Mass Spectrometry of SOFC Fuel Mixtures Containing Phosphine

Harry O. Finklea,a,** Wei Zhang,a Mahfuzur Jony,a and Berk Demirgokb

aDepartment of Chemistry, West Virginia University, Morgantown, West Virginia 26506, USA
bDepartment of Mechanical & Aerospace Engineering, West Virginia University, Morgantown, West Virginia 26506, USA

Phosphine (PH₃) is present at ppm concentrations in coal syngas, a potential fuel source for solid oxide fuel cells (SOFCs). A mass spectrometer is used to monitor fuel mixtures of hydrogen and phosphine after exposure to two environments. In the first environment, the gas mixtures are passed through a heated zone in a tube furnace. In the second environment, the gas mixtures are passed across the anodes of operating SOFCs, both electrolyte- and anode-supported. Phosphine appears to react with residual oxygen in dry hydrogen at intermediate temperatures (400–600 °C) but is stable above 600 °C. Phosphine reacts with water in wet hydrogen mixtures and with a Ni/YSZ anode at temperatures above 400 °C. Evidence is presented for deposition of non-volatile contaminants following prolonged phosphine exposure. The contaminants react with dry hydrogen to generate PH₃ at 800 °C. Mass spectra of the anode exhaust of an electrolyte-supported SOFC show that a few torr of water, either present initially or electrochemically generated by fuel oxidation, is sufficient to suppress the phosphine signal. At all gas compositions and currents, no new mass signals were detected in the mass range of 45–100, suggesting that HPO, HPO₂ and HPO₃ are not products of phosphine reaction or electrochemical oxidation.

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The abundance of coal and the high theoretical efficiency of solid oxide fuel cells (SOFCs) have led to proposed power plants based on syngas as the fuel for SOFC stacks.1 The performance of a Ni/YSZ anode is stable in a syngas mixture containing the major components of coal syngas: H₂, CO, H₂O and CO₂. However, coal syngas contains several volatile impurities, including hydrogen sulfide (H₂S) and phosphine (PH₃) at part-per-million levels.2 Phosphine at 1–10 ppm levels have been shown to be detrimental to the Ni/YSZ anode in a number of studies.3–13 Depending on conditions, the SOFC may exhibit immediate and continuous degradation of performance, or may operate stably for a hundred hours before exhibiting performance degradation. Post-mortem studies reveal new phases, most often various nickel phosphides, which migrate to the surface of the anode or into large voids in the anode structure. Non-nickel anode, LaSrFe₂CrO₉, is also degraded by ppm levels of phosphine.14

Phosphine is a highly reactive substance, and its fate in SOFC fuels at high temperatures is the focus of several thermodynamic predictions in the literature. Phosphine is predicted to be stable in hydrogen with 3% water at 800 °C,12 to form various phosphorus oxides depending on the oxygen partial pressure,15 and to form HPO₂ and HPO₃ in the presence of water.16 Using an effusion beam source at low pressure, Bao et al. determined that phosphine was stable at 995 K in dry hydrogen with 40 ppm phosphine, and helium. The hydrogen could be routed through a humidifier to create “wet” hydrogen (~22 torr H₂O based on the temperature of 22 °C). Compressed air from a tank was delivered to the cathode of the SOFC. Gas flow rates were set using mass flow controllers.

In the temperature studies, the fuel mixtures were passed through an alumina or quartz tube (19 mm ID) in a programmable tube furnace at a flow rate of 100–200 sccm. The length of the heated zone was 30 cm, and with a linear flow rate 0.5–1.0 cm/s, the gas was at or near the set point temperature for at least 20 s. Upon exiting the heated zone inside the furnace, the gas mixture passed through a T-junction to which the mass spectrometer capillary was attached. In order to minimize leaks, the fuel gas continued through a narrow-bore copper tube to generate a slight back pressure. The temperature program was typically a linear ramp from room temperature to 800 °C, a hold period at that temperature, and then a linear ramp back to room temperature. In some experiments, an anode piece (NiO/YSZ) was placed in the center of the heated tube.

Electrolyte-supported cells (50 micron Ni-GDC/Ni-YSZ anode, a 150 micron Ni-GDC electrolyte and a 50 micron LSM/GDC cathode) were purchased from Fuel Cell Materials. An anode-supported half cell (0.9 mm NiO/YSZ support and active layer, 10 micron YSZ electrolyte) from MSRI was modified with a LSM/YSZ paste cathode. Data are normalized with respect to the cathode areas in each design. Gold paste or silver paste current collectors were applied to the electrodes. Care was taken to leave most of the anode uncovered by the metal paste.

Cells were mounted in a Probostat unit. The electrolyte on the cathode side of each cell was sealed to an alumina tube using a proprietary glass tape. Gas exhaust from the fuel side passed through the T-junction and narrow bore copper tube as described above. The mass spectrometer capillary was connected to the T-junction. Typical fuel and air flows were each 200 sccm. The cell was heated to 800 °C with helium passing over the anode. Effective sealing was noted by the
Mass 34 (black line, PH$_3$) and temperature (gray line) versus time in "dry" H$_2$ + 20 ppm PH$_3$. The temperature program starts at 2 hours, increases from room temperature to 800 °C from 2 to 14 hours, remains at 800 °C from 14 to 24 hours, and then cools down to room temperature from 24 hours to 36 hours.

sharp drop in air signals (N$_2$ and O$_2$) in the mass spectra. Hydrogen was added in increments to reduce NiO to Ni in the anode. The reduction was followed by the mass 18 signal and the rise in the open circuit voltage (OCV). In “dry” H$_2$, the OCV exceeded 1.2 V, and in “wet” hydrogen, the OCV reached the predicted Nernst voltage. Electrochemical testing was performed either with a Gamry Reference 3000 system or a Solartron SI 1287 potentiostat and a 1252A frequency response analyzer. Impedance measurements were performed from $1 \times 10^5$ Hz to 0.02 Hz in 10 log linear steps per decade.

Results and Discussion

Analysis of heated gas mixtures.— In Figure 1, the signal at mass 34 (PH$_3$) are displayed as a function of time while 20 ppm PH$_3$ in “dry” hydrogen (P(H$_2$O) < 1 torr) is passed through an alumina tube. The temperature profile is included in the plot. After 2 hours at room temperature, the temperature increases to 800 °C linearly with time over a 12 hour period, remains at 800 °C for 10 hours, and then decreases linearly to room temperature during the next 12 hours. Since the mass 32 signal does not exceed 0.5 torr (see below), the contributions of molecular oxygen to the mass 34 signal (di-oxygen 34 has a natural abundance of 0.4%) is less than 0.002 torr on this plot. The mass 34 signal shows a dip during both the heating and cooling steps, and is stable both at low and at high temperatures. The mass 34 and mass 32 signals versus temperature are shown for the heating step in Figure 2. The dip in the mass 34 signal occurs between 400 °C and 600 °C. There is a corresponding dip in the mass 32 signal over the same temperature range. Mass spectra recorded at 300 °C and 500 °C show the presence of water (masses 17–21), N$_2$ (mass 14, 28 & 29), O$_2$ (masses 16 & 32), PH$_3$ (masses 31, 33, 34), argon (mass 40) and CO$_2$ (mass 44) (Figure 3). Only the signals for O$_2$ and PH$_3$ exhibit significant changes between these two temperatures. In particular, the H$_2$O signals are nearly constant (the P(18) signal in Figure 3 is not calibrated).

In “wet” H$_2$ (11 torr H$_2$O), the mass 32 and mass 34 signals drop steeply between 300 °C and 400 °C, but this time do not recover above 600 °C (Figure 4). In other experiments, the mass 34 signal does recover but to a lower value (~60% loss) than at room temperature. As in “dry” hydrogen, the mass 34 signal recovers to the original level once the temperature drops below 400 °C. Mass spectra at room temperature and temperatures of 400 °C or 800 °C only show changes in the mass 31–34 range consistent with loss of PH$_3$ and reaction of residual O$_2$.

In Figure 5, the evolution of the mass 34 signal vs temperature is shown when a NiO/YSZ piece (~1 cm$^2$) is present in the gas stream containing “dry” H$_2$ with 20 ppm PH$_3$. During the heating step, the nickel oxide is reduced to nickel with an accompanying spike in the water signal (mass 18) at 400–500 °C. The mass 34 signal decreases at approximately the same temperature. The mass 34 signal remains low with no recovery at temperatures above 600 °C. During the cooling phase, the mass 34 signal dips and then recovers to the initial level.

The preceding patterns are observed in both alumina and quartz tubes, so reactions are presumed to be occurring in the gas phase. Since the gas mixture cools as it exits the tube furnace and passes the T-junction connecting with the capillary, there is the question of whether changes may happen to gas compositions during this time. Based on the dimensions of the tube and furnace and the linear flow rate, the gas is exposed to the set temperature inside the furnace for at least 20 seconds. The gas exiting the tube furnace reaches the T-junction within 1 to 2 seconds, where the temperature is estimated to...
be on the order of 100 °C. The following discussion assumes that the rapid cooling kinetically freezes the gas composition so that measured partial pressures reflect the chemistry at the set point temperature of the furnace.

We hypothesize that the correlation between the mass 32 and mass 34 signals in Figures 2 and 4 indicate that residual oxygen reacts with phosphine above 400 °C. One example of a possible reaction is given in Equation 1:

\[ 2\text{PH}_3 + 4\text{O}_2 \rightarrow \text{P}_2\text{O}_5 + 3\text{H}_2\text{O} \]  

Equation 1

The recovery of the mass 34 signal above 600 °C in “dry” \( \text{H}_2 \) is attributed to the loss of \( \text{O}_2 \). The auto-ignition hydrogen with oxygen occurs in this temperature range. An Ellingham diagram generated by Kishimoto et al. predicts that \( \text{PH}_3 \) is stable when oxygen partial pressures are less than the equilibrium pressure for the \( \text{H}_2/\text{O}_2 \) system at 700–1100 K, and that phosphorous oxides are the major species at higher oxygen partial pressures, in reasonable agreement with the experimental results. Because water pressures of 10 torr result in total or partial loss of the mass 34 signal above 300 °C, water is also implicated as a possible reactant in “wet” fuels. One possible reaction is given in Equation 2:

\[ 2\text{PH}_3 + 5\text{H}_2\text{O} \leftrightarrow \text{P}_2\text{O}_5 + 8\text{H}_2 \]  

Equation 2

The experimental observations above disagree with the thermochemical calculations of Haga et al. In their calculations, an equilibrium mixture obtained from 20% hydrogen with 3% water (22 torr) and 5 ppm phosphorous species predicts that \( \text{PH}_3 \) is the dominant species from 400 to 800 °C with \( \text{P}_2 \) as the species with the second highest concentration. \( \text{P}_2 \) (mass 62) is not detected in the mass spectra (pressure less than 10⁻⁴ torr).

In the experiment with NiO/YSZ piece in the heated gas (Fig. 5), nickel is generated by reduction during the heating step. The reduction of NiO is complete by 600 °C as shown by the return of the mass 18 signal to its base level. The low mass 34 signal at the higher temperatures suggests that nickel is effectively reacting with \( \text{PH}_3 \) in the gas stream. The recovery of the mass 34 signal during the cooling phase indicates that the reaction of nickel with phosphine diminishes as the temperature is decreased to room temperature. The dip near the beginning of the cooling phase (at 18 h) is similar to the dip present in Fig. 1 and is assigned to the reaction of \( \text{PH}_3 \) with residual oxygen at temperatures below the auto-ignition temperature of hydrogen and oxygen.

One anomalous observation is the correlation of the mass 32 signal with the mass 34 signal in both Figures 2 and 4. The oxygen partial pressure is expected to fall to negligible levels for hydrogen gas exposed to temperatures above the auto-ignition temperature. There are two potential sources for the mass 32 signal, a fragment of phosphine (PH) and residual oxygen due to leaks in the mass spectrometer. An experiment with just hydrogen (no added \( \text{PH}_3 \)) passing through the heated tube shows that the mass 32 signal drops to 0.1 torr above 600 °C. This signal is assigned to residual oxygen due to leaks in the mass spectrometer. The rise in the mass 32 signal above 600 °C in Fig. 2 is attributed to the PH fragment whose concentration is tracking the \( \text{PH}_3 \) concentration.

No significant new signals appear above mass 45 at any temperature and in both “dry” or “wet” \( \text{H}_2 \). Potential reaction products of \( \text{PH}_3 \) include \( \text{P}_2 \) (mass 62), HPO (mass 64), HPO₂ (mass 80) and HPO₃ (mass 96). These products are not observed in the preceding experiments. Other possible products include phosphorus oxides (\( \text{P}_2\text{O}_5 \)) which, if volatile, are beyond the mass range of the mass spectrometer.

Non-volatile products may be depositing inside the alumina tubes. There is evidence for a contaminant in alumina and quartz tubes exposed to phosphine for prolonged times. In Figure 6, the mass 34 signal is monitored vs temperature while passing “dry” \( \text{H}_2 \) with no added \( \text{PH}_3 \) through a quartz tube. The quartz tube had been exposed to \( \text{PH}_3 \) at high temperatures in several preceding experiments. The initial signal is consistent with residual \( ^{34}\text{O}_2 \) (0.4% of the mass 32 signal). Above 650 °C, the mass 34 signal rises and continues to rise after the furnace reaches 800 °C. A concomitant signal rise occurs at mass 31. Consequently, \( \text{PH}_3 \) appears to be forming at the higher temperatures in “dry” hydrogen. This hypothesis is supported by one report in which \( \text{PH}_3 \) is generated by passing “wet” \( \text{H}_2 \) over \( \text{P}_2\text{O}_5 \) at 300 °C or 400 °C. Attempts to remove solid contaminants from the alumina or quartz by water or alcohol washes reduce the mass 34 signal but do not eliminate it. The \( \text{PH}_3 \) signal is sensitive to the partial pressure of \( \text{H}_2 \) as well as the temperature. Dilution of \( \text{H}_2 \) with \( \text{He} \) greatly attenuates the mass 34 signal when the relative concentration of \( \text{H}_2 \) drops below 50%.

It is clear that phosphine reaches the anode when the temperature is above 600 °C and the fuel is “dry” \( \text{H}_2 \) (Fig. 2). Rapid reaction with nickel is confirmed by the loss of phosphine in the presence of a NiO/YSZ piece (Fig. 5). Phosphine concentrations appear to be reduced to very low levels in “wet” hydrogen at high temperatures. Most importantly, contamination of the hot surfaces of a SOFC support structure from prior phosphine exposure can result in phosphine generation despite the absence of \( \text{PH}_3 \) in the fuel gas. Removal of phosphine from coal syngas should be implemented well away from the anode.  

**Electrolyte-supported cell.** The electrolyte-support cell is conditioned in a fuel mixture of 50% “wet” \( \text{H}_2 \) and 50% \( \text{He} \) to minimize generation of \( \text{PH}_3 \) from internal contamination. At each fuel composition, the cell is subjected to electrochemical testing (measurement of the OCV, impedance at OCV, and a polarization curve). Polarization curves are recorded by scanning the cell voltage from OCV to 0.2 V and back at 2 mV/s. Mass spectra are recorded continuously during the experiments (1 scan every 40 s). The Nyquist plot for the cell at OCV in 50% “wet” hydrogen is shown in Figure 7. Ohmic...
resistance is 0.62 ohm cm$^2$ and the polarization resistance is 2.51 ohm cm$^2$. The cell generates 0.6 A/cm$^2$ at 0.2 V and reaches a peak power of 0.16 W/cm$^2$ at 0.36 A/cm$^2$. During acquisition of the polarization curve, the mass 18 signal rises from 11 torr to a peak value of 19 torr due to the electrochemically generated water. The mass 32 and mass 34 signals remain constant at all current densities.

Subsequently, the fuel is changed to 50% “dry” H$_2$ and then 50% “dry” H$_2$ with 20 ppm PH$_3$. Impedance spectra collected at OCV before adding PH$_3$ and 1.5 hours after adding PH$_3$ are shown in Figure 8. The low frequency arc in the impedance spectra extends beyond the measured frequency range and the polarization resistance cannot be determined. The polarization resistance of the high frequency arc increases noticeably with the addition of PH$_3$. Visible effects of PH$_3$ exposure appear within a few hours in the impedance spectra in the electrolyte-supported cell. However, polarization curves recorded with and without PH$_3$ display no significant differences (data not shown).

In Figure 9, the mass 18 signal and the current are plotted during acquisition of a polarization curve in 50% “dry” H$_2 + 20$ ppm PH$_3$. The horizontal axis is the scan number for the mass spectrometer. During the initial open circuit condition, the measured mass 18 signal is 1.3 torr (actual P(H$_2$O) = 0.3 torr based on the OCV of 1.27 V). The cell voltage starts at 1.27 V at scan 19, reaches 0.2 V between scans 32 and 33, and returns to 1.27 V by scan 46. The dashed line shows the current with respect to the scan number. The mass 18 signal is proportional to the current as expected, but is delayed by the time between water generation at the anode and its arrival at the exhaust of the Probostat. The mass 34 signal is relatively constant at OCV but drops to base levels (due to oxygen-34) when the anode reaction generates a few torr of H$_2$O (Figure 10). Clearly, PH$_3$ reacts quantitatively with the electrochemically generated water at 800°C.

In Figure 11, the mass spectra are displayed at OCV (scan 10) and at the scan corresponding to the maximum water signal (scan 33). There are no detectable ions with masses between 45 and 100 (Fig. 11A). The changes between the two conditions are confined to masses 16–21 (H$_2$O) and masses 31 and 34 (PH$_3$) (Fig. 11B). This result is consistent with the hot tube experiments, and it suggests that PH$_3$ is reacting with water as well as the anode to form non-volatile products. The site of the reactions is likely to be on and close to the anode, where the PH$_3$ first encounters elevated H$_2$O concentrations.

The gas flow is returned to the original fuel mixture of 50% “wet” H$_2$ with no added PH$_3$ and the cell performance evaluated. From an impedance measurement (Figure 7), the polarization resistance increases from 2.51 ohm cm$^2$ to 2.76 ohm cm$^2$. The ohmic resistance also increases from 0.62 to 0.65 ohm cm$^2$. The latter increase might indicate loss in the active area of the anode, which would account for some of the increased polarization resistance. The rapid degradation of the cell continues for the next two days with the series resistance doubling and the total polarization resistance tripling during that period. Relative to the anode-supported cell (see below), the electrolyte-supported cell appears to be more rapidly degraded by PH$_3$ exposure.

**Anode-supported cell.**—The data set for the anode-supported cell is similar to the data set for the electrolyte-supported cell. The OCV in “dry” H$_2$ is 1.19 V, corresponding to a partial pressure of 3 torr for water, and 1.12 V in 50% “wet” H$_2$, corresponding to a partial pressure of 14 torr. The mass 18 signal is approximately proportional.
Figure 11. Mass spectra recorded at scan 10 (OCV, gray bars) and scan 33 (maximum mass 18 signal, black bars). (A) Mass range 10–100. (B) Mass range 10–35.

Figure 12. Nyquist plots of the anode-supported cell in “wet” H2 with no PH3 (squares) and in “wet” H2 with 20 ppm PH3 (diamonds) recorded 13 days later. The data are corrected for ohmic resistance and inductance.

to the current flowing through the SOFC. However, the mass 34 signal remains close to base values consistent with residual 34O2 at all currents, with and without added H2O, and with and without added PH3. The anode appears to be quantitatively reacting with PH3. No new masses are observed above 45 m/z for any fuel composition and 50% “wet” H2 with no PH3 and in 50% “wet” H2 with PH3 13 days later. During that period, the cell was operated in fuel containing 20 ppm PH3 at fixed voltages for approximately half of the time and at OCV for the remaining time. The polarization resistance increased at OCV for the remaining time. The data are corrected for ohmic resistance and inductance. Despite prolonged exposure to 20 ppm PH3 for 19 days, only modest changes. Figure 12 shows impedance data recorded in the cell performance (peak power, polarization resistance) exhibits spectra consistent with nickel phosphide phases.

In both cells, a visible coating is present on the anode surface after the experiment. As in previous studies, this coating yields XRD spectra consistent with nickel phosphate phases.

Summary

Mass spectroscopic analysis of gas mixtures passing through heated zones or over anodes of SOFCs have provided insight on the fate of phosphine in selected fuel mixtures. Phosphine reacts with water at partial pressures above a few torr at high temperatures. No volatile products of phosphine reactions, including the thermodynamically predicted products P2, HPO, HPO2 and HPO3, are detected either for gases passing through heated zones or for anode exhaust gases of operating SOFCs. There is evidence for non-volatile products deposited in the heated zones which can subsequently form phosphine when exposed to “dry” hydrogen at 800°C. The electrolyte-supported cell with its thin anode exhibits rapid degradation over a few days in the presence of phosphine while the thicker anode-supported cell survives for several weeks. This study demonstrates the need to remove phosphine from syngas before the fuel enters the heated zone of a SOFC.

References

1. F. N. Cayan, M. Zhi, S. R. Pakalapati, I. Celik, N. Wu, and R. Gemmen, *J. Power Sources*, 185, 595 (2008).
2. J. P. Trembly, R. S. Gemmen, and D. J. Bayless, *J. Power Sources*, 163, 986 (2007).
3. M. Zhi, X. Chen, H. Finklea, I. Celik, and N. Q. Wu, *J. Power Sources*, 183, 485 (2008).
4. C. Xu, J. W. Zondlo, H. O. Finklea, O. Demircan, M. Gong, and X. Liu, *J. Power Sources*, 193, 739 (2009).
5. O. Demircan, C. Xu, J. Zondlo, and H. O. Finklea, *J. Power Sources*, 194, 214 (2009).
6. O. Demircan, W. Zhang, C. Xu, J. Zondlo, and H. O. Finklea, *J. Power Sources*, 195, 3091 (2010).
7. O. A. Marina, L. R. Pederson, R. Gemmen, K. Gerdes, H. Finklea, and I. B. Celik, *ECS Trans.*, 26, 363 (2010).
8. Y. Chen, S. Chen, G. Hackett, H. Finklea, J. Zondlo, I. Celik, X. Song, and K. Gerdes, *Solid State Ionics*, 234, 25 (2013).
9. C. Xu, J. W. Zondlo, M. Gong, and X. Liu, *J. Power Sources*, 196, 116 (2011).
10. O. A. Marina, C. A. Coyle, E. C. Thomsen, D. J. Edwards, G. W. Coffey, and L. R. Pederson, *Solid State Ionics*, 181, 430 (2010).
11. W. Liu, X. Sun, L. R. Pederson, O. A. Marina, and M. A. Khalileel, *J. Power Sources*, 195, 7140 (2010).
12. K. Haga, Y. Shiratori, Y. Nojiri, K. Ito, and K. Sasaki, *J. Electrochem. Soc.*, 157, B1693 (2010).
13. J. Bao, G. N. Krishnan, P. Jayaweera, J. Perez-Mariano, and A. Sanjurjo, *J. Power Sources*, 193, 607 (2009).
14. M. Gong, D. Bierschenk, J. Haag, K. R. Poeppelmeier, S. A. Barnett, C. Xu, J. W. Zondlo, and X. Liu, *J. Power Sources*, 195, 4013 (2010).
15. H. Kishimoto, K. Yamaji, M. E. Brito, T. Horita, and H. Yokokawa, *J. Mining & Metallurgy, Geol.*, 44B, 39 (2008).
16. J. Bao, G. N. Krishnan, P. Jayaweera, K.-H. Lau, and Angel Sanjurjo, *J. Power Sources*, 193, 617 (2009).
17. Z. Zhan, J. Liu, and S. A. Barnett, *Appl. Catal. A*, 262, 255 (2004).
18. Z. Zhan and S. A. Barnett, *Science*, 308, 844 (2005).
19. Z. Zhan, Y. Lin, M. Pillai, I. Kim, and S. A. Barnett, *J. Power Sources*, 161, 460 (2006).
20. I. Kim, M. Pillai, N. McDonald, T. Shastry, and S. Barnett, *ECS Trans.*, 25, 271 (2009).
21. C. Guerrra, A. Lanzini, P. Leone, M. Santarelli, and N. P. Brand, *J. Power Sources*, 245, 154 (2014).
22. B. Hu, M. Keane, K. Patil, M. K. Mahapatra, U. Pasaoagullari, and P. Singh, *Appl. Energy*, 134, 342 (2014).
23. M. Rohshanfarshar, J.-L. Luo, A. L. Vincent, K. T. Chuang, and A. R. Sanger, *Int. J. Hydrogen Energy*, 37, 7762 (2012).
24. C. Xu, J. W. Zondlo, and E. M. Sabolsky, *J. Power Sources*, 196, 7665 (2011).