for $\text{Ar} + \text{PH}_3 + \text{H}_2\text{O}$ mixture at 995 K. [27]

Species	Partial Pressure (atm)		
	Measured (without H_2O)	Measured (With H_2O)	Calculated
Ar	3.96×10^{-4}	3.96×10^{-4}	4.17×10^{-4}
PH_3	2.36×10^{-8}	1.26×10^{-8}	1.51×10^{-28}
H_2O		7.60×10^{-5}	8.33×10^{-5}
HPO			1.22×10^{-15}
HPO_2		1.70×10^{-9}	1.20×10^{-9}
HPO_3		7.20×10^{-9}	1.54×10^{-8}
H_2			6.55×10^{-8}
O			1.27×10^{-16}
OH			4.30×10^{-12}
O_2			8.97×10^{-14}
PO			1.12×10^{-14}
PO_2			3.20×10^{-12}
P_2	5.57×10^{-11}		2.95×10^{-27}
P_4	2.13×10^{-9}		9.29×10^{-51}

The data in Table 2.5 also showed that the hydrolyzed HPO_3 is significantly less than the calculated value, suggesting the reaction is kinetically slow although the product is thermodynamically stable. The decomposition of PH_3 is also slow. So, the unconsumed

PH₃ remains in the fuel stream with the coal syngas, and may finally reach the anode of SOFC.

H. Kisimoto et al. generated Ellingham diagrams of P-O-H and Ni-P-O-H multi-gas systems. [30] This study was based upon computer calculations using a thermodynamic database. Ellingham diagrams are phase diagrams drawn to show the temperature dependence of the stability for compounds. In the diagrams, the partial pressure of H₂ is fixed at 1 atm. The horizontal axis is temperature. The vertical axis is the Gibbs free energy of oxygen, given by the equation from partial pressure:

$$\Delta G(\text{O}_{2(g)}) = RT \ln(P_{\text{O}_2}) \quad (2-21)$$

Figure 2.5 Two dimensional Ellingham diagram of a P-O-H system. [30]

The straight lines are borders of different phases. A sloping line indicates the equilibrium of $2\text{H}_2 + \text{O}_2 \leftrightarrow 2\text{H}_2\text{O}$. In the P-O-H diagram of Figure 2.5, the possible phosphorus species at 1000K include (P₂O₅)₂, P₄O₉ and PH₃. For some of the species with molecular weight greater than 200, a mass detection range of 1-300 is needed. A vertical line

indicates the 1000K position. The total partial pressure of all phosphorus species ($P(P_X)$) is 10^{-6} atm. The P_4O_9 area is narrow as a boundary between $(P_2O_5)_2$ and PH_3 at calculated $P_{O_2}=2.6 \times 10^{-20}$ atm ($\Delta G=-400$ kJ/mol). The SOFC working condition at the anode is near this border line. This is consistent with Bao's finding: with O_2 present, PH_3 may be oxidized. But there is no kinetic data available showing how fast the process occurs.

In the extended Ellingham diagram of Ni-P-O-H system (Figure 2.6), Ni and P show strong chemical interactions at 1000K. The researchers also suggested that the following reactions may occur:

Figure 2.6 Ellingham diagram of a Ni-P-O-H system. [30]

Both Bao and Kishimoto predicted the formation of Ni-P compounds on the anode by calculation. Nickel phosphide and nickel phosphate may cause loss of performance on the SOFC anode.

Thermodynamic calculations by K. Sasaki et al. predicted that the PH_3 is a stable form of phosphorus in wet hydrogen under the SOFC anode conditions from 400-1000 °C. [49]

The software HSC Chemistry (Version 4.1, Outokumpu Research Oy, Finland) was used in the calculations. Equilibrium compositions of 20% humidified H_2 fuel containing 5 ppm phosphorus is shown in Figure 2.7. At 800 °C, PH_3 is dominant over other phosphorus species.

Figure 2.7 Equilibrium concentration in 3% humidified H_2 fuel and containing 5 ppm P species calculated between 400 and 1000 °C, representing PH_3 as the most stable P-based compound. [49]

Based upon the calculations, Sasaki et al. also used P_2O_5 heated to 300 °C in humidified H_2 to generate PH_3 . The concentration of PH_3 in the fuel is estimated to 2.04 ppm when

the P_2O_5 was maintained at 300 °C. The chemical reactions explaining the generation of PH_3 from the source P_2O_5 can be represented by

The fuel containing PH_3 was then fed into the SOFC. The SOFC showed loss of power and increased resistances over 100 hours of operation. Post-mortem analyses showed that a layer of nickel phosphide had formed on the anode surface. The loss of performance and the appearance of the new material are similar to the previous PH_3 poisoning studies by Xu, Zhi and Demircan et al., which implies that the PH_3 generated by the heating of P_2O_5 has the same poisoning effects on the anode of the SOFC. [30-33]

2.5 Poisoning effects of PH_3 and H_2S on Ni/YSZ anodes.

Current studies have shown that many trace impurities including H_2S , PH_3 , AsH_3 , NH_3 , HCl , Hg , etc. in the coal syngas will cause the loss of performance in SOFC anodes. [21] At West Virginia University, a large amount of work on PH_3 and H_2S has been performed. In this dissertation, discussions will focus mainly on PH_3 effects. Several researchers have discussed the effect of phosphine in coal syngas on Ni/YSZ anodes. J.P. Trembly reported formation of Ni_5P_2 on the anode surface in PH_3 exposure tests. [30] M. Zhi et al. examined the anode after exposure to 20 ppm of PH_3 , and found nickel phosphate and zirconium phosphate phases formed on the surfaces. [31] X. Song et al. also reported findings of YPO_4 phase with TEM analysis after PH_3 exposure. [38]

The loss of performance caused by exposure to PH_3 is immediate and irreversible. [22, 30-31, 34] The following research was conducted by Xu et al. [33] In Figure 2.8, the

cell was kept at 0.5 A/cm^2 current density at 800°C with syngas as fuel. The cell voltage began dropping immediately upon the introduction of 10 ppm PH_3 into the fuel stream. The voltage degraded at a constant rate of approximately 0.46 mV/h . The cell OCV remained at about 0.962 V during the entire experiment.

In the EIS tests, both the series resistance (R_s) and polarization (R_p) resistance increased with time exposed to PH_3 . Figure 2.9 are the overlaid and normalized impedance spectra of the cell collected at different times of PH_3 exposure. The R_s increased at a constant rate of $0.42 \text{ m}\Omega \text{ cm}^2/\text{h}$, and the increasing rate of R_p was about $0.87 \text{ m}\Omega \text{ cm}^2/\text{h}$.

Figure 2.8 The cell voltage versus time under load 0.5 A/cm^2 operating on syngas before and after adding 10 ppm PH_3 at 800°C . [33]

Figure 2.9 Impedance spectra before and during exposure to 10 ppm PH_3 . [33]

Post-mortem examination of the cell showed a significant difference from the clean reduced cell. The anode area exposed to PH_3 appeared to have a shiny metallic look, (Figure 2.10) which implies that a new phase may have formed on the surface.

Figure 2.10 Clean reduced cell anode (left), and after PH_3 exposure (right). [33]

A SEM image of the top surface in Figure 2.11 showed that the surface is less porous after PH_3 exposure. XPS analysis detected peaks of phosphorus 2s/2p and nickel 3p, which implies the possible existence of Ni_3P and Ni_5P_2 . XRD data confirmed the Ni_5P_2

composition. This new phase is dense and not as conductive as metallic nickel, so the resistance of the cell increases, and the performance is degraded.

Figure 2.11 SEM images of clean reduced cell anode (left), and after PH_3 exposure (right). [33]

Another study done by O. Demircan et al. examined the effect of different overpotentials of Ni/YSZ anodes. [32] Overpotential is defined as the difference between the open circuit voltage and the applied voltage. In Figure 2.12, the power density was monitored over time under constant 0.5 A/cm^2 load for various fuels and overpotentials. PH_3 was added into the fuel at point (e). There was an immediate and continuous power loss after the addition of PH_3 . Three overpotentials (0.1V, 0.2V and 0.3V) were investigated. At point (k), PH_3 was shut off but the degradation caused to the anode was irreversible. The data showed no direct relation between degradation rate and the overpotential. Figure 2.13 showed the R_s and R_p (obtained from impedance measurements) of the cell. After the PH_3 was added, both R_s and R_p had significantly increased because a new layer formed on the top surface and Ni metal was drawn from the active layer.

Figure 2.12 Long term power density vs time under $0.5\text{A}/\text{cm}^2$ load [32]

Letters in the figure: (a) start with 97% H_2O , 3% H_2 . (b) 30% H_2 , 26% H_2O . (c) Clean syngas. (d) Continue clean syngas. (e) Syngas+10 ppm PH_3 , apply 0.1V over potential. (f) Apply 0.2V. (g) Apply 0.3V. (h) Apply 0.1V. (i) Apply 0.2V. (j) Apply 0.3V. (k) Syngas without PH_3 . (l) 30% H_2 , 26% H_2O (m) End. [32]

Figure 2.13 R_s (left) and R_p (right) for the cell before and after exposure to PH_3

Letter captions are the same as Figure 2.10. Diamonds measured at OCV and squares measured at 0.2 V applied potential. [32]

Figure 2.14 is the cross-section SEM image of the post-mortem cell. Image “a” is a clean reduced whole anode cross section. The two thin layers at the top are the cathode and the

electrolyte. The large area in the bottom is the anode and the anode surface is at the very bottom of the image. Image “b” is magnified to show the part of anode after exposure to PH_3 . The solid bottom half is the surface of anode, with a thick and dense layer attached. Analysis in Figure 2.15 indicated the presence of a new phase layer on top of the anode surface similar to that observed in previous papers. [33]

Figure 2.14 Cross section SEM images of the cell, before and after PH_3 exposure. [32]

Figure 2.15 SEM images of clean reduced anode top surface (left) and after exposure to PH_3 (right) [32]

The XRD spectrum in Figure 2.16 shows the existence of YSZ, Ni_3P and metallic Ni phases on the top surface after comparing the peak positions with the literature values. Ni_5P_2 , Ni_3P , Ni_8P_3 and Ni_{12}P_5 peaks could not be assigned because their diffraction angles are very close together.

Figure 2.16 XRD analysis of PH_3 exposed anode surface. (◆YSZ ■ Ni_3P ● Ni) [32]

Figure 2.17 is an XPS survey scan of the anode surface region exposed to PH_3 . There are no Y or Zr peaks seen, which means that the dense layer completely covers the top surface, and thus is an extra layer on top of the anode. A detailed Ni-2p3 regional scan is in the left insert. The peak at 852.8eV can be either elemental Ni or Ni-P compounds. The detailed P 2p region scan is in the insert. There are two P(2p) peaks at 130.1 and 134.1 eV, and they can be assigned to elemental or reduced phosphorus and +5 oxidation state, respectively. This observation indicates the existence of the Ni_3P phase again. The top layer may be aggregations of Ni and/or Ni_3P chunks.

Figure 2.17 XPS survey of the PH₃ exposed area on the surface of the anode. [32]

Figure 2.18 is a 20 μm spot analysis on the active area of the cell anode. The presence of C, O, Ni, Y, Zr, Si and P are shown by their peaks. The peak in the detailed P(2p) area indicates that only oxidized phosphorus was detected.

Figure 2.18 20 μm spot XPS analysis on the cross-section of the active layer of anode.

[32]

Micro-structural studies done by X. Song et al. point out the presence of YPO_4 phase on the Ni/YSZ anode after 117 hours of exposure to PH_3 . [38] Ni-P products, primarily Ni_5P_2 , are observed on the anode top surface. This observation is similar to results in the previous studies. TEM examination was performed on the anode of a cell operated in syngas with 20 ppm of PH_3 for 117 hours. Crystals with about 100 nm dimension are deposited at the YSZ-YSZ/Ni boundaries. Figure 2.18 is the TEM image of the anode active layer. The EDX study implies that the particles are composed of Y, P and O. The electron diffraction pattern in Figure 2.20 confirms that the identification as YPO_4 , with a tetragonal structure. The YPO_4 particles are pointed out by arrows in Figure 2.19.

Figure 2.19 TEM image of anode active layer in a cell exposed to PH_3 for 117 hours [38]

Figure 2.20 (a) Chemical compositions of the deposited particles. (b) Diffraction pattern taken from the Y-P-O phase and YSZ phase [38]

The new YPO_4 phase is considered to be a corrosion product of the YSZ material. When it develops in the YSZ/YSZ/Ni tri-boundary, the reaction site is blocked, leading to loss of cell performance. The YPO_4 is stable at SOFC operation temperature around 800°C , but decomposes at 900°C . [39]

2.6 In-situ analyses during SOFC operation.

There are several types of in-situ methods currently being used in the SOFC research. Some of the methods are material analysis such as in-situ Raman Spectroscopy, surface deformation and temperature measurements [35-36]. The standard electrochemical tests are carried out during operation, so they can be classified as in-situ methods, as well. In this section, the discussion will mainly focus on in-situ analyses during SOFC operation. Methods will include Mass Spectroscopy, Gas Chromatography, tunable diode laser spectroscopy and high-temperature Raman Spectroscopy.

J. Bao et al. from SRI International [29] used a high-temperature (997 K) mass spectrometer to measure the partial pressures and to determine the thermochemical properties of gases. This instrument has a 30.5 cm radius, is single focusing, and utilizes magnetic deflection. The instrument has been employed more than 30 years to determine the thermodynamic properties of many inorganic chemicals.[37] Figure 2.21 is a schematic illustration of the system. It consists of a molecular effusion-beam vapor source, an electron impact ion source, and a magnetic mass analyzer. The analyte gases are admitted from the base through the inlet tube. The chemistry of the species in the cell is frozen in the collision free molecular path from the quartz Knudsen cell orifice (1.0 mm in diameter) to the ion source without encountering any instrument surfaces. The ionized particles are then accelerated and analyzed by the magnetic mass analyzer.

Figure 2.21 High-temperature Mass Spectrometer [29]

This high-temperature Mass Spectrometer is believed to give accurate measurements of partial pressure within a factor of two. The detection limit for most observed species is on the order of 5×10^{-11} atm (3.8×10^{-8} torr). The thermal decomposition behavior of PH_3 and CH_3Cl was studied using the mass spectrometer. Effects of sub-ppm level of impurities in syngas including Hg, AsH_3 , PH_3 , CH_3Cl and H_2S were also investigated. Part of the data related to PH_3 studies was described in previous text in this dissertation (Section 2.4).

The conditions in these tests are selected to be similar to SOFC operating conditions. However, this mass spectrometer was not used on-line with a working SOFC. The degradation effects and the high temperature chemistry were tested in separate experiments. [29]

Another article by H. You et al. probed the conversion among reactions at the SOFC anode with dry methane. [40] In-situ gas chromatography (GC) was used in this study to measure the anode exhaust gases. The reactions of methane were investigated at various current densities. The GC system measured the production rates of anode exhaust gases. Figure 2.22 is a typical data plot vs current density. The GC measurements were carried out 15 mins after changing the current density.

Figure 2.22 Production rates of anode exhaust gases in SOFC with Ni-YSZ anode and 3.85% methane. [40]

The detection limit and sensitivity of the GC system is suitable for major fuel gas and water vapor measurements, but not for sub-ppm level studies of impurities.

C. Guerra et al. also reported a study of dry methane direct reforming at the SOFC anode with the help of Mass Spectrometry. [45] The gas composition at the reactor outlet was monitored using a mass spectrometer. The kinetics of the reactions occurring over the anode were investigated by means of Isotherm reactions and Temperature-programmed reactions.

Figure 2.23 CH₄, CO, H₂ and CO₂ flow rates for inlet CH₄=6 ml/min and chemical equilibrium composition calculated at 800°C with varying inlet CO₂/CH₄ ratio. [45]

In Figure 2.23, the solid lines are the calculated equilibrium composition from theory. The subscript “i” means the inlet. The symbols are observed data points collected at different CO₂ to CH₄ ratios at the inlet. There are clearly two regions. One is the carbon deposition (“coking”) region, the other is the no carbon formation (“non-coking”) region. This result is consistent with the previous predictions. [41]

The catalytic properties of the Ni/YSZ anode in methane reforming are also investigated under different temperatures. Temperature programmed reforming reactions showed that the catalytic activity is poor at temperatures lower than 450°C. The reforming reaction is very close to equilibrium when the temperature is higher than

620°C. The conditions chosen to avoid coking are further confirmed by other studies.

[43-44]

The Mass Spectrometer used by C. Guerra et al. was employed to detect gases with molar ratios, which means large amount of gases. [45] The details of the instrument such as model, ion source, type of detector, detection limit and sensitivity are not mentioned in the paper. Whether it is suitable for trace amount of impurities is unknown.

2.7 Summary

While SOFCs are a promising source of power in the future, there are many challenges to overcome. The most significant problem with direct utilization of coal syngas is the poisoning effect of many impurities. The degradation behavior and mechanism have been investigated but are still not fully clear. New methods are continuously introduced into the Solid Oxide Fuel Cell research. Further investigation of impurities tolerance, fuel flexibility and efficiencies are on-going.

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Chapter 3 Leak check and cell test with H₂S.

3.1 Introduction to the Cirrus Residual Gas Analyzer

The main instrument for detection of gas-phase species in this study is a special type of quadrupole mass spectrometer called Residual Gas Analyzer (RGA). The RGA in this study is the CirrusTM from MKS International (Figure 3.1). The Cirrus RGA is designed to monitor and analyze gases and gas mixtures including trace amounts of contaminants. Gas compositions can be tracked over a wide dynamic range (sub-ppm to percentage levels).

Figure 3.1 Cirrus Residual Gas Analyzer from MKS Instruments

RGAs are widely used for gas-phase analyses and monitoring, such as in leak tests, high vacuum systems, environmental controls, catalyst optimization and controlled gas sources. Researchers in Keele University, UK for example, used the Cirrus to

determine and control the gas phase composition while testing for the optimized conditions of the reduction of a NiO/SiO₂ catalyst precursor. [1]

The ion source in the Cirrus RGA is a cylindrically symmetric closed ion source. It is a type of electron impact ion source. A tungsten filament is heated to emit electrons towards the accelerator. The electrons are accelerated to energies of 25 to 105 eV, depending on the operation mode. Usually in the normal RGA mode, 70 eV is chosen for general-purpose analyses. The electrons impact the gas molecules from the sampling capillary. The ion energy is about 4 to 8 eV. This low energy will break a small fraction of the chemical bonds in small inorganic molecules. Sometimes doubly ionized species can be observed. After focusing, these ions move into the quadrupole mass analyzer.

For most analytical purposes, the quadrupole MS has the ability to resolve ions whose mass to charge ratio (m/z) differs by one atomic mass unit (amu). The Cirrus unit used in this study has a detectable m/z range of 1-100 amu. The scan direction is always from lowest mass to highest mass. The major gases in the SOFC fuel stream are H₂, and H₂O, with trace amounts of N₂, O₂, Ar, CO₂, PH₃ and possibly HPO₂, HPO₃ and P₂O₅. There are three models of Cirrus systems available from MKS, with mass range 1-100, 1-200 and 1-300 amu. The 1-100 amu model is chosen here because most of the analytes of interest are within 100 amu, and the 1-100 amu model offers better sensitivity and a lower detection limit than the other two models. [2]

The Cirrus RGA achieves a wide dynamic range, from atmosphere pressure (760 torr) down to 10⁻⁴ torr through the use of two detectors, a Faraday cup and an electron multiplier. Signals at 10⁻³ torr and above are considered to be reliable. So if an analyte

has a partial pressure of 1×10^{-3} torr, in other words, about 1ppm in concentration, it is detectable. Usually the contaminant studied in coal syngas such as PH_3 , AsH_3 and H_2S varies from 1 ppm to 10 ppm. The contaminants and their derivatives are expected to be reliably analyzed.

The RGA can sample gases from atmospheric pressure through a thin capillary with inner diameter of 1 μm . The silica capillary is heated to 120°C to prevent water condensation. The sampling connection is a standard 1/4 inch Swagelok fitting. This sampling capillary is a pressure adapter between the atmospheric pressure gas and the high vacuum inside the Mass Spectrometer chamber (usually $\sim 10^{-6}$ torr). The pumping consists of a four-stage mechanical diaphragm pump and a high-speed turbo pump.

In most cases, the RGA is used to monitor both the gas inlet and exhaust, especially the exhaust. The purpose is to study which gas species get to the anode and which species come out from it. So two sampling points, both with shut off valves, and a valve controlling the selection between the two points are included in the experimental design. The block diagram is shown in Figure 3.2:

Figure 3.2 Block diagram of RGA application on Solid Oxide Fuel Cells

The mass scan with the RGA is programmed always from lowest mass to highest mass. The speed of the scan can be set by adjusting the time spent at each mass number. The signal is integrated over the time at one mass, and then the mean of the signal is determined as the output. A full spectrum scan from mass 1 to 100 usually takes less than 1 minute. The repeat scan interval is often set to 1 minute.

The calibration of the RGA begins with the Faraday Cup detector. In this calibration, the N₂ composition in the room air is assumed to be stable at 585 torr (78% of 750 torr). The Faraday Cup is calibrated against the partial pressure of N₂. A test run of the Faraday detector is usually done after the calibration process to verify the N₂ reading at mass 28 is still 585 torr. Generally, the mass spectrometer exhibits a measurable loss of sensitivity over a period of 1 day.

The electron multiplier detector is more sensitive than the Faraday Cup, has lower detection limits and lower maximum detectable pressures. It can handle gas pressures only up to about 100 torr. So it is calibrated against a reading of the Faraday Cup, usually Argon at mass 40 in this study.

The RGA detector measures a current due to the ions reaching the detector. This current is assumed to be proportional to the partial pressure of the residual gas in the ionization chamber. The ions must pass through the quadrupole chamber without collision with other molecule or ions, so the mean free path must be longer than the length of the chamber. To ensure the large mean free path, a high vacuum is necessary. Usually the RGA operates under 10^{-6} torr pressure. In the MKS Cirrus unit, a turbo pump backed by a four stage diaphragm pump is installed to achieve the high vacuum needed.

The amount of current at particular masses can be affected by a number of factors some of which are described below [3]:

1. The probability that a molecule will be ionized due to the electron impact. This can be determined by the cross section for ionization for each species.
2. The probability that an ion is produced by a particular molecule fragment.
3. The probability that an ion will make it into the quadrupole chamber and finally pass through the chamber to be detected.

The first factor, which is defined by the cross section for ionization, is believed to be dominant. A list of cross sections for ionization of some selected species taken at incident energy of 70 eV is provided in Table 3.1 [4]. Based on the cross sections for ionization data, O₂, N₂ and H₂O are predicted to have the same calibration. H₂S is listed because the cross section of PH₃ is predicted to be roughly the same or marginally bigger than H₂S.

Table 3.1 Cross sections for ionization of selected molecules at 70 eV [4]

Gas Species	Cross section for ionization (Å ²)
H ₂	1.021
O ₂	2.441
N ₂	2.508
CO ₂	3.521
H ₂ O	2.275
H ₂ S (in place of PH ₃)	4.145

The probability of fragmentation of a particular mass is also brought into consideration. For example, H_2S produces peaks at masses 32, 33 and 34. The peak height at mass 32 and 33 each is about 40% of the peak height at mass 34. The sum of signals of all possible fragments is the total amount of current generated by a particular molecule. This summed value gives a first approximation to relative peak heights.

However, the RGA is only calibrated to a certain mass, often mass 28 (N_2). This calibration is based on the cross section of nitrogen and used across all masses within the detection range. The calibration method is often good within a few percent but may be off by a large amount occasionally.

In an actual observation, immediately after calibrating the RGA detectors in air, mass spectra of “dry” and “wet” H_2 were obtained. In the “dry” H_2 , the reading for mass 2 (for H_2) and 18 (for H_2O) were 830 torr and 1.5 torr. In the “wet” H_2 , the reading for mass 2 and 18 were 794 torr and 88.2 torr. The partial pressure readings for H_2 are somewhat reasonable but the H_2O readings are off by a factor of 4 in this case. The correct value of H_2O in the wet H_2 should be around 20 torr.

3.2 Experimental setup in WVU Chemical Engineering.

The gas handling system in WVU Chemical Engineering Department is illustrated in Figure 3.3. The gas flows are controlled by Alicat Scientific Mass Flow Controllers (MFC). The mixture of the fuel gas can either go through or around the humidifier. PH_3 or H_2S can be added after the humidifier. On the cathode side, the compressed air is also regulated by a mass flow controller and then fed into the furnace.

Figure 3.3 Illustration of gas handling system in WVU CHE Fuel Cell Test Stand.

The joints of the gas lines are mainly 1/4 inch stainless steel Swagelok® fittings with ferrules. These joints are believed to be highly gas tight and reliable. The seals around the cell are flanges pressed together with spring loading (Figure 3.4). Mica gaskets are installed on both sides of the cell to minimize leaks. Although much effort has been put in to reduce the leaks, the seals are still not completely gas tight around the cell (see below).

Figure 3.4 Detailed setup around the fuel cell in the WVU CHE test stand.

The gases coming out of the cylinders can either go through or bypass the humidifier, and then PH_3 can be added to the fuel gas downstream. The inlet sampling point is just before the fuel stream enters the furnace, and the outlet sampling point is just after the exhaust leaves the furnace.

3.3 Pure gas and leak checks

Before the actual cell or gas tests, a complete leak check of the whole gas handling system was performed. This step is necessary mainly because one of the isotopes of oxygen will interfere with the mass 34 signal, the most interesting analyte in this study, the $\text{PH}_3 \cdot {}^{34}\text{O}_2$ has a natural abundance of about 0.4%.

Figure 3.5 Mass spectra of room air.

A typical room air spectrum from 1 through 50 amu taken with the faraday cup detector is shown in Figure 3.5. In this figure, the mass spectrometer was calibrated in room air against Ar. The partial pressure of Ar at mass 40 is 7.2 torr, very close to its natural abundance. The detector can be calibrated for only one mass at a time, so other partial pressures including N₂, O₂, H₂O, etc. are not corrected. The partial pressure values are relative, not absolute.

Ultra High Purity (UHP) level gases are used with the mass spectrometer to avoid any possible impurity sources. The specification of UHP level claimed by Air Liquide America is at least 99.999% purity. These gases were passed through a T-junction to which the mass spectrometer capillary was connected. The mass spectrum of UHP He is shown in Figure 3.6. This spectrum is taken using the electron multiplier detector. The mass 4 was skipped when scanning due to the saturation of the electron multiplier detector. The peak at mass 8 is assigned to the bi-atomic He formed inside the ion source.

There is small amount water content (~ 0.02 torr) in the UHP He. Other than that, the UHP He is very pure. The partial pressures of N_2 and O_2 are down in the 10^{-3} torr range, very close to the noise level.

Figure 3.6 Mass spectra of UHP grade He.

Figure 3.7 Mass spectra of UHP grade N_2 .

The mass spectrum of UHP N₂ is shown in Figure 3.7. The N₂ contains more impurities than the He, although they are claimed to be the same purity grade. Mass 14, 28 and 29 are skipped in the mass scans. However, the RGA detection tends to exhibit a “carry over” effect. After a very large, sometimes out of range peak is detected in the spectrum, the signal at the next higher mass number will be much larger than expected. A hypothesis of this type of observation is that the mass analyzer resolution is not sufficient to exclude the large signal from one mass from infringing the next higher mass. For example, the mass 14 was skipped due to the large amount of double ionized N₂, but at mass 15 a large signal still appears on the spectrum. Mass 28, which is the N₂ molecule, is well above the detector limit range, and, the carried over mass 29, is still out of range. The “carry over” effect is still seen at mass 30. Residual Ar made its contribution to mass 40. The peak at mass 42 cannot be assigned to any gas that exists in the room air, but might be a pair of some hydrocarbons from the compressor oil.

A leak check of the system was performed with the UHP N₂. There was no cell in the furnace, only a seal block (elastic film over the tube opening normally pressing against the mica seal of a SOFC). The furnace was not heated. UHP N₂ was fed into the fuel lines. The mass spectrometer was hooked up to the exhaust sampling point and used to monitor the gas compositions in mass range 20-80 amu continuously for 24 hours. After 5-10 minutes from the start of mass scanning, 20 ppm of PH₃ (mass 34) was fed into the stream. The plot of mass 34 and 44 versus time is in Figure 3.8. Mass 44 (CO₂) is chosen here because the CO₂ level in the UHP N₂ is very low, and CO₂ serves as a leak marker.

Results in Figure 3.8 show that there is an air leak in the system. CO₂ levels of about 0.005 - 0.04 torr are detected, while CO₂ in room air is about 0.2 torr on average. The mass 34 signal stays low below 10⁻³ torr level.

Figure 3.8 Leak check with UHP N₂ and 20 ppm PH₃.

Another leak check was conducted by squirting He at every joint of the system and monitoring the exhaust gas with the RGA leak check mode (rapid scanning of mass 4). If a higher than normal level of He is detected, it means the joint being squirted is leaking.

Much effort was put into locating the leaks. Leaks in the gas transfer lines were eliminated by tightening or changing the Swagelok fittings. Leaks were also found in the humidifier, but not fixed. For many subsequent measurements, the fuel gas was routed around the humidifier.

To ensure the ability of the Cirrus unit to detect analytes within the entire range of mass to charge ratio of 1-100, some volatile organic compounds are placed near the tip of the sampling capillary for the Cirrus unit to inhale the vapor. The air is also drawn into the

mass spectrometer with the organic compounds. The mass spectra of ethyl acetate ($\text{CH}_3\text{COOC}_2\text{H}_5$) with a molecular weight of 88 are shown in Figure 3.9.

Figure 3.9 Mass spectra of ethyl acetate vapor in room air.

The molecular peak at 88 (the molecular weight of ethyl acetate) and fragments at mass 73, 70, 61, 45 and 43 are seen on the spectra. This result confirms the capability of the mass spectrometer to detect any mass within the range of 1-100 amu.

3.4 Cell preparation

The cells used in this study are commercially available MSRI (Materials and Systems Research, Inc) anode-supported button cells. Both the test bed in WVU Chemical Engineering and the Probostat can hold cells with a diameter of about 2.5 cm. The cell usually is supported by the NiO/YSZ anode, which is $\sim 900\mu\text{m}$ in thickness. The dense YSZ electrolyte is coated on the anode as a very thin layer of about $10\mu\text{m}$. The cathode is screen-printed on the electrolyte, with a smaller diameter than the anode and

electrolyte. These three layers are sandwiched together to make a full solid oxide fuel cell.

Figure 3.10 is an illustration of the SOFC cross-section.

Figure 3.10 Sandwich structure of anode supported SOFC (Not to scale)

The current collectors are gold meshes attached to the cathode and anode using conducting gold paste. After applying the gold paste, the cell is heated slowly to 600-800°C to dry the paste and burn out any organic compounds. This step also places the gold mesh in firm contact with the cathode and anode. Figure 3.11 shows the current collector on both sides of the SOFC.

Figure 3.11 Current collectors of the anode-supported MSRI cell

On each side of the cell, there are two wires. One is for the major current flow and the other one for the voltage sense. This configuration minimizes the interference of wire resistance on the voltage measurements.

The potentiostats in this study (Solartron or Gamry) provide four leads: working electrode (current), working sense (voltage sense), counter electrode (current) and reference electrode (voltage sense). Either the cathode or the anode were connected as the working electrode.

Before each cell test, the cell was fully conditioned. The preparation of the cell consisted of several steps. Firstly the cell was correctly wired. Then the cell was secured firmly on the test bed and sealed to minimize leaks between the fuel and air. Then the furnace was programmed to heat up slowly, usually with a rate of 1-2 °C/min. The anode side was fed with inert gas (typically N₂) and the cathode side was fed with air while heating up. Once the temperature reached 800°C and was stable, the reduction of the anode began with diluted H₂, usually 10% H₂ in N₂ for the first 2 hours, and then the H₂ was increased to 50% for another 4-6 hours. The H₂ was finally increased to 100%. The cell was kept at this point for ~10 hours with open circuit (no current flow). Then a small current was applied (typically 100 mA) to ensure that the anode was fully reduced. A new cell has a green color from the NiO in the anode, but when it is reduced, the anode color becomes metallic grey because of the Ni metal.

3.5 Cell tests in WVU Chemical Engineering with H₂S

3.5.1 Ni-GDC cell test with different levels of H₂S

An anode-supported Ni-GDC cell was reduced in H₂ and pre-conditioned with a small current to achieve a stable performance before the mass spectrometry tests. In this test, the Mass Spectrometer was connected to the exhaust of the SOFC test stand and it

was set to scan the 30-100 amu mass range. The partial pressures of the gases were monitored over 100 hours of operation time. The total gas flow to the anode was kept at 200 sccm. The cathode was fed with 300 sccm of air throughout the entire experiment.

In the experiment, the Ni-GDC cell is operating on dry H_2 initially, then 3% water (~20 torr) was added (“wet” condition) at 800°C. Then 100 ppm of H_2S was introduced into the fuel stream after 25 hours from the beginning of the mass scans. After 50 hours, the amount of H_2S was increased to 200 ppm. After 92 hours, the H_2S flow was shut off. The major signal of H_2S is mass 34. The plot of mass 34 versus time is shown in Figure 3.12.

Figure 3.12 Mass 34 (H_2S) signal in the exhaust gas during cell operation at 800 °C.

During the first 18 hours, the cell was running on “dry” H_2 without water added. At about 18 hours, the fuel stream was passed through a humidifier. The humidifier has a relatively large dead volume of air about 10 liters, so the air peaks increased sharply after

it was turned on. The mass 34 signal also increased as a spike peak because of the contribution of $^{34}\text{O}_2$. The air was gradually purged over several hours. The addition of H_2S was delayed until a stable baseline was achieved at mass 34.

Immediately after the addition of 100 ppm H_2S , there was a small amount of residual air in the gas transfer line and this causes the small “bump” in the graph. Then the mass 34 signal increased very slowly to 0.14 torr (roughly double the true pressure of 0.08 torr). This transient took more than 20 hours to reach a steady value. However, the power loss of the SOFC occurred almost instantly after addition of 100 ppm H_2S . After the H_2S was increased to 200 ppm, another transient behavior occurred, but with an initial sharp jump and much shorter time. One hypothesis of the transient phenomena is that the H_2S tends to be adsorbed on to the walls of the gas transfer system, test stand, mass spectrometer transfer line and cell itself. There might be a saturation volume of the H_2S onto the inner surfaces. The surface area is so large that it takes a long time to be fully saturated. But after the saturation, the response of signal becomes more sensitive to the change of H_2S concentration, although the increased concentration may lead to a larger saturation volume of adsorption. Another hypothesis is that the H_2S adsorbed by and reacted with the Ni in the cell anode. Liu et al. reported that Ni_3S_4 , NiS , and Ni_3S_2 were detected at the anode surface by in-situ Raman spectroscopy if the anode was cooled down in a fuel contaminated by H_2S . [5]

When the H_2S was shut down, the signal at mass 34 dropped immediately and sharply to the baseline level. The sharp drop implies that the adsorption is not reversible or kinetically very slow. Also, the H_2S may have reacted irreversibly with the cell anode

and bonded to the nickel to form solid products that is not volatile. Thus, no H_2S was released when the supply is shut off.

Mass 34 and 33 are the only two mass numbers that exhibit change correlating to the addition of H_2S within 30-100 amu range. Mass 34 is believed to be H_2S and mass 33 is possibly HS. The HS may be formed from H_2S during the ionization impact with the accelerated electrons, with one hydrogen atom knocked out. The plot of mass 33 signals versus time is shown in Figure 3.13. The shape of the graph is very similar, almost identical with the mass 34 graph, just with a smaller scale.

Figure 3.13 Mass 33 (HS) signal in the exhaust gas during cell operation at 800 °C.

3.5.2 MSRI anode supported cell test with H_2S and current change

In order to obtain a fast response of the mass spectrometry signals when the H_2S is added, the gas handling system and the furnace were pre-saturated with H_2S . A YSZ

disk is put in place of the cell to block the anode (fuel) side from air. The furnace was heated up to 800°C slowly. H₂S was added into the gas stream for a few hours before turning on the mass spectrometer, but a “ramp up” was still seen at mass 34. The transient of H₂S is faster than the cell described above. Not only does the furnace system need time to be saturated, but also the mass spectrometer transfer line requires saturation. The nitrogen signal indicates a significant air leak inside the furnace or in the exhaust system. The water signal also suggests the presence of a leak. These leaks are very difficult to eliminate and they are incorporated in the tests.

A MSRI anode-supported cell was mounted onto the SOFC test stand in WVU Chemical Engineering similar to the cell described previously. The mass spectrometer was hooked up to the sampling point at the exhaust of the SOFC. The cell was prepared and pre-conditioned as before.

This cell test is conducted to investigate any change of H₂S due to the cell current during actual operation. The fuel gas was “dry” H₂ and the mass spectrometer was programmed to scan the mass range 30-100 amu. The plot of mass 34 in the exhaust gas over time is in Figure 3.14.

Figure 3.14 Mass 34 signal in the exhaust gas with current on and off. The cell was operating at 800 °C with H_2 . 100 ppm of H_2S added at 0.21 hours.

100 ppm of H_2S was added to the fuel stream at 0.21 hours. A transient behavior is seen in the first few hours. The mass 34 signal increased slowly during the current tests. The cell was loaded with 1 A of current at 3.8 hours. The mass 34 signal went up in 2 minutes, with no significant change of mass 64 (SO_2) or 60 (COS) signals. Then the mass 34 signal started to decay slowly, but was still higher than it was before applying the current. The cell current was turned off at 6.2 hours. The mass 34 signal dropped in 2 minutes, then slowly went up, but was lower than when the cell current was on.

For comparison, the inlet gas was also checked in the next experiment. The gas stream was the same as in the exhaust tests, just with the sampling point to the gas inlet before the SOFC. The mass 34 plot is in Figure 3.15. 100 ppm of H_2S was added at 0.46 hours. In this experiment, the apparent steady state pressure of 0.35 torr is substantially

higher than the true pressure of 0.08 torr. The cell current was turned on and off several times during the operation time but the mass 34 signal did not show a change according to the current. Without passing through the furnace area, the mass 34 signal still showed a transient, which implies that the H_2S will adsorb on to the sampling line of the RGA.

Figure 3.15 Mass 34 in the inlet gas with current on and off. The cell was operating at 800 °C with H_2 . 100 ppm of H_2S added at 0.46 hours.

The data from the exhaust and inlet with current flow are compared by determining the average of 5-6 hours of the exhaust data, and the average of 2-3 hours of the inlet data. In these regions, the mass signals are relatively stable. The following important masses are compared in Figure 3.16: 17(OH group, for H_2O , Mass 18 is out of range), 14 (atomic N or double ionized N_2), 32(O_2), 34(H_2S), 40(Ar), 60(CSO), 64(SO_2).

Figure 3.16 Comparison of inlet and exhaust gases during cell operation at 800 °C.

Because the O_2 signal is on the order of 1 torr, the expected contribution of $^{34}O_2$ to the mass 34 signal is on the order of 0.004 torr. Such a high O_2 content is not predicted by thermodynamic calculations. The equilibrium pressure of O_2 in pure H_2 at 800 °C is on the order of 10^{-13} torr. The O_2 signal at mass 32 is due to the small leaks at the place that the sampling capillary enters the mass spectrometer. Consequently, mass 34 signals are largely attributed to H_2S , even with a noticeable air leak (higher mass 32 signal in the exhaust). The changes in mass 34 signal in Fig. 3.13 are attributed to desorption of H_2S from the cell during current flow (possibly due to heating of the cell during oxidation of H_2 and ohmic heating), and re-adsorption of H_2S to the cell when the current is shut off.

The air peaks at mass 14, 32 and 40 are higher in the exhaust than in the inlet gas, suggesting there was an air leak between the two sampling points. The most likely place was around the cell. The water signal was also much higher in the exhaust due to the reaction of H_2 in the fuel and the oxygen in the air leaking into the fuel side. Mass 34

signals were almost the same in the two points. Considering some of the contribution to mass 34 in the exhaust is because of the oxygen isotope, some of the H_2S must have reacted. Mass 60 and 64 signals are in the noise level. There is no other mass signals above the noise level within the 30-100 mass range.

3.6 Conclusion and discussions.

The application of RGA on solid oxide fuel cell study offers a new way to determine the gas-phase composition. The trace gases and the major gases can be detected at the same time. However, due to the limitation of single point calibration, the absolute value of the partial pressure reading for some of the gases can be inaccurate.

A slow transient behavior is observed after the H_2S is added to the fuel stream. The H_2S might have reacted with the Ni in the cell anode or adsorbed on to the inner surfaces of the test stand or the sampling capillary of the RGA. However, when the H_2S was shut off, the signal dropped sharply and immediately. This implies that the reaction and adsorption of H_2S on to the gas handling system including the transfer lines to the mass spectrometer is irreversible.

The amount of H_2S detected at the exhaust of the cell is found to have a relationship with the current change. The current or the resulting local heating on the cell releases some of the adsorbed H_2S . Without current, the H_2S adsorbs back on to the cell anode.

The test stand at WVU Chemical Engineering had numerous leak points that were very difficult to eliminate. The seal around the cell was not designed to be gas tight. The small leaks at the inlet of the Cirrus unit lead to an unusually high amount of O₂ from the air contaminants as well. Despite the leaks in the system, the H₂S at 100 ppm is reliably detectable with the Cirrus RGA unit. At no point were significant amounts of SO₂ or COS detected. A comparison of inlet and exhaust gas composition further confirms the large amount of leaks around the cell. Due to the difficulties caused by the leaks, the work was moved to another test platform.

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Chapter 4 Cell test in WVU Mechanical Engineering (Dr. Kang' lab)

4.1 Experimental set up.

The cell test in the WVU MAE laboratory was performed using a commercial testing platform named the Probostat. The Probostat is a versatile SOFC testing system designed in the Kofstad/Norby group at the University of Oslo, Norway. It consists of a two-foot long supporting tube made of alumina and a stainless steel base. When testing a fuel cell, the sample is held with a spring-loaded alumina assembly. Wires for the current leads, thermocouples and the gas in/out ports are on the metal base. Figure 4.1 is a photograph of assembled Probostat. [1-2]

Figure 4.1 Picture of assembled Probostat testing platform for SOFC button cells.

The gas delivery system in WVU MAE is illustrated in Figure 4.2. All the gases were regulated by the Alicat Scientific Mass Flow Controllers. H_2 , CO and CO_2 can be mixed

to make a fuel gas mixture. The fuel mixture can either go through or around the humidifier. Helium can be fed to either or both the anode and cathode sides. PH₃ can be added to the fuel stream after the humidifier from a tank containing 1000 ppm PH₃ in nitrogen. The typical operating flow rate is 100 sccm of fuel in the anode side, and 300 sccm of air in the cathode side.

There are four sampling ports for connection to the mass spectrometer: the anode inlet and exhaust, and the cathode inlet and exhaust.

Figure 4.2 Gas delivery system in WVU MAE.

In the Probostat, the cell was usually glued with Aremco Ceramabond™ to the inner support tube with the cathode side facing down toward the base. This alumina tube has an outer diameter of 2.5 cm. In order to minimize the air leak between the cathode side and anode side, an alternate approach for connecting the current collector and voltage leads

was applied to the original design. In the previous tests, the current leads are usually brought out from the cell between the cell and the inner supporting tube (Figure 4.3 [1]). This leads to a gap and potential gas leaks between the cell and the tube.

Figure 4.3 Original cell testing set up in the Probostat. The leads to the anode and cathode are the blue wires.

In the new approach, an inner current lead was attached to the cathode side. The inner lead that connected the cathode ran through the base inside the inner support tube. The cell was secured directly on the tube. A new sealing method was used in the study in contrast to the conventional ceramic glue, usually alumina or zirconia-based adhesives from Aremco. The new method used a gold O-ring with a diameter of 23 mm, and gold paste to serve as glue. A photo of the actual cell is shown in Figure 4.4. The cathode current collector is inside the tube. The gold O-ring can be seen attached to the cell. The cell is pressed on to the tube with a spring-loaded assembly. In the test, the temperature was first ramped up to 900°C. At this temperature, the gold O-ring becomes soft and

deforms slightly in order to seal any possible gaps and cracks. Then the temperature was brought down to normal SOFC operation around 800°C.

Figure 4.4 Cell assembly on to the Probostat using a Gold O-ring, showing the cathode current lead coming off the bottom of the cell.

4.2 MSRI anode supported cell test

An MSRI anode-supported cell was mounted using the method described above. The cell was reduced in diluted and pure H_2 as discussed in Chapter 3. There were a total of 8 steps in this test. For each step, the data were taken when the mass scan was stable after changing the gas compositions and cell loads. In all the steps, the cell was at 800 °C.

1. He in both anode and cathode sides. This step was done to track any leak of air through the outer tube. The selected masses in the anode and cathode exhaust are shown in Figure 4.5. The N_2 signals are in the order of 0.1 torr, which implies that the air leak at this point is very small. The N_2 may also be coming from the impurities in the He cylinder as mentioned earlier in Chapter 3.

Figure 4.5 He in both anode and cathode sides. The cell was at 800 °C.

2. He in the anode side and air in the cathode side. Select masses taken from the anode and cathode exhausts are shown in Figure 4.6. This step was done to measure the leaks between the anode and cathode side. About 10 torr of N₂ signal was seen in the anode side. The mass 28 signal in the cathode is skipped because it is too high and out of the detection range. Meanwhile, the He signal was also seen in the cathode side. These results confirm the presence of a leak in the gold ring seal. The experiment continued with the leaks present.

Figure 4.6 Anode with He and cathode with air. The cell was at 800 °C.

3. H₂ in the anode side and air in the cathode side, the cell at open circuit. Selected masses are shown in Figure 4.7 for both the inlets and outlets. Air peaks of N₂ (shown in mass 29), O₂, Ar and H₂O signals are seen in the anode exhaust. The H₂O at the exhaust

comes from the reaction of the leaked H_2 and air. Although the cell was left at open circuit, with no electrochemical reactions, water was still generated by the spontaneous combustion of hydrogen and oxygen at $800\text{ }^{\circ}\text{C}$. Excess water and some hydrogen also appeared in the cathode exhaust, suggesting that hydrogen was leaking into the air and combusting. The small amount of O_2 in the anode outlet is from air leaks.

Figure 4.7 Anode with H_2 and cathode with air, Cell at OCV and temperature at $800\text{ }^{\circ}\text{C}$.

4. H_2 in the anode side and air in the cathode side, the cell is loaded 0.7V cell voltage ($\sim 170\text{ mA}$ current). Selected masses are shown in Figure 4.8. The gas compositions were very similar to the ones in step 3. The only significant difference is that the water signal at the anode exhaust went up from 24 torr to 60 torr. This incremental amount of water is attributed to oxidation of hydrogen at the anode of the fuel cell. The generated water leaks into the cathode side also, and leads to an increase of the H_2O signals.

Figure 4.8 Anode with H₂ and cathode with air, Cell loaded with 0.7V and temperature at 800 °C.

5. H₂ with 3% water added in the anode side and air in the cathode side, the cell at open circuit. Selected masses are shown in Figure 4.9. The N₂ signal at mass 28 is not shown. Mass 29 signal is chosen to represent the amount of N₂ instead. A very high water signal at mass 18 was seen above 90 torr at both in the inlet and exhaust of the anode. The water at the exhaust was still a little higher than the inlet, because of the combustion of H₂ with the leaked air. Air leaks are apparent in the anode exhaust (O₂, N₂, Ar) and cathode exhaust (H₂).

Figure 4.9 Anode with H₂ + 3% H₂O and cathode with air, cell at OCV and temperature at 800 °C.

6. H₂ with 3% water added in the anode side and air in the cathode side, the cell voltage loaded at 0.7V. Selected masses are shown in Figure 4.10. Relative to the results in step 5, the amount of water in the anode exhaust increased slightly to 94 torr. This water increase is due to the additional electrochemical reactions of the cell.

Figure 4.10 Anode with H₂ + 3% H₂O and cathode with air. Cell loaded with 0.7V and temperature at 800 °C.

7. Dry H₂ with 10 ppm PH₃ added in the anode side and air in the cathode side, the cell at open circuit. Selected masses are shown in Figure 4.11. The N₂ signal at mass 28 in the fuel increased because the PH₃ stock cylinder is balanced with N₂. The difference of mass 28 signals at the anode inlet and exhaust still shows the existence of air leaks. The PH₃ signal at mass 34 is seen in the anode inlet, but is very small (down to the noise level) at the anode exhaust. The PH₃ was present in the fuel gas stream, but was not detected after the fuel stream passed the fuel cell in the hot zone of the furnace. There was also a transient behavior observed in the inlet stream for the PH₃ signal at mass 34 shown in Figure 4.12. The mass 34 signal was dominated by the oxygen isotopes in the first few hours. Then the PH₃ started to increase slowly. After about 5 hours, the mass 34 signal reached a stable value of about 0.02 torr. This slow increase was due to the slow flow (1

mL/min) of gas from the 1000 ppm PH_3 supply. The mass 34 signal (0.02 torr) is approximately three times higher than the expected signal for a gas pressure of 10 ppm (0.008 torr).

Figure 4.11 Anode with $\text{H}_2 + 10\text{ppm } \text{PH}_3$ and cathode with air. Cell at OCV and temperature at 800°C .

Figure 4.12 Transient behavior of PH_3 signal at the anode inlet. The cell was operating at 800°C .

8. Dry H₂ with 10 ppm PH₃ added in the anode side and air in the cathode side, the cell voltage at 0.7V. Selected masses are shown in Figure 4.13. Comparing these results to the results in step 7, the water signal at the anode exhaust was very high at about 98 torr, much higher than the test of “dry” H₂ with 0.7V cell voltage (60 torr in step 4). The reason for the discrepancy is due to the calibration change. The amount of PH₃ detected at the anode inlet and outlet was roughly the same as in step 7, meaning the current change did not have a significant effect of the amount of PH₃.

Figure 4.13 Anode with H₂+10ppm PH₃ and cathode with air. Cell voltage was at 0.7V and temperature at 800 °C.

The cell test was terminated after 6 days of exposure the anode to 10 ppm of PH₃. However, there was no significant degradation of cell performance. The cell was kept at constant 0.7 V cell voltage. The beginning current was 192 mA and after 6 days, the current was 190 mA.

There were no signals of masses greater than 44 (CO₂) detected in the outlet during the test. In particular, there were no increases in the signals at mass 48 (HPO), mass 64 (HPO₂) or mass 80 (HPO₃). The PH₃ added may have quantitatively reacted to form non-

volatile products, or products with mass larger than 100, or the PH_3 was strongly adsorbed onto the inner surfaces of the system. The cell was removed from the test platform after operation. There was a new shiny metallic new layer of material formed on top of the anode surface seen by visual examination of the cell. It is suspected that this new layer is from nickel phosphides formed during the exposure of the cell to trace level of PH_3 . This has been documented many times in the literature. [3-5]

4.3 Conclusions and discussions.

Despite the careful bonding of the gold o-ring to the electrolyte, the cell leaked between the anode and cathode sides. Gases transferred in both directions across the o-ring seal. H_2 reacted with air to form water in both the anode and cathode exhausts. When the current was turned on, the water signal at mass 18 increased quickly in less than 5 minutes. For a current of 190 mA, only 10 torr of water generated by the cell is expected by the calculation. However, the change of pressures of water was more than 30 torr, in some cases about 60 torr. This may due to the fact that the calibration coefficient of water in the Cirrus unit is different from the mass used for calibration. PH_3 at 10 ppm level was detectable at the gas inlet, but was not seen at the exhaust. The change of current did not affect the detected PH_3 partial pressures.

Due to safety regulation changes, the cell testing in WVU MAE had to be terminated. The Probostat testing platform and the mass spectrometer were moved to the Chemistry Research Laboratory. Later tests were carried out in WVU Chemistry.

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Chapter 5 Study of Reactions of PH_3 , H_2O and Ni/YSZ at high temperatures.

5.1 Gas-phase composition study with a tube furnace configuration.

5.1.1 Experimental set up.

In order to understand the possible reactions of PH_3 in the fuel stream in the absence of the fuel cell, a tube furnace with a ceramic tube was employed. The tube furnace configuration is illustrated in Figure 5.1. The temperature was programmed to heat at a linear rate from room temperature to 800 $^{\circ}\text{C}$, to hold at that temperature for several hours, and then to cool to room temperature at a linear rate. The mass spectrometer could be hooked up at the inlet or exhaust to monitor any change of gas phase compositions. This test was carried out in the WVU Chemistry Department.

Figure 5.1 Diagram of tube furnace configuration for testing possible PH_3 reactions.

A gas manifold was built to handle the gas supplies. An illustration of the gas handling system is in Figure 5.2. A typical flow rate was 100 sccm. The PH_3 stock cylinder was 40 ppm balanced with H_2 .

Figure 5.2 Gas manifold used in the gas phase tests.

5.1.2 Gas purity check and calibration curves

The H_2 and He used in this section were ultra-high purity grade. The compressed air was breathing grade. The 40 ppm ($\pm 10\%$) of PH_3 in H_2 balance was custom made by Air-Liquid Company and it was claimed to be industrial grade (lower than UHP). The purity of H_2 , He and PH_3 from the cylinders was checked using the mass spectrometer. Calibration curves of H_2 in He up to 1 atm and ppm levels of PH_3 in H_2 were generated. In these tests, the mass spectrometer was connected to the sampling point right after the mass flow controllers to minimize any leaks in the transfer lines.

1. Gas purity checks of H_2 , He and 40 ppm PH_3 in H_2 .

The H₂ cylinder was connected to the mass flow controller and the mass spectrometer was connected to the port nearest to the mass flow controller. H₂ flow was turned on at 100 sccm for several hours to purge the air and water vapor in the transfer lines. The partial pressures reading from the RGA of the major impurities are: H₂O at 1.5 torr, N₂ at 0.17 torr and O₂ at 0.03 torr. The purity of He was checked using the same method. The major impurities in UHP grade He are: H₂O at 0.22 torr, N₂ at 0.13 torr and O₂ at 0.05 torr. The 40 ppm PH₃ in H₂ was checked at a flow rate of 200 sccm. The major impurities are: H₂O at 2.75 torr, N₂ at 0.47 torr and O₂ at 0.19 torr. The partial pressure of PH₃ in the 40 ppm cylinder is 0.123 torr at mass 34. As noted in the preceding chapter, the measured partial pressure of PH₃ is substantially higher than the actual partial pressure (40 ppm = 0.03 torr) A summary of the impurities in different gases are listed in Table 5.1.

Table 5.1 Major impurities in the gas cylinders.

Gas Cylinder Grade and Content	Partial Pressure of Impurities (torr)		
	H ₂ O	N ₂	O ₂
UHP H₂	1.5	0.17	0.03
UHP He	0.22	0.13	0.05
Industrial 40 ppm PH₃ in H₂	2.75	0.47	0.19

2. Calibration curves.

Calibration curves of H₂ are generated both for dry and wet conditions by varying the H₂ flow rate with a fixed 100 sccm He as balance. The Faraday cup detector was used for

this study. In Figure 5.3, the partial pressure of the dry H₂ reading at mass 2 is plotted versus the calculated pressure of H₂ in He based on the pre-set flow rates. The curve is approximately linear over the entire range of pressures but with a noticeable positive deviation at the higher pressures. A linear regression fit of all data points yields a slope of 1.22(+/-0.05) and an intercept of -35(+/-14) torr. The corresponding fit to the lowest three pressures yields a slope of 1.01(+/-0.03) and an intercept of -7(+/-4) torr. The wet H₂ (10 torr water) calibration curve and linear fits shown in Figure 5.4 are similar. Linear regression slopes and intercepts are 1.14(+/-0.03) and -23(+/-8) torr for all data points and 0.99(+/-0.01) and -4(+/-2) torr for the lowest three pressures. The positive deviations at higher pressures are attributed to changing viscosities of the gas blends. A higher hydrogen content lowers the viscosity and increases the mass flow through the capillary to the ionization chamber.

Figure 5.3 Calibration curve for dry H₂ in He. Symbols: measured P(H₂); solid line: linear regression fit to all data points; dashed line: linear regression fit to the lowest three pressures.

Figure 5.4 Calibration curve for wet H₂ in helium. Symbols: measured P(H₂); solid line: linear regression fit to all data points; dashed line: linear regression fit to the lowest three pressures.

The calibration curve of PH₃ was generated using nominal concentrations of 0, 10, 20 and 40 ppm. The reading at mass 34 was determined at each concentration using the electron multiplier. The curve is shown in Figure 5.5 with a linear regression fit. In mixed units, the slope is 0.00325(+/-0.00014) torr/ppm and the intercept is -0.012(+/-0.004) torr.

Conversion of ppm to torr yields a slope of 4.3(+/-0.2). Again, the measured pressure is substantially higher than the actual pressure. All the calibration curves generated confirmed the linear behavior of the mass spectrometry method from the ppm level up to 1 atm. However, the values are relative but not absolute.

Figure 5.5 Calibration curve and linear regression fit of PH₃ in hydrogen. Symbols: measured pressures; line: linear regression fit to all data points.

5.1.3 Blank gas tests (No cell)

1. “Dry” H₂ test: Pure H₂ from the gas cylinder was passed into the ceramic tube.

The furnace was kept at room temperature for 2 hours. Then the temperature was ramped up to 800°C at a linear rate over 8 hours, held at 800°C for 4 hours, and then cooled to room temperature at a linear rate over 8 hours. Figure 5.6 is an overview of gas profile of mass 18 (H₂O), 28 (N₂) and 32(O₂). The H₂O pressure (mass 18) increased slightly during heating and then dropped to its lowest level during cooling. Nitrogen pressures (mass 28) show a linear change with temperature. The cause for this linear change is not known since it is not observed for the Probostat tests (see below). However, it is a convenient temperature gauge in this plot. Oxygen pressures (mass 32) drop during the

heating phase at temperatures above 400 °C to 0.15 torr (Figure 5.7) and rise again during the cooling phase.

Figure 5.6 "Dry" H₂ blank test gas pressures vs time.

Figure 5.7 Oxygen (mass 32) vs temperature during the heating phase in "dry" H₂.

From this test, it can be said that the sealing of the tube furnace configuration is acceptable with impurities below 5 torr and the ^{18}O isotope will not interfere with the detection of PH_3 at mass 34. The N_2 signal is below 2 torr. There is some O_2 in the system, about 0.3 torr at room temperature. The decrease of O_2 at higher temperatures is due to the auto-ignition with the major component H_2 . However, there is still a small amount of O_2 even at 800 °C. One hypothesis is that the O_2 may be the fraction that did not combust. However, the combustion reaction of H_2 with O_2 is very fast at 800 °C. The equilibrium partial pressure of O_2 in pure H_2 is in the order of 10^{-11} torr. Another source of the O_2 is small leaks in the fittings around the ceramic tube after the heated zone and the place that the sampling capillary enters the mass spectrometer. The slight increase of H_2O signals also confirms the reaction of H_2 and the residual O_2 . The “dry” H_2 test sets a baseline of gas compositions for the next experiments.

2. “Wet” H_2 test: Pure H_2 from the gas cylinder was first passed through the humidifier, generating a gas stream with about 20 torr of H_2O . The furnace was kept at room temperature for 4 hours, then was ramped up to 800 $^{\circ}\text{C}$, held at 800 $^{\circ}\text{C}$ for 4 hours, and then cooled down in 6 hours. An overview of gas compositions versus time is in Figure 5.8.

Except for a blip at the beginning of the heating step, H_2O pressures (mass 18) remain at around 130-140 torr, which is much higher than expected due to the different calibration coefficients. Again, nitrogen pressures (mass 28) show a linear change with temperature.

Figure 5.8 “Wet” H₂ blank test gas pressures vs time.

Oxygen pressures (mass 32) drop during the heating phase and rise again during the cooling phase. The auto-ignition appears to start around 300 °C in this case (Figure 5.9). Surprisingly, the oxygen signal remains at about 0.1 torr even at 800 °C. The oxygen in the “wet” H₂ test is lower than in the “dry” test because it is partially displaced by the water vapor.

Figure 5.9 Oxygen (mass 32) pressure vs temperature during heating phase in the “wet” H_2 test.

In comparison to the “dry” H_2 test, the major gas compositions are similar except the H_2O signal. The water content detected is much higher than the calculated value (~120 torr vs 20 torr).

3. “Dry” H_2 with 20 ppm PH_3 test: The pure H_2 was 1:1 blended with stock 40 ppm PH_3 in H_2 , making the actual concentration of PH_3 20 ppm. The furnace was held at room temperature for 2 hours, then was ramped up to $800^{\circ}C$ in 12 hours, held at $800^{\circ}C$ for 10 hours, and then cooled to room temperature over 12 hours.

An overview of the major gases is shown in Figure 5.10. Water (mass 18 in Figure 5.11) shows a continuous decrease in signal, particularly during the cooling phase. The signal for nitrogen (mass 28) tracks the furnace temperature, again. The phosphine (mass 34) shows two dips during the heating and cooling of the furnace.

Figure 5.10 “Dry” H_2 + 20 ppm PH_3 test gas pressures vs time.

Figure 5.11 H_2O , N_2 and O_2 signals in “Dry” H_2 +20 ppm PH_3 test pressures vs time.

During heating in Figure 5.12, the PH_3 signal at mass 34 remains nearly constant until about 400 °C. It drops abruptly from 0.12 torr to 0.008 torr, and then rises abruptly back to 0.12 torr just above 600 °C. The O_2 signal at mass 32 also drops abruptly at 400 °C, and then rises at 600 °C. The contributions of PH_3 at mass 32 are believed to be minor. The signal for PH at mass 32 is probably in the order of 0.03 torr. Consequently, the loss of PH_3 at 400-600 °C is probably due to reaction of PH_3 with O_2 . There are no visible fluctuations in the H_2O signal (mass 18 in Figure 5.11); however, H_2O has a much higher concentration (~10 torr apparent signal, ~1 torr true pressure) because of the different calibration coefficient. The reaction of PH_3 and oxygen at 400 °C is not surprising. Possible products are HPO , HPO_2 , HPO_3 , H_3PO_4 or P_4O_{10} . Only HPO (mass 48), HPO_2 (mass 64) and mass HPO_3 (mass 80) are in the mass range of the mass spectrometer, and there are no visible signals at these masses. The biggest surprise is the reappearance of the mass 34 signal at 600 °C. A hypothesis is that the product that is formed between 400 and 600 °C is thermally unstable above 600 °C and consequently PH_3 is regenerated. Additional support for this hypothesis is provided by the cooling curve data plotted in Figure 5.13, which shows the same pattern in reverse. The reaction of PH_3 may have a negative change of Gibbs free energy below 600 °C and a positive change above 600 °C, and the entropy change is negative. So the reaction does not happen below 400 °C because of an activation energy barrier.

Figure 5.12 Details of mass 32 and 34 vs temperature during the heating process in “dry” $\text{H}_2 + 20 \text{ ppm PH}_3$.

Figure 5.13 Details of mass 32 and 34 vs temperature during the cooling process in “dry” $\text{H}_2 + 20 \text{ ppm PH}_3$

Mass spectra comparison of 300 °C and 500 °C are shown in Figure 5.14. There are no significant signals above mass 44 (CO₂). Masses 31 (P), 32 (O₂ and PH), 33 (PH₂) and 34 (PH₃) show decreases going from 300 °C to 500 °C. There is no signal increase which correlates with the loss of PH₃. All other signals can be related to gases present in the mixture (H₂, H₂O, N₂, Ar, CO₂). So there is no HPO, HPO₂ or HPO₃ generated with 20 ppm PH₃ and low water content. PH₃ does react at higher temperatures. However, the products are undetectable with the current instrument.

Figure 5.14 Mass spectrum comparisons of 300°C and 500°C in “dry” H₂ + 20 ppm PH₃

5.1.4 Gas tests with PH₃ and NiO/YSZ sample piece inside the ceramic tube.

A loose piece of fresh, unreduced NiO/YSZ sample was put into the ceramic tube, approximately in the center of the heated zone. The sample was a piece of an anode-supported half cell with an area about 1 cm².

1. “Dry” hydrogen with 20 ppm PH_3 test: Pure H_2 was mixed 1:1 with 40 ppm PH_3 in H_2 as described before. The furnace was kept at room temperature for 2 hours, then ramped up from room temperature to 800 °C in 6 hours, then held for 10 hours, and then programmed to cool over 6 hours. The overview of mass 28, 32 and 34 is in Figure 5.15.

Figure 5.15 Gas pressures vs time in “Dry” H_2 + 20 ppm PH_3 with NiO/YSZ sample

The N_2 signal at mass 28 appears to correlate well with the actual furnace temperature. The heating step is linear as programmed, but the cooling step is nonlinear because the furnace did not cool as fast as the programmed temperature. As in the preceding case of PH_3 in “dry” H_2 , the PH_3 signal decreases, but it remains low at 800 °C (compared with PH_3 signal in “dry” H_2 without a NiO/YSZ sample present in Figure 5.10). During cooling, the PH_3 signal decreases further and then rises back to the initial

level. After the experiment, the reduced Ni surface did not appear to have any visible new phases on the outer surface, although PH_3 could have reacted with the Ni.

Figure 5.16 H_2O and N_2 pressures vs temperature during the heating phase in “dry” H_2 + 20 ppm PH_3 with NiO/YSZ present.

The water signal (mass 18) in Figure 5.16 shows a spike between 400 °C and 600 °C. This spike is not present during the cooling phase. The green NiO is converted to metallic Ni during this step. The amount of water generated is enough to replace some of the N_2 and cause a dip in the N_2 signal (mass 28). The O_2 signal (mass 32) in Figure 5.17 shows a similar pattern as before, decreasing sharply at the same temperature as the drop in the PH_3 signal.

In comparison to the results without a Ni/YSZ sample piece, the PH_3 signal at mass 34 is much lower at 800 °C, which implies that the PH_3 is reacting with the Ni/YSZ sample. But the products are either non-volatile or out of the detectable mass range (above 100 amu).

Figure 5.17 O₂, N₂, and PH₃ pressures vs temperature during the heating phase in “dry” H₂ + 20 ppm PH₃ with NiO/YSZ sample

2. “Wet” hydrogen with 20 ppm PH₃ test: The pure H₂ was passed through the humidifier first, and then mixed with 40 ppm PH₃ in H₂. A loose piece of an anode-supported half cell with an area about 1 cm² was put inside the ceramic tube near the center of the heating zone. The furnace was kept at room temperature for 2 hours, then ramped up from room temp to 800 °C in 6 hours, then held for 10 hours, and then programmed to cool down in 6 hours. An overview of masses 28, 32 and 34 at the outlet during the whole process is shown in Figure 5.18.

Figure 5.18 Gas pressures vs time with “wet” H_2 + 20 ppm PH_3 with a NiO/YSZ sample.

With high water content added, the PH_3 signal at mass 34 drops steeply upon heating from 0.097 torr to 0.002 torr and then rises to 0.008 torr. The trend is reversed during furnace cool down.

Figure 5.19 H_2O and N_2 pressures vs temperature during heating in “wet” H_2 + 20 ppm PH_3 with NiO/YSZ sample.

Despite the very high amount of added water background at about 100 torr, the spike in H_2O signal when the NiO is reduced still very evident in Figure 5.19. The peak pressure for mass 18 appears to have reached the saturation level for the electron multiplier. Again, the generated water replaces some of the N_2 so the N_2 signal shows a dip in the same temperature range. O_2 decreases with the dip of PH_3 as well.

The PH_3 level at 800 °C is lower than the blank tests without a Ni/YSZ sample, and also lower than the “dry” PH_3 with sample test. The PH_3 actually gets to the sample and reacts with it. With higher water content, more PH_3 is reacted. However, the products are still not detected with the Cirrus unit. The sample was removed from the furnace for a visual examination; the reduced Ni surface appeared to have a thin new shiny layer. The new material is believed to be the nickel phosphide. However, there was not an opportunity to have the sample tested with SEM or EDS to have the microstructure and elemental information.

5.1.5 P_2O_5 sample test

P_2O_5 and other phosphorus oxides are predicted by calculations to be possible PH_3 reaction products [1,6]. PH_3 can be generated by heating the P_2O_5 to 300 °C as described in Chapter 2. [6] It is necessary to know that if the phosphorus oxide is detectable using the current instrument. A small amount of P_2O_5 sample was placed in a crucible. The crucible was then placed inside the alumina tube in the furnace. There is no other sample or cell inside the furnace. The gas flow was H_2 at 200 sccm. After the air had been purged, the furnace was heated from room temperature to 350 °C in steps of 50 °C. The melting point of P_2O_5 is 340 °C and the boiling point is 423 °C, so sufficient vapor pressure of P_2O_5 and its possible fragments should have been generated to permit detection by the mass

spectrometer. The mass spectrometer was connected to the exhaust. All visible signals in the mass spectra are assigned to H_2 and air impurities. No new masses associated with phosphorus appear, indicating that fragment ions of P_2O_5 are not seen with the current instrument. A mass spectrum taken at $350^\circ C$ is shown in Figure 5.20. This result contradicts the predictions by Sasaki et al.[6] One of the hypotheses is the generated PH_3 has reacted before it reaches the mass spectrometer.

Figure 5.20 Mass spectrum of exhaust gas with P_2O_5 sample at $350^\circ C$.

5.2 Gas-phase studies with the ProbostatTM.

5.2.1 Experimental set up

The preceding experiments are repeated in the Probostat to verify the patterns of reactivity and as a prelude to mounting a cell in the Probostat. In these high-temperature gas-phase studies inside the Probostat, there is only one chamber, not separated by a cell

or sample into the anode and cathode side. The gas comes in from the base, passes through the inner tube (normally the cathode side) to the top, and then flow back down the outer tube (normally the anode side) to the base and the exhaust. The mass spectrometer is connected with a T-joint to the exhaust gas port.

5.2.2 Blank gas tests (No cell)

These tests replicate the ones described previously using the alumina tube in the tube furnace. Leak checks are performed before the gas tests to confirm that there is no significant air leaking into the Probostat chamber from the atmosphere air. With 200 sccm H_2 fed into the inlet, N_2 pressure was about 1.0 torr at the outlet sampling point by the mass spectrometer. This result confirms the presence of an acceptably gas tight seal.

1. “Dry” H_2 test: H_2 from the gas cylinder was directly fed into the Probostat. The furnace was heated up in 10 hours, kept at 800 °C for 10 hours, and then cooled down on its own. The furnace surrounding the Probostat can only be programmed to ramp up the temperature during heating. Cooling is achieved by cutting the power to the furnace.

Figure 5.21 is an overview of the pressures of masses 18, 28 and 32. In this test configuration, the N_2 signal (mass 28) shows a different behavior from the ceramic tube set up. The N_2 signal goes down linearly with temperature change. At 800°C, the N_2 is about 1.1 torr. In comparison, the N_2 signal becomes higher at high temperatures in the tube furnace set up. The water signal (mass 18) decreases continuously as the water trapped is being purged and then stays at 6.7 torr. Based on the 100 torr signal obtained with 10 torr of water in the wet hydrogen, the actual pressure of water in “dry” H_2 is less than 1 torr. Figure 5.22 shows the mass 34 signal together with N_2 and O_2 over time. Both

the mass 34 and mass 32 signals show slight decreases upon heating to 800 °C and increases during the cooling step.

Figure 5.21 Gas pressures vs time in the “dry” H₂ test with the Probostat.

Figure 5.22 Mass 34, N₂ and O₂ pressures vs time during the “dry” H₂ test with the Probostat.

2. “Wet” H₂ test: H₂ from the gas cylinder was passed through the humidifier, and then fed into the Probostat. The true partial pressure of water was about 20 torr. The temperature was ramped up with a 1.5 °C/min rate to 800°C, taking 8 hours. The furnace was kept at 800 °C for 9 hours and cooled down afterwards. The gas pressure overview is shown in Figure 5.23.

The water signal (mass 18) stays very high without a significant change with the temperature. The O₂ signal (mass 32) decreases sharply when the auto ignition starts, and goes back up when the temperature drops below the ignition point during cool down. The N₂ signal at mass 28 shows a linear change with temperature as described above. Figure 5.24 shows the signal at mass 34 over time with other gases. The pattern here is essentially the same as in “dry” H₂. The “dry” and “wet” H₂ tests are performed to define a necessary baseline of background gas compositions.

Figure 5.23 Gas pressure vs time in the “wet” H₂ test with the Probostat.

Figure 5.24 Mass 34, N₂ and O₂ pressures vs time during the “wet” H₂ test with the Probostat.

3. “Dry” H₂ with 20 ppm PH₃ test: H₂ was mixed 1:1 with the 40 ppm PH₃ stock cylinder. The temperature was controlled to ramp up with a 1.5 °C /min rate to 800 °C in about 8 hours. Then the furnace was kept at 800 °C for 12 hours, and was cooled to room temperature afterwards. The gas pressure overview is in Figure 5.25.

Figure 5.25 Gas pressures vs time in the “dry” H_2 + 20 ppm PH_3 test with the Probatat.

Figure 5.26 is a plot of mass 28, 32 and 34 vs temperature during the heating up process. N_2 and O_2 pressures are similar to the previous blank tests. The PH_3 signal was about 0.1 torr initially. After the temperature reaches 300°C , the PH_3 signal quickly drops to nearly zero, below 10^{-3} torr range. With the temperature rising, after 600°C , the PH_3 climbs up and reaches a peak about 0.12 torr, and then it stabilizes around 0.09 torr at 800°C . The “dipping” occurs during the cooling down within roughly the same temperature range. These results are consistent with the tube furnace results described previously. The PH_3 may react with O_2 at $300\text{--}600^\circ\text{C}$ to form either a non-volatile product or a product with mass greater than 100 that is out of the detectable mass range. The products then becomes thermally unstable after 600°C and the PH_3 re-appears.

Figure 5.26 Pressures vs temperature during the heating phase of “dry” H_2 + 20 ppm PH_3 test with the Probostat.

4. “Wet” H_2 with 20 ppm PH_3 test on the Probostat: The H_2 was passed through the humidifier before being mixed 1:1 with the 40 ppm PH_3 in H_2 . The temperature was ramped up to 800°C over 8 hours with a rate of $1.5^\circ\text{C}/\text{min}$. Then the furnace was kept at 800°C for 12 hours, and then cooled down (not controlled) afterwards. An overview of gas pressures can be seen in Figure 5.27.

Figure 5.27 Gas pressures vs time during the “wet” H_2 + 20 ppm PH_3 test with the Probostat.

Water is not included in Figure 5.27 because the water level is high around 100-120 torr. N_2 and O_2 signals behave just as in previous tests. A detailed plot of gas pressures vs temperature during heat up is shown in Figure 5.28. The PH_3 (mass 34) starts dropping a little earlier at 220 $^\circ\text{C}$. This drop is quick and at about 400 $^\circ\text{C}$, the signal of PH_3 is at the noise level. Unlike the “dry” test, the PH_3 does not rise up when the temperature approaches 800 $^\circ\text{C}$. The PH_3 signal stays in the noise range until the temperature reaches a low enough point during the cool down process. The PH_3 signal finally recovers to the initial value about 0.08 torr after the furnace is cooled down.

Figure 5.28 Gas pressures vs temperature during the heating phase of “wet” H_2 + 20 ppm PH_3 test with the Probostat.

Summary of the gas tests with the Probostat:

The leaks between the inner chambers of the Probostat and the outside air are acceptably low. The existence of water vapor does not affect the N_2 and O_2 behavior. In dry hydrogen, the PH_3 reacts with other gases, or is adsorbed into the walls of the Probostat at temperature range of roughly 300-600 °C. The product of PH_3 reaction is either a non-volatile compound or a product with a molecular mass greater than 100 amu. In “wet” hydrogen, PH_3 reacts quantitatively above 300 °C. Again, no products containing phosphorus are detected by the mass spectrometer.

5.2.3 Gas tests with a loose NiO/YSZ sample piece inside the Probostat.

The NiO/YSZ sample is similar to the ones used in tube furnace tests. The sample piece is placed into the supporting alumina tube of the Probostat, not blocking the inner tube. The cathode side and anode side are still connected as before.

“Dry” H_2 and the NiO/YSZ sample in 20 ppm PH_3 with the Probostat test: The sample was a piece of anode supported half cell (NiO/YSZ) with an area of about 1 cm^2 . The temperature was controlled to ramp up to 800°C with a $1.5^\circ\text{C}/\text{min}$ rate, and was held at 800°C for 40 hours and then cooled to room temperature. The profile of gases overview during the entire experiment is shown in Figure 5.29.

Figure 5.29 Gas pressures vs time during the “dry” H_2 + NiO/YSZ sample in 20 ppm PH_3 with the Probostat test

As described in other experiments, the N_2 signal decreases linearly with increasing temperature. Due to reduction reaction of the NiO with H_2 to form metallic Ni, a large amount of water is released, replacing part of the N_2 signal at mass 28. The dip in the N_2 signal is clearly seen in detail in Figure 5.31, with a water peak at 300-400°C.

Figure 5.30 is a plot of gases during the heating phase. The PH_3 signal drops with temperature rise to about 0.02 torr, starting at 200°C. When the furnace temperature approaches 800°C, the PH_3 signal rises back to a spike peak of 0.09 torr, and then slowly coasts to a stable 0.03 torr level (Figure 5.29). There is also a dip of PH_3 during the cooling down process. Then the PH_3 signal climbs back to its initial value above 0.1 torr after complete cool down. The presence of PH_3 in the exhaust at 800 °C with a piece of Ni/YSZ in the Probostat suggests that some of the PH_3 passes by the Ni without reaction.

Figure 5.30 Pressures of O_2 , N_2 and Mass34 vs temperature during the heating phase of “dry” H_2 + NiO/YSZ sample in 20 ppm PH_3 with the Probostat.

Figure 5.31 Pressures of water and N_2 vs temperature during the heating phase of “dry” H_2 + NiO/YSZ sample in 20 ppm PH_3 with the Probostat

“Wet” H_2 and NiO/YSZ exposed to 20 ppm PH_3 test with the Probostat: A NiO/YSZ piece was placed inside the inner alumina tube of the Probostat. The gases were prepared as described in other “wet” PH_3 tests. The temperature was ramped up with a 1.5 $^{\circ}C/min$ rate to 800 $^{\circ}C$ and stayed at 800 $^{\circ}C$ for about 40 hours. Then the furnace was cooled down.

Figure 5.32 is the gas overview of the whole process. The water signal (not shown) is very high (100-120 torr) and stable. The other major differences between “dry” and “wet” conditions are the PH_3 levels at 800 $^{\circ}C$. In “wet” conditions, the PH_3 signal drops to the noise level and does not recover when the temperature is close to 800 $^{\circ}C$. Figure 5.33 is a detailed plot of gases vs the temperature during the heating step. However, the PH_3 still climbs up to the initial value near the end of the experiment, when the temperature is cool enough.

Figure 5.32 Gas pressures vs time during the “wet” hydrogen + 20 ppm PH₃ with NiO/YSZ in the Probostat.

Figure 5.33 Gas pressures vs temperature for water, N₂ and PH₃ signal during heating phase of “wet” hydrogen + 20 ppm PH₃ test with NiO/YSZ present in the Probostat.

The PH₃ signal at mass 34 in the Probostat tests shows a similar behavior with the tests using tube furnace configuration. PH₃ drops when the temperature is ramping up, and then recovers when the temperature reaches 800 °C in some of the tests. The signal of N₂

is much different. In the ceramic tube tests, the N_2 increases with temperature while in the Probostat tests it decreases. The reason is unknown. One hypothesis is that small leaks develop around the fittings of the ceramic tube during heating.

5.3 Gas test with quartz tube.

A quartz tube with outer diameter of 1 inch was used to replace the alumina tube. The purpose is to investigate any possible reactions between the alumina or quartz tube with the PH_3 . As before, 20 ppm of PH_3 in “dry” H_2 was fed through the tube. The furnace was kept at room temperature for 3 hours to allow air impurities to be purged out. Then the temperature was ramped up to $800^\circ C$ over 6 hours, kept at $800^\circ C$ for 10 hours, and then cooled down over 6 hours. The overall view of masses 28, 32 and 34 is shown in Figure 5.34. A detailed gas pressure vs temperature is in Figure 5.35. The PH_3 at mass 34 is at 0.03 torr initially. When the temperature reaches $348^\circ C$, the PH_3 signal decreases very sharply. Within 3 minutes, the signal at mass 34 drops to nearly zero (noise level). With the temperature still rising, the mass 34 signal gradually recovers at about $600^\circ C$. After $800^\circ C$, the PH_3 signal stabilizes at 0.02 torr, about 60% of the initial amount. This same “dip” behavior occurs also during the cool down phase. The final sharp rise of PH_3 signal occurred at $277^\circ C$.

Figure 5.34 Gas pressures vs time in "dry" H_2 + 20 ppm PH_3 with the quartz tube..

Figure 5.35 Gas pressures vs temperature for water, N_2 and PH_3 signal during the heating phase of the test with the quartz tube.

A comparison of mass spectra taken at 300°C and 500°C is shown in Figure 5.36. Masses 31, 32, 33 and 34 signals all show a decrease with the increased temperature. No new species appear above mass 44. The pattern with a quartz tube is very similar to the pattern with an alumina tube, suggesting that reactions of PH_3 are not associated with the surface or the material of the tube. After the experiment, the quartz tube was checked visually and no deposits were found in the inner surface.

Figure 5.36 Comparison of mass spectra at 300°C and 500°C.

5.4 Conclusion and discussions

Loss of PH_3 is observed in most of the tests at various temperatures. However, at no point in any of the tests and at any of the conditions are any significant mass signals observed at masses above 44. One hypothesis is that the loss of the PH_3 is due to reactions, and that the products of these reactions are not detected because either they are

not volatile or they have molecular mass greater than 100 amu. The “nonvolatile” hypothesis is inconsistent with the known effect of phosphine on the anode of a SOFC.

In the “dry” H_2 without water added, PH_3 reacts at intermediate temperatures in the range of about 300-600°C. But the PH_3 does not react at high temperatures (close to 800°C). With the presence of NiO/YSZ sample, PH_3 reacts with the Ni/YSZ once the NiO is reduced in H_2 . The trends in loss/recover of PH_3 signals are tracked by O_2 signals (mass 32), but not by water signals (mass 18).

The result in the test with quartz tube in Section 5.4 is similar to the results on the alumina tube in Section 5.1.3. This result suggests that there is no reaction between the PH_3 and the tube wall. The “dip” of PH_3 signal during heating is reproducible with both tubes even though they are made from different material.

From the observations discussed above, a conclusion is drawn that in “dry” H_2 conditions at 800 °C, PH_3 will retain its form and reaches the anode of the SOFC. And, in “wet” conditions, PH_3 reacts to form other species that not detected by the RGA. Thus, the species reaching the anode in “wet” conditions are currently not known. However, in the previous cell tests, the anode reacts with PH_3 in both dry and wet conditions. Nickel phosphides (Ni_xP_y) are observed on the anode surface as a product. [3-5] The phosphorous species is reaching the anode in either dry or wet case and reacting with the nickel to form nickel phosphides.

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Chapter 6 In-situ cell tests with Mass Spectrometry in WVU

Chemistry Research Lab

6.1 Experimental set up

The gas manifold described in Chapter 5 is modified to deliver gas to the Probostat for the cell test. The modified diagram is in Figure 6.1. In this set up, H_2 goes to the anode side, air goes to the cathode side and He can be fed to both sides if needed. The air source is a compressed air cylinder.

Figure 6.1 gas manifold used in the cell test

The Probostat was used as the testing platform and a MSRI anode-supported cell was mounted in the Probostat. The original cell had a diameter of 27 mm. It was polished down to 25 mm to fit in the Probostat. The cathode area of the cell was 1.54 cm^2 , smaller

than the anode. In the experiments that follow, the normalization of the electrochemical data is based on the area of the cathode. The connection to the cell cathode was made through the inner tube as described earlier in Chapter 4. A new method using a glass tape sealing material to prevent leaks was employed in this test. Two layers of O-ring shaped glass tape were nested together to make a gasket between the cell and the supporting tube. A photo showing the assembling of the cell is in Figure 6.2. The cell was pressed down with a spring-loaded alumina assembly. High tension springs were chosen in this test.

Figure 6.2 Assembling a cell with glass tape seals.

The electrochemical tests were performed using a Gamry potentiostat, which was connected to the cell using four leads: working electrode (for current), working sense (voltage sense), counter electrode (current) and reference electrode (voltage sense). The anode was connected as the working electrode. The polarization curves were obtained from the cyclic voltammetry tests. The impedance was tested from 100 kHz to either 0.1 or 0.01 Hz.

6.2 Cell test I – pre-conditioning.

After the mounting the cell, the cathode side was fed with air and the anode side with He. The mass spectrometer was connected to the exhaust of the anode. The furnace was heated to 800°C at a rate of 0.8 °C/min. The heating phase took 16.4 hours. N₂ and O₂ pressures during heating are plotted vs time in Figure 6.3. Water and mass 34 signals are in Figure 6.4. During this heating step, the N₂ and O₂ and mass 34 (mainly from ³⁴O₂ as a leak indicator) pressures increased and then abruptly decreased, suggesting that the glass tape had sealed the cell. The abrupt drop in pressures appears to occur before the furnace reached the set point temperature (800 °C) at 16.4 hours, suggesting that the glass seal had formed at a lower than expected temperature (850°C). The water signal at mass 18 dropped to about 0.25 torr.

Figure 6.3 Gas pressures vs time for N₂ and O₂ during the initial heating phase, the cell reached 800 °C at 16.4 hours.

Figure 6.4 Gas pressures vs time for water and mass 34 during the initial heating phase, the cell reached 800 °C at 16.4 hours.

The cell was then reduced in 10% H₂ in helium (at 32.1 hours in Figure 6.5), 50% H₂ in helium (at 43.9 hours) and 100% H₂ (at 48.5 hours). The open circuit voltage of the cell was 1.174V at this point. The N₂ and O₂ pressures are in Figure 6.5, and the water and mass 34 signals are in Figure 6.6. The spike in mass 28 at 32 hours corresponds to the addition of 10% H₂ to the He. There are usually some residual air impurities in a gas line that appear when that line is switched on. The water pressure rises to ~10 torr for 3.5 hours and then suddenly drops. This step corresponds to the water generated by the reduction of NiO to Ni. During this time, N₂ and O₂ signals show a slight rise. At 44 h, the change to 50% H₂ causes step rises in N₂, O₂, and H₂O. Steps also appear at the change to 100% of 100 sccm H₂ at 48 hours. These changes are attributed to the impurities in the hydrogen supply. The open circuit voltage was 1.189V after the cell was reduced. This high OCV is consistent with a leak-free seal and with “dry” H₂ as the fuel. 200 sccm of air was fed to the cathode during the entire experiment.

Figure 6.5 N₂ and O₂ pressures vs time during cell reduction. H₂ was introduced to 10% at 32 hours, increased to 50% at 44 hours and 100% at 48 hours.

Figure 6.6 Water and mass 34 pressures vs time during cell reduction. The time of gas changes are the same as in Figure 6.5

A polarization curve from cyclic voltammetry was acquired after the cell was reduced (Figure 6.7). There is a slight hysteresis on the forward and reverse scan, possibly caused by generated water vapor near the anode during the reverse scan. The cell current density reaches nearly 0.64 A cm^{-2} at 0.1 V . The peak power is 0.18 W cm^{-2} at 0.35 A cm^{-2} .

Impedance data in Figure 6.8 show that the normalized R_s is $1.18 \Omega \text{ cm}^2$ and that R_p is above $3.0 \Omega \text{ cm}^2$. The impedance scan extends from 100 kHz to 0.1 Hz in this data set. The arc does not come down to the real axis at low frequencies, so the later impedance data sets were collected down to 0.01 Hz. The high series resistance found in the impedance data accounts for the poor power performance of this cell. If the cell voltage is corrected for the iR drop by assuming a more realistic series resistance of 0.2 ohm cm^{-2} , then the corrected cell voltage at 0.64 A/cm^2 is 0.74 V , and the corresponding cell power is 0.48 W cm^{-2} .

Figure 6.7 Cyclic voltammetry and power curve after cell reduction. Cell was in pure H_2 at 800°C .

Figure 6.8 Nyquist plot in dry H_2 after cell reduction. The cell was at 800 °C.

The N_2 , O_2 , water and mass 34 signals during the CV test are in Figures 6.9 and 6.10. The CV test was at 76 hours. Beginning from 76.4 hours, the cell was loaded at 1.0 V cell voltage to burn in the cell (a standard technique in SOFC research). The air peaks (mass 28 and 32) increase during current flow after 76.4 hours. This may be due to a slight leak developed around the cell when the current is applied. The water generated during current flow is detected.

Figure 6.9 N_2 and O_2 pressures during the CV test. The cell was at 800 °C.

Figure 6.10 Water and mass 34 signals during the CV test. The cell was at 800 °C.

The current flow is stopped at 100 hours. In Figure 6.11, the H₂O signal drops, but the O₂ and N₂ signals do not. This observation suggests that the formation of a leak occurs at the onset of current flow. The mass 34 signal tracks the mass 32 signal, suggesting that this small signal is caused by ³⁴O₂.

Figure 6.11 N₂, O₂, water and mass 34 pressures when a small current is applied. The cell was in “dry” H₂ at 800 °C.

6.3 Cell test II – different gas composition and cell voltages.

In this section, the cell was the same single cell described in Section 6.2 with the same glass seal. The cell was first operated in “dry” H₂, then the fuel flow was changed

to “wet” H₂, “dry” H₂ + 20 ppm PH₃ and “wet” H₂ + 20 ppm PH₃, respectively. Mass spectrometry, cyclic voltammetry (CV) and electrochemical impedance (EIS) data were obtained for each gas composition.

6.3.1 “Dry” hydrogen test.

The fuel flow for this test is pure H₂ at 100 sccm from the cylinder. The cell is kept at open circuit except during electrochemical tests. The open circuit voltage is 1.189 V. A polarization curve with the dry hydrogen as fuel is shown in Figure 6.12. The peak power density of 0.18 W cm⁻² is seen at 0.49 V. The current is 0.49 A cm⁻² at 0.3 V. While this cell performance improved after current burn-in, the figures of merit here are considered to be lower than cell performances in the previously published studies by Xu et al. [2-3] The current density of the cells tested by Xu can be up to 1 A cm⁻² at 0.3 V. As noted previously, the low performance is caused by the high series resistance. There are some hysteresis and noise in the polarization and power curves. This may due to the water generated during the scan to higher currents accumulating near the anode surface.

Figure 6.12 Polarization and power curves in “dry” H₂ after burn-in. The cell was at 800 °C.

The EIS data (Nyquist plot) is in Figure 6.13 for a scan from 100 kHz to 0.01 Hz. The peak frequency is at 0.10 Hz. The normalized R_s is $1.2 \Omega \text{ cm}^2$ and the R_p is larger than $5 \Omega \text{ cm}^2$. Both of the resistances are very high compare to the cell tested by Xu et al., which is $0.2\text{-}0.3 \Omega \text{ cm}^2$ for the R_s and less than $1 \Omega \text{ cm}^2$ for the R_p [2]. Correcting the cell voltage for iR drop and assuming a true series resistance of $0.2 \Omega \text{ cm}^2$ for R_s leads to a minimum cell voltage of 0.78 V and a power of 0.38 W cm^{-2} at the maximum current of 0.48 A cm^{-2} . With this correction, this cell’s performance is closer to that of Xu et al. As will be shown later, the high polarization resistance arises from the low water pressure in the “dry” hydrogen. The test stand used by Xu et al. likely had higher water pressure due to leaks across the anode seal.

Figure 6.13 Nyquist plot for the cell in “dry” H₂. The cell was at 800 °C.

The cell is then subjected to 0.9 V, 0.7 V and 0.5 V for one hour at each voltage. The N₂ and O₂ pressures are in Figure 6.14. Water and mass 34 data are shown in Figure 6.15.

The effects of electrochemical tests are clearly seen at 3.4, 3.8, 6.3 and 10.0 hours. The water shows large rises when the current is turned on due to the water generated by hydrogen oxidation. Other gas signals have slight dips because of partial displacement of each gas by the large amount of water generated. The relation of cell current and the partial pressure of water are shown in Table 6.1. The water concentration is not linear with the cell current. At high water content, the detector may have been nearly saturated.

Figure 6.14 N_2 and O_2 pressures in "dry" H_2 during applied cell voltages. The cell was at $800\text{ }^{\circ}\text{C}$.

Figure 6.15 Water and mass 34 pressures in "dry" H_2 during applied cell voltages. The cell was at $800\text{ }^{\circ}\text{C}$.

Table 6.1 Cell current and the water concentrations

Cell Voltage (V)	Current (A)	Partial pressure of water (torr)
1.2	0	1
0.9	0.15	8
0.7	0.34	15
0.5	0.52	16

By comparing the mass spectrometry data taken at open circuit and 0.5 A current, it is evident that no new products above mass 44 are found.

6.3.2 “Wet” hydrogen test.

The H₂ from the cylinder is passed through the humidifier at room temperature. The air trapped inside the dead volume of the humidifier is purged over one hour. The polarization and power curves are in Figure 6.16. The peak power is 0.17 W/cm² at 0.46 V, slightly lower than the peak power in dry H₂. There is less hysteresis at low currents because of the presence of water at open circuit. The Nyquist plot from the EIS data is in Figure 6.17. The normalized R_s is 1.2 Ω cm² and the R_p is 1.1 Ω cm². Correcting the series resistance from 1.2 to 0.2 Ω cm² yields a cell voltage of 0.77 V and a cell power density of 0.36 W cm⁻² at the maximum current density of 0.47 A cm⁻². The polarization resistance drops dramatically from over 5 Ω cm² in the dry H₂ to 1.1 Ω cm² in the wet H₂. This behavior is caused by the well-known decrease in activation resistance in the presence of higher water content. [7]

Figure 6.16 Polarization and power curves in “wet” H₂. The cell was at 800 °C.

Figure 6.17 Nyquist plot at OCV in “wet” H₂. The cell was at 800 °C.

The cell is then subjected to applied voltages of 0.9 V, 0.7 V and 0.5 V for one hour starting at times of 1.3, 3.0 and 5.4 hours, respectively. Signals of N₂ and O₂ are in Figure 6.18. Water and mass 34 signals are in Figure 6.19. Changes in N₂ and O₂ are apparent during the electrochemical tests. The water signal at mass 18 stays high at about 15 torr until the fuel stream is turned back to “dry” H₂ at 7.4 hours. This high water level is close

to the saturation of the electron multiplier detector in this data set. The water generated by the electrochemical reactions is not seen due to the high water background. However, the mass 18 pressure does not start dropping until 9.6 hours. This lingering water signal may be because liquid water trapped in the system (possibly in the base of the Probostat) needs time to be swept out.

Figure 6.18 N₂ and O₂ pressures during current flow in the “wet” H₂ test. The cell was at 800 °C.

Figure 6.19 Water and mass 34 pressures during current flow in the “wet” H_2 test. The cell was at $800\text{ }^\circ\text{C}$.

6.3.3 “Dry” hydrogen with 20 ppm PH_3 .

The H_2 from the cylinder is 1:1 mixed with the 40 ppm PH_3 in H_2 . The cell voltage is applied 0.9 V, 0.7 V and 0.5 V at 23.5, 29.7 and 31.7 hours. Each voltage is applied for one hour. Signals of N_2 and O_2 are in Figure 6.20. Water and mass 34 signals are in Figure 6.21. Addition of PH_3 at 19.2 hours causes spikes in the air signals (N_2 and O_2), but there is no increase in the mass 34 signal. The current flow yields increases in the water signal at mass 18 during the electrochemical tests. The air signals also show dips according to the current flow. The signal at mass 34 stays almost unchanged during the entire experiment. In comparison to the “dry” clean H_2 without PH_3 , the mass 34 level is not changed. The PH_3 is not getting out of the furnace at any time during the test.

Figure 6.20 N₂ and O₂ signals during addition of phosphine and application of voltages in “dry” H₂ + 20 ppm PH₃. The cell was at 800 °C.

Figure 6.21 Water and mass 34 signals during addition of phosphine and application of voltages in “dry” H₂ + 20 ppm PH₃. The cell was at 800 °C.

Polarization and power curves with 20 ppm phosphine present are shown in Figure 6.22. The peak power density is 0.19 W/cm² at 0.47 V, which is better than in clean “dry” H₂, despite the presence of PH₃ in the fuel stream. EIS data in Figure 6.23 shows that the normalized R_s is 1.0 Ω cm² and the R_p is about 5 Ω cm². The series and polarization

resistances are slightly smaller than in the clean H_2 . This improvement of performance may be because the cell is better conditioned in the “wet” hydrogen for a while. The high series resistance, whatever its cause, appears to be decreasing. Correcting the cell voltage and power for iR drop from 1.0 to 0.2 ohm cm^2 yields a voltage of 0.72 V and a power of 0.37 W cm^{-2} at the maximum current density of 0.52 A cm^{-2} .

Figure 6.22 CV and power curve in “dry” H_2 + 20 ppm PH_3 . The cell was at 800 °C.

Figure 6.23 Nyquist plot at OCV in “dry” H_2 + 20 ppm PH_3 . The cell was at 800 °C.

6.3.4 “Wet” hydrogen with 20 ppm PH_3 .

For this test, only the pure hydrogen is passed through the humidifier at room temperature. Then the “wet” H_2 is 1:1 mixed with the 40 ppm PH_3 in H_2 (dry). So the actual humidity of this gas mixture is expected to be half of the “wet” H_2 test in Section 6.3.2. The cell voltage is set at 0.9 V, 0.7 V and 0.5 V at 3.8, 5.3 and 10.4 hours, respectively. Each voltage is applied for one hour. Signals of N_2 and O_2 are in Figure 6.24. Water and mass 34 signals are in Figure 6.25.

The dips in air signals and rises in water due to the electrochemical tests are similar to the signal changes in previous tests. The water background signal is about 8 torr in this test because of the half humidity set up. However, the water signal does not go down until 1.5 to 2.8 h after the current is turned off. Also, the water signal is nearly the same (15 torr, believed to be saturation) for all 3 currents. There is no detectable PH_3 in the exhaust gas.

Figure 6.24 N₂ and O₂ signals during application of voltages in “wet” H₂ + 20 ppm PH₃. The cell was at 800 °C.

Figure 6.25 Water and mass 34 signals during application of voltages in “dry” H₂ + 20 ppm PH₃. The cell was at 800 °C.

A polarization and power curves are shown in Figure 6.26. The peak power is 0.18 W/cm² at 0.49 V, which is comparable to the results in wet H₂ without PH₃. The Nyquist plot is shown in Figure 6.27. The normalized R_s is 1.0 Ω cm² and R_p is 1.7 Ω cm². The R_p increased from the wet clean H₂ test (1.3 Ω cm²). This increase may due to the change in the water concentration near the cell anode. Correcting the series resistance from 1.0 to

$0.2 \Omega \text{ cm}^2$ yields a cell voltage of 0.70 V and a power density of 0.345 W cm^{-2} at a maximum current density of 0.495 A cm^{-2} .

Figure 6.26 CV test in “wet” $\text{H}_2 + 20 \text{ ppm PH}_3$. The cell was at 800°C .

Figure 6.27 Nyquist plot of the cell at OCV in “wet” $\text{H}_2 + 20 \text{ ppm PH}_3$. The cell was at 800°C .

6.4 Cell test III – long term constant cell voltage tests.

The tests in this section are still on the same cell described earlier with the glass seal.

Dry H₂ test. The cell voltage was set to 0.9 V for 20 hours. The normalized power density is plotted vs time in Figure 6.28. The power density starts at 0.107 W cm⁻² and shows a slight decay although no PH₃ is added. This decay may be due to the residual PH₃ left over. The power loss rate is 0.345 mW cm⁻² h⁻¹, which is comparable to the results with the presence of 20 ppm PH₃. The mass signals of N₂ and O₂ are in the first 20 hours of Figure 6.29. Similarly, water and mass 34 signals are in the first 20 hours of Figure 6.30.

At 20 hours, the cell voltage was returned to OCV, and at 24.8 hours, 3% water vapor was added into the fuel stream. Changes in the common gas signals are shown in Figures 6.29 and 6.30. During current flow in dry H₂ (0-20 hours), the water signal at mass 18 was about 10 torr. When the current was turned off, water signal dropped to 1 torr. When water vapor was added to the fuel, the water signal rose to 14 torr. All other masses reflected the changes in the water signal.

Figure 6.28 Power density vs time in “dry” H₂ with 0.9 V cell voltage. The cell was at 800 °C.

Figure 6.29 N₂ and O₂ signals vs time in “dry” H₂ at 0.9 V (first 20 hours), open circuit (20-22 hours) and in “wet” H₂ (24-50 hours). The cell was at 800 °C.

Figure 6.30 Water and mass 34 signals vs time in “dry” H₂ at 0.9 V (first 20 hours), open circuit (20-22 hours) and in “wet” H₂ (24-50 hours). The cell was at 800 °C.

“Wet” H₂ test. The fuel was H₂ with ~20 torr of water vapor. The cell voltage was set at 0.9 V for 20 hours. The power density is plotted vs time in Figure 6.31. The power density was approximately 0.09 W cm⁻² with some fluctuations.

Figure 6.31 Power density vs time in “wet” H₂ with 0.9 V cell voltage. The cell was at 800 °C.

The mass signals of N₂, O₂, water and mass 34 signals are in Figure 6.32. The air peaks (N₂ at mass 28 and O₂ at mass 32) were fluctuating by a large amount during the current flow. When the current was turned off, the fluctuation disappeared. This fluctuation may be because of the changes in water content in the exhaust stream. The water signal showed a “blip” at 18-20 hours. The reason for the “blip” is unknown.

Figure 6.32 Gas pressures vs time in “wet” H₂ at 0.9 V. The cell was at 800 °C.

“Dry” H₂ with 20 ppm PH₃ test. After the gas composition was stabilized at 20 ppm PH₃ in “dry” H₂, the cell was set for an applied cell voltage of 0.9 V. The power density at this setting is plotted vs time in Figure 6.33. The power decayed continuously over time with

the presence of 20 ppm PH_3 . The degradation rate is $0.346 \text{ mW cm}^{-2} \text{ h}^{-1}$, determined by linear fit of part of the curve shown in Figure 6.33. This rate is comparable to the values in the literature around $0.3\text{-}0.6 \text{ mW cm}^{-2} \text{ h}^{-1}$ [2-3]. The mass signals of N_2 , O_2 , water and mass 34 signals are shown in Figure 6.34. The spikes at 24 hours correspond to the change from dry H_2 to wet H_2 with PH_3 . During the next 23 h, the water (mass 18) signal dropped rapidly to 2 torr and then slowly to 1 torr. The air impurities signals (mass 28 and 32) show corresponding increases. Mass 34 signal shows a slight increase which is likely due to the drop in water and not due to PH_3 getting to the exhaust port. The PH_3 concentration at the exhaust point remains low. The low PH_3 concentration is similar to the results of the tests in Chapter 5. The PH_3 level was low with a Ni/YSZ piece in the gas stream, under both dry and wet conditions. However, the PH_3 in dry conditions is slightly higher than in wet gas stream, which is also consistent with the results in Chapter 5. At 47 h, when the current is turned on, water signal shoots up to 10 torr, and all other signals show a slight decrease.

Figure 6.33 Power density vs time in “dry” H_2 + 20 ppm PH_3 with 0.9 V cell voltage. The cell was at 800 °C.

Figure 6.34 Gas pressures vs time in “dry” H_2 + 20 ppm PH_3 . See the text for details about cell voltage and gas composition. The cell was at 800 °C.

A comparison of mass spectra at 40 hours (dry H_2 with 20 ppm PH_3 , no current) and 60 hours (dry H_2 with 20 ppm PH_3 , $\sim 120 \text{ mA/cm}^2$ current flow) is shown in Figure 6.35. The only changes are due to the higher pressure of water at 60 hours. There are no new signals appearing at masses higher than 44.

Figure 6.35 Mass spectra in dry H_2 with 20 ppm PH_3 without (40 hours) and with (60 hours) current flow.

“Wet” H_2 with 20 ppm PH_3 test. The H_2 from the gas cylinder is passed through the humidifier at room temperature before it is 1:1 mixed with the 40 ppm PH_3 in H_2 . The cell voltage is set at 0.9 V for 20 hours. The power density vs time is plotted in Figure 6.36. The degradation of cell performance is very fast initially with a rate of $0.498 \text{ mW cm}^{-2} \text{ h}^{-1}$, and then dropping to a moderate rate. After 7 hours, the degradation rate becomes very slow at $0.077 \text{ mW cm}^{-2} \text{ h}^{-1}$. The low degradation rate is unusual. Xu and Zhi et al. reported that the degradation occurs at a constant rate in the range of 0.4-0.6 $\text{mW cm}^{-2} \text{ h}^{-1}$. [3-4]

Figure 6.36 Power density vs time in “wet” $\text{H}_2 + 20 \text{ ppm PH}_3$ with 0.9 V cell voltage. The cell was at 800 °C.

The mass signals of N_2 , O_2 , water and mass 34 signals are in Figure 6.37. The water signal at mass 18 was at 8 torr before the current was turned on at 2.4 hours. Then the water increased to 14 torr with ~160 mA of current. The water signal dropped to 8 torr after the current was turned off at 22.4 hours. The water signal then dropped to less than 2 torr corresponding to the time that the humidifier was bypassed at 25 hours. Other gases showed decreases with current flow due to partial replacement by the water vapor.

Figure 6.37 Mass signals in “wet” $\text{H}_2 + 20 \text{ ppm PH}_3$. See the text for details about applied voltage and changes in fuel composition. The cell was at 800 °C.

6.5 Post-mortem analysis of the cell

After the cell is taken out of the furnace, a shiny layer of new crystalized material is visible on the anode surface. This new phase is also seen in previous studies [2-3, 5].

SEM images of the top surface of the anode are shown in Figure 6.38. The clean reduced anode surface (left) is very porous and consists of fine grains of Ni and YSZ. The grain size is very small, in the order of 0.5-1 μm . The porous structure is favorable for the fuel gas to penetrate through the thick anode and reach the active layer. This structure is consistent with the structures of previous cells from MSRI. [5, 7] After exposure to 20 ppm of PH_3 , there is a new phase formed on top of the anode surface. The new phase exhibits well-defined facets and is believed to be crystalline. The grain size is about 100 μm , much larger than the YSZ particles on the clean reduced anode. The formation of the additional phase is also described in the previous studies. [5, 7]

Figure 6.38 SEM image of the clean reduced anode (left) and the area exposed to 20 ppm PH_3 (right).

EDX analyses were performed within the same area of clean and PH_3 -exposed anode mentioned above. Figure 6.39 is the EDX spectra of the clean reduced anode. The graph

is shown with a smaller scale on the right to emphasize the smaller peaks. The major elements are Ni, Zr, Y and O. The small C peak is from impurities on the anode.

Figure 6.39 EDX analysis of the clean reduced anode surface.

The EDX spectra of the anode area that was exposed to 20 ppm PH_3 is shown in Figure 6.40. In comparison to the clean anode, the PH_3 -exposed anode exhibits peaks for nickel and phosphorus. Zr and Y peaks are strongly suppressed indicating that the new nickel phosphide layer is completely covering the entire area on the anode that exposed to PH_3 . The new phase formed is identified in previous studies by Xu and Demircan et al. as nickel phosphide. [2, 5, 7]

Figure 6.40 EDX analysis of the PH_3 exposed anode surface.

The XRD pattern of the PH_3 exposed anode in Figure 6.41 provides the evidence of the presence of nickel phosphide. The signature peaks for YSZ are at 2θ of 30.10° , 34.98° , 50.21° , 59.79° and 62.86° (PDF# 01-082-1241). The two peaks at 44.65° and 51.99° are assigned to metallic nickel (PDF# 4-850). Nickel phosphide (mainly Ni_5P_2) peaks are at 38.31° , 41.77° and 46.32° . However, some of other nickel phosphide peaks (Ni_3P , Ni_8P_3 , etc.) may overlap with the stronger Ni_5P_2 signals. [8-9] The dominant form of nickel phosphide in the anode after PH_3 exposure is Ni_5P_2 . Xu and Tremblay et al. also reported that the dominant phase is Ni_5P_2 under similar conditions. [2] Thermodynamic calculations by Xu et al. suggest that the most stable form of nickel phosphide under SOFC anode conditions is Ni_5P_2 as well. [2] The presence of Ni_3P has been reported by Marina et al. [11]

Figure 6.41 XRD analysis of the PH₃ exposed anode surface. (♦ YSZ ■ nickel phosphide ● metallic Ni)

6.6 Conclusions.

The electrochemical performance of the SOFC tested in this chapter fueled by H₂ is significantly lower than similar cells reported in previously published work. The peak power is lower and both series and polarization resistances are much higher. The SOFC degrades with a power loss after a long time operation in wet and dry H₂, with and without 20 ppm PH₃. However, by comparing the peak power obtained at the very beginning and very end of the entire test, the overall performance did not show a significant loss. The water generated from the electrochemical reactions (oxidation of hydrogen) and chemical reactions (reduction of NiO) is readily detected. The product water volume is large and is displacing the other gases in the exhaust. No new masses

above mass 44 were detected at any time. In particular, HPO (mass 48), HPO₂ (mass 64), and HPO₃ (mass 80) are not detected as products of PH₃ reactions. Due to the change of the calibration of the RGA during the experiment, the gas partial pressures are considered reliable only for their relative values. The accuracy of the measured pressures may be compromised. The post-mortem SEM, EDX and XRD analyses showed the evidence of a new layer of nickel phosphide on the top surface of the PH₃ exposed anode similar to the results in previous studies.

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Chapter 7 Discussion, Conclusions and Future Work

7.1 Discussion

The major observations in Chapter 3 are the transient behavior of H_2S when introduced into the gas stream and the change of H_2S signal at mass 34 when the current is turned on and off. The slow rise of impurities signal is very reproducible and was seen numerous times in the data. In the mass detection range, only H_2S and PH_3 at mass 34 show a slow rise with time. No other gases exhibit this behavior. However, there is no direct evidence showing that either PH_3 or H_2S reacts with alumina. In the current test with H_2S in Chapter 3, the signal at mass 34 jumped up when the current is turned on, and then slowly decayed to the background value. The signal also decreased sharply when the current is turned off, and then returned slowly back to the normal value. These changes are only seen once in the experiments. After the apparatus has been moved, there was not a chance to repeat the H_2S and current test to confirm the reproducibility. A hypothesis for this phenomenon is due to the local heating of the cell. Both thermodynamic calculations and experimental studies confirmed that when current is loaded to the cell, the temperature rises up to 10°C higher than at open circuit (also depends on the current flow) [1-3]. The H_2S adsorbed onto the cell may be released when the temperature becomes higher. However, the amount of the released H_2S is limited, so the mass 34 signal slowly went back to track the normal level. Another possible oxidation product is SO_2 at mass 64. Mass 64 signals were in the noise level at all times during the experiment. The H_2S may have also adsorbed on to the sampling capillary to the RGA or reacted with the Ni.

In Chapter 4, the H_2O generated by the oxidation of H_2 via the fuel cell reaction is detected by the mass spectrometer as anticipated. Although the results are compromised by the leaks to the air, the amount of H_2O generated is so large that it can be easily detected. Part of the H_2 in the fuel stream was oxidized by the leaked air to form H_2O , causing a high background level of H_2O signal. The H_2O formed by the electrochemical reaction is seen as an increase on top of the background when current is turned on.

From the gas tests in Chapter 5, PH_3 is found to be stable from room temperature up to at least 300°C and 1 atm in H_2 , regardless of the humidity (up to 10 torr of H_2O) or the presence of Ni/YSZ sample. The PH_3 fed into the system is detected unchanged at mass 34 at the exhaust sampling point. Although Trembly and Bao et al. predict that the PH_3 will decompose and react with H_2O or the residual O_2 due to impurity gas or leaks, these predictions are based on thermodynamic calculations. [4-5] No kinetic data are provided such as a reaction rate or an equilibration time. One hypothesis is that the reaction may be slow at lower temperatures, so the phosphorus remains as PH_3 . As the temperature rises, the PH_3 starts to react. The initial temperature of the reaction in dry hydrogen is 400°C and in wet hydrogen is about 300°C . The onset of reaction of PH_3 is rapid after reaching this critical temperature. The product is so thermodynamically favorable and the reaction rate is so fast that little or no phosphorus as PH_3 at mass 34 is detected in the exhaust gas. No products of the phosphine reaction are detected.

As the temperatures continue to rise, the discussion separates into three cases.

1. Under the dry condition, the PH_3 reappears at $600 - 800^\circ\text{C}$ at a pressure almost the same as the initial pressure. The products of the reaction at intermediate temperatures are

presumably unstable at high temperatures. Thus the reaction direction is reversed and PH_3 is regenerated or the reaction simply stops. Again, the return of the PH_3 signal during temperature increases occurs over a narrow range of temperatures. This process is observed during both the heating and cooling phases of the experiment. It is also observed in alumina and quartz tubes, suggesting that the reaction occurs in the gas phase and not on surfaces or between the surface and gas. The O_2 pressure at mass 32 tracks the PH_3 signal at mass 34, suggesting that oxygen is a possible reactant, although some of the changes are due to changes in concentration of PH , a fragment of PH_3 . The H_2O signal at mass 18 shows no correlated changes. However, this result may be due to the large pressure of water relative to the pressure of PH_3 . In any event, it is evident that PH_3 will reach the anode of the SOFC with dry hydrogen as the fuel.

2. Under wet conditions, the PH_3 stays at noise level and is not regenerated at 600-800°C. The water vapor plays a critical role in the PH_3 reaction. The products are more thermodynamically stable with water vapor present, although the products are not detected with the current instrument. The species reaching the anode is not known.

3. With a Ni/YSZ sample present in the gas stream, the PH_3 reacts with the sample. The Ni/YSZ is very attractive to PH_3 at high temperatures [6]. So even in dry conditions, only a small signal at mass 34 is seen (less than 10% of the initial amount). This result is consistent with rapid gettering of PH_3 by nickel mesh (a proposed filter for PH_3). [9-10] After the furnace is cooled, the sample is taken out and a shiny layer of new material has formed on the surface, which is similar to the results for cells exposed to PH_3 in the previous studies described in Section 2.5. At low temperatures, PH_3 does not react with nickel at a rapid rate, and the mass 34 signal returns to its initial levels.

In the gas tests in Chapter 5, there are no signals detected above mass 44 (CO_2). This implies that no product of PH_3 reaction is detected by the mass spectrometer. HPO (mass 48), HPO_2 (mass 64) and HPO_3 (mass 80) are excluded as possible products. The other types of compounds that may be products are phosphorus oxides. In the P_2O_5 sample test, there is no new signal detected in the exhaust gas from room temperature to 350°C . The products of decomposition and hydrolysis of P_2O_5 may have masses beyond the mass range of 100 amu. This result contradicts the finding in the paper by Sasaki et al. [11] PH_3 was generated by heating P_2O_5 to 300°C by Sasaki. Also, no fragments of P_2O_5 or P_4O_{10} under 100 amu are detected. The mass spectrometer readily detects organic vapors with masses in the 40-100 range, so the fault does not lie with the spectrometer. The quartz tube test shows similar results with the alumina tube. The “dip” of PH_3 is not related to the alumina material but due to the gas reactions.

In Chapter 6, all the three stages of testing were on the same single cell. The cells tested by Xu et al. exhibited a voltage of 0.72 V at 0.5 A cm^{-2} in clean H_2 . [2] This cell in the present study, after correcting the series resistance to the same value, exhibits a voltage of 0.73 V at the same current density. The performance of this cell is comparable to the performance of previous cells from the same vendor. The main problem is the high series resistance. Since four leads (two current, two voltage sense) extend from the potentiostat to a point near the SOFC, lead wire resistance is not the source of the series resistance. Usually, such a high series resistance arises from one of two sources, a faulty contact with the current collectors or delamination flaws within the SOFC. However, the current collectors and the cell was well intact under visual examine. Whatever the cause of the high series resistance, that resistance decreased slightly during the experiment. The

polarization resistance of the current cell with 20 torr of water in clean hydrogen is 1.1 ohm cm². A similar cell in hydrogen + 3% water (23 torr) exhibited a polarization resistance of 1.4 ohm cm². [7] The polarization resistances at OCV in dry hydrogen are much larger because of the effect of low water concentration on the kinetics of hydrogen oxidation at OCV.

Deconvolution analysis provides greater detail of the number and types of processes appearing in the impedance spectra. [8] Deconvolution analysis of this cell's impedance data shows that the polarization resistance can be assigned to three parts, the anode at low frequency, the electrolyte at intermediate frequency and the cathode at high frequency. In the deconvolution plot of dry and wet H₂ conditions shown in Figure 7.1, the presence of water vapor makes a significant difference in the R_p values. The large peak at 0.1 Hz in dry H₂ largely disappears due to the lower activation energy of H₂ oxidation with the presence of water, leaving behind a small peak at 0.16 Hz.

Figure 7.1 Deconvolution overlay comparison for dry and wet H₂ conditions with no PH₃.

Another comparison of deconvolution spectra in dry hydrogen with and without PH_3 is shown in Figure 7.2. The two plots overlap well above 1 Hz. At lower frequencies, the slight discrepancies are attributed to noise in the impedance data.

Comparison of deconvolution spectra of wet condition with and without added PH_3 is shown in Figure 7.3. The multiple peak patterns of the two plots are very similar. The only difference is the absolute value of the impedance. One possible cause of the difference is a change in the water concentration. The “wet” H_2 with 20 ppm PH_3 has only half the humidity of the pure “wet” H_2 (10 torr vs 20 torr), as described in section 5.1.3.

Figure 7.2 Comparison of deconvolution of impedance in dry H_2 , with and without PH_3

Figure 7.3 Comparison of deconvolution of impedance in wet H₂, with and without PH₃

In the long term tests of constant voltage with 20 ppm PH₃, the cell showed a loss of power. The degradation rate in dry condition is 0.35 mW cm⁻² h⁻¹, which is comparable to previous results by Xu. However, in the wet condition, the degradation rate did not stay constant. The starting rate was 0.50 mW cm⁻² h⁻¹ and after 8 hours it gradually decreased to 0.077 mW cm⁻² h⁻¹. Xu et al. observed a constant degradation rate of 0.4-0.6 mW cm⁻² h⁻¹ through the entire testing period. By comparing the power density data collected near the end of the test to the data in the very beginning, the cell tested in Chapter 6 does not show a significant change of performance over 16 days of operation. At a current density of 0.3 A cm⁻², the iR-corrected power densities are (dry H₂) 0.25 W cm⁻², (wet H₂) 0.26 W cm⁻², (dry H₂ + PH₃) 0.26 W cm⁻² and (wet H₂ + PH₃) 0.25 W cm⁻². Although a continuous run in the presence of PH₃ caused some degradation, this cell surprisingly recovers between runs. The 20 hours of run time may not be long enough to see significant degradation. However, most literature data show that the PH₃ will cause immediate and irreversible loss of performance to the SOFC anode. The post-mortem analyses (see below) prove that phosphine is reacting with the anode during this extended

test. It is possible that the PH_3 or its reaction products are not reaching the active layer of the anode.

During the cell test, the H_2O generated by the electrochemical reaction of the cell is detected by the mass spectrometer. The detection of H_2O is highly reproducible and reliable. When the current is turned on, a significant increase in signal appears at mass 18. All other gases show a decrease in their mass signal because the amount of generated water is so large that all other gases are displaced. A larger current load applied to the cell yields a higher signal at mass 18. However, the linearity of H_2O concentration with the mass 18 signal is valid only for water levels lower than 16 torr. At higher current densities, the electron multiplier detector is saturated with water so it cannot further increase in signal. In some cases, the water vapor may have condensed in the exhaust lines so it took some time to evaporate and purged out the water after turning off the current. Again, no mass above 44 amu is detected under any experimental configuration or any gas composition.

After the cell test was finished, the cell was taken out for further analysis. The cell and the current collectors were intact under visual check. The inner surface of the cell-supporting tube was examined visually, but there were no significant amount of deposits found. A shiny, highly crystalline new phase formed on top of the anode surface. SEM, EDX and XRD tests were performed on the post mortem cell. The SEM images show there is an additional dense phase formed on top of the anode with a much larger grain size than the clean reduced anode. This new phase is similar to the one observed by Xu and Demircan et al. in similar experiments. [2, 7, 9-10] The EDX analyses confirmed the

existence of nickel and phosphorus in the new phase. XRD indicated that the new phase was nickel phosphide.

7.2 Conclusions

The Residual Gas Analyzer is applied to the study of fuel and exhaust gases of the Solid Oxide Fuel Cell. It is capable of detecting major gases (H_2 , N_2 , O_2 , H_2O , etc.) and trace amount of gases (H_2S , PH_3 , CO_2 , etc.).

The results obtained in the experiments in WVU MAE laboratory are consistent with the data collected later in WVU Chemistry laboratory, despite the significant leak in the system. The electrochemical reactions of the operating SOFC can be seen as a distinct rise of water content in the exhaust gas.

The PH_3 is readily detectable at 10 ppm level with the Cirrus unit. Mass spectrometry observations confirm that the PH_3 reaches the cell anode. The degradation of the cell performance is due to the presence of PH_3 , even at 10 ppm level.

The gas phase reactions of PH_3 at high temperatures were investigated. The PH_3 reacts at temperatures above $\sim 400^\circ\text{C}$. However, no expected products (HPO , HPO_2 , HPO_3 , fragments of P_4O_{10} , etc) were detected under any gas compositions with the current instrument. The possible products may be non-volatile or have mass numbers larger than 100 amu.

The use of Residual Gas Analyzer in the study of SOFC is a novel application. This analytical method has its great advantages and some drawbacks. The most remarkable feature of this instrument is the large dynamic range from sub ppm level to atm level. The

large dynamic range provides the ability to detect trace gases and major gases at the same time. The continuous gas phase sampling is another advantage. The RGA can be connected on to the gas system and perform on-line analyses of the gases. The response time is very fast. However, there are some limitations. The RGA is usually calibrated with only one point and this calibration is used over its entire dynamic range. And, the RGA can be calibrated based on one single mass. While different molecules have different calibration coefficients, the readings of some gases may be inaccurate. During operation, the RGA gave different readings for the same gas compositions. The results are not precisely quantitative, but only provides relative readings or semi-quantitative data. For qualitative purposes, the RGA will provide reliable results.

7.3 Future work

For the Cirrus RGA unit, it is better to develop a new version of software that will have the capability to calibrate with multiple points. The ratios of calibration coefficient of different masses are to be set and stored in the software. For the study of trace amount of PH_3 in the ppm level, it is necessary to have the instrument calibrated with a standard PH_3 gas within the working range. For example, an accurate 40 ppm standard PH_3 balanced in N_2 or H_2 will be sufficient.

The tests and analyses in Chapter 6 were on the same single cell. More repeated cell tests are necessary to further understand the gas-phase composition both at the inlet and exhaust of the fuel cell. The problem of high series resistance needs to be solved.

The state of PH_3 and the products of the PH_3 reactions under SOFC operating conditions are still unclear. One approach is to purchase a mass spectrometer with an increased mass detection range. The new instrument will have the possibility to reveal any products over the mass number of 100. Another approach is to investigate the inner surfaces of the furnace for any deposited products of the PH_3 reaction. The residual deposits can be collected and studied using microscopic methods. The elemental information can be obtained by XPS. The crystal structure can be determined by diffraction patterns to identify the compound.

The mechanism of the degradation of cell performance caused by PH_3 is yet to be discovered. More in-situ methods need to be developed to reveal the gas reactions close to the anode surface.

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