Effects of PH₃ Contaminant on Solid Oxide Fuel Cells Performance and Related Anode Surface Temperature Measurements

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Solid oxide fuel cells (SOFCs) are being extensively researched for clean power generation from coal-derived syngas. Some of the contaminants in syngas such as phosphine (PH₃) may interact with the SOFC anode material, and degrade its electrochemical performance and material properties. In this paper, a modified Sagnac interferometry method is utilized to monitor the anode surface transient temperature as a function of applied current densities under hydrogen and simulated coal syngas. Moreover, the poisoning effects of PH₃ contaminant on the SOFCs performance are investigated in dry and moist conditions. The experimental results indicate that the Ni-cermet-based SOFC anode is more susceptible to degradation due to PH₃ in the presence of steam than under dry conditions. These experiments are valuable for the validation and the development of SOFC electrochemical models, and understanding the anode-contaminant interaction.

Introduction

Solid oxide fuel cell (SOFC) is an attractive technology for power generation with a high efficiency and a low level of NOₓ and SOₓ emissions. As a high-temperature fuel cell, SOFC can tolerate many of the contaminants found in the coal-derived syngas. Although several studies¹,² have shown the feasibility of utilizing coal-derived syngas as fuel for SOFC system,
its electrochemical performance and materials properties are affected when exposed to certain contaminants (e.g., As, P) in the syngas.\textsuperscript{3–7} Coal syngas cleanup techniques such as absorption and filters have been used to bring down the contaminant concentration. However, these processes are not cost effective and are carried out at lower temperature, and hence a significance portion of syngas thermal energy is lost.\textsuperscript{7} It is important to establish the tolerance of SOFCs for coal-derived syngas contaminants to facilitate the proper design of the fuel feed system that would not catastrophically degrade the SOFCs electrochemical performance during their expected life.

Presently, electrochemical impedance spectroscopy and voltammetry are the most popular methods for studying SOFC electrochemical performance.\textsuperscript{8} In situ Raman spectroscopy and Fourier transform infrared spectroscopy have been utilized to identify the molecular structure of an SOFC electrode surface.\textsuperscript{9–14} However, these techniques are carried out at a temperature lower than the standard SOFC operating temperature. The lack of suitable experimental methods that could directly probe the chemical transformations and microstructural changes of SOFC electrodes limits the research and development of realistic numerical models for the long-term prediction of SOFC operation.

In this paper, two tasks are carried out: (a) a modified Sagnac interferometry, integrated with infrared (IR) thermometry, is utilized for \textit{in situ} anode surface temperature measurement as a function of applied current density; (b) the effects of PH$_3$ contaminant on the SOFC performance are studied under hydrogen environment with and without steam. The experimental results obtained under SOFC operating conditions could be used for the validation and development of SOFC electrochemical models, and understanding the anode–contaminant interaction.

**Experimental Arrangement**

Anode-supported SOFC button cells, manufactured by Materials and Systems Research (MSRI, Salt Lake City, UT), were tested in this study. The MSRI cell fabrication procedure and material parameters are described in detail by Zhao and Virkar.\textsuperscript{15} Each button cell was about 2.6 cm in diameter with an anode composed of a 1-mm-thick Ni-8YSZ support structure and a 25-μm-thick interlayer of a highly catalytic Ni-8YSZ mixture. The electrolyte (8YSZ) was 20 μm thick and the cathode was composed of a 25-μm-thick La$_{0.8}$Sr$_{0.2}$MnO$_3$ (LSM)-8YSZ interlayer and a 25-μm-thick current-collection layer of LSM.

A NexTech Probostat\textsuperscript{TM} (Lewis Center, OH) button cell test apparatus was modified and integrated with a Sagnac interferometric optical setup and IR thermometer (OMEGA OS3707, OMEGA Engineering, Stamford, CT).\textsuperscript{16–18} The optical setup consisted of a 20 mW diode laser (wave length $\lambda = 658$ nm, laser spot size diameter = 2 mm), beam splitters, a polarizer, and beam-directing mirrors. A long-distance microscope fitted with a CCD camera was used to record the fringe patterns corresponding to out-of-plane surface rotation and a PhotriX IR pyrometer (Oakland, NJ) was used to measure the cell surface temperature on the same spot. Concurrently, electrochemical performances were measured using a Solartron electrochemical interface (SI 1287) and Solartron impedance analyzer (SI 1260) (Farnborough, U.K.). The impedance spectra were collected with an AC amplitude of 10 mV at frequencies ranging from 1 MHz to 0.1 Hz. Detailed description of the experimental setup and approach can be found in Guo et al.\textsuperscript{18}

**Result and Discussion**

We have reported\textsuperscript{18} the integration of a modified Sagnac interferometry with a NexTech Probostat\textsuperscript{TM} for \textit{in situ} out-of-plane surface deformation measurement of SOFC anode. The setup is capable of measuring the anode surface deformation on a small spot (~2 mm) and is immune to the system vibration and temperature fluctuation. In this research, an IR thermometer is incorporated with the test setup to monitor the anode surface temperature under the SOFC operation. With a modified and narrower field of view, the surface IR emission from the same spot of the anode surface is captured by the PhotriX IR pyrometer, albeit with only limited spectrum transmission (300–1650 nm).

**IR Calibration**

After complete reduction of anode material, IR pyrometer calibration was carried out with 5°C steps, from 750°C to 800°C. At discrete temperature steps, data were simultaneously recorded from the IR pyrometer and an embedded thermocouple close to the button cell under steady state conditions. As shown in Fig. 1,
the thermal calibration data was linear that could be extrapolated to transform the IR signal into temperature under cell operating conditions. It should be noted that IR temperature calibration was different for each test due to the optical alignment even though the trends remain linear. Thus, on-line calibration is needed in order to obtain accurate temperature measurement.

**Surface Temperature Variations**

To investigate the polarization effect on electrode reaction, *in situ* surface IR temperature measurement was carried out as a function of loading current densities. Figure 2 shows the surface temperature variation with the current density in steps, from 0 to 0.8 A/cm² under 100 sccm H₂/3 vol% H₂O. As shown in Fig. 2, cell surface temperature increase with increase in current density and it takes about 20–60 s to reach steady-state temperature depending on the applied current density. It is also found that the final steady-state surface temperature is independent of the intermediate current steps and only depends on the final current density (e.g., 0.8 A/cm²) but it takes less time to reach the steady-state temperature when the current is applied in larger steps. Figure 2b shows the corresponding power densities. Similar trends were obtained under H₂/3 vol% H₂O and simulated coal syngas (30% H₂, 23% CO, 21% CO₂, and 26% H₂O).

The changes in steady-state temperature of the anode surface are plotted against loading current densities for different fuel gas in Fig. 3a. As shown, the relation between surface temperature and current density is found to be nonlinear. It also shows that the correlation coefficient is higher under simulated coal syngas than under wet hydrogen fuel. It is due to different heat generation under different cell operating conditions such as exothermic water gas shift reaction under coal syngas. Moreover, the heat generation within a cell increases with the current drawn due to the fuel cell internal resistance. As illustrated in Fig. 3b, the cell is less efficient under simulated coal syngas than under hydrogen and thus generates more excess heat at the same operating current density. Figure 3a also shows a comparison between the experimental and numerical results from DREAM-SOFC, a three-dimensional computational fluid dynamics solver developed by Dr. Celik’s research group at West Virginia University. The numerical results indicate that the temperature variation through the cell thickness is negligible and the major source of the surface temperature rise is entropic heating from fuel oxidation, and a minor source is ohmic heating, while the water gas shift reaction provides negligible contributions to the temperature changes in coal syngas. In this case, the experimental data are used to assess the validity of the numerical model.
Surface Temperature during Hydrogen to Coal Syngas Transition

Anode surface temperature was also monitored while the fuel gas was switched from hydrogen to simulated clean coal syngas. To avoid damage to the button cell, it was operated under open circuit potential OCV as the humidifier was heated from room temperature to 66°C in order to increase water vapor concentration from 3% to 26%. Once the cell was stabilized, operating current density of 0.5 A/cm² was applied to the button cell. The corresponding surface temperature variation is plotted in Fig. 4a.

As the fuel gas was switched to simulated coal syngas, the power density fluctuated initially and then stabilized to a steady state after 33 mW/cm² of power density drop as shown in Fig. 4b. Because of the change of fuel gas composition, H/C and O/C atom ratios were decreased and slowed down the reaction rate, especially near the active anode/electrolyte interface and the concentration polarization becomes significant. Thus, the performance of button cell under syngas is lower and more excess heat is generated as shown in Fig. 3.

PH₃ Effects on SOFC Performance

The button cell was also tested with 10 ppm of PH₃ to study its poisoning effect on SOFC performance under dry and moist hydrogen. In this section, the preliminary results of SOFC electrochemical performance are presented under PH₃. Because the temperature measurement is limited by the sensitivity of the IR sensor, it was not detected due to PH₃ injection in the fuel stream. It indicates that 10 ppm of PH₃ does not significantly change the cell temperature field but it is expected that the cell temperature field will change in the long run. This change in temperature may be for the
two reasons: reaction between PH$_3$ and Ni and/or IR emission variation due to the Ni–P secondary phase formation. It is a subject of our future research.

The variation of cell power density history at a constant loading current density of 0.7 A/cm$^2$ is shown in Fig. 5. The cell was initially exposed to dry hydrogen gas and then 10 ppm of PH$_3$ was injected into the fuel gas for 48 h. It can be seen from Fig. 5 that the cell power density remained constant during exposure to PH$_3$ with dry H$_2$. The cell performance did not show degradation until the steam was introduced into the fuel gas. The power density of the button cell decreased gradually over time, for example 0.12 mW/cm$^2$/h degradation under H$_2$/3 vol% H$_2$O with 10 ppm PH$_3$. It also illustrated that the cell performance degradation was more severe under a higher steam content in the PH$_3$-containing fuel gas.

The electrochemical impedance data is also obtained at the open circuit condition. Two arcs were observed in the Nyquist plots of impedance as shown in Fig. 6. The $Z^*$-intercept of the high frequency arc yielded the ohmic polarization resistance of the cell. It exhibited a low value of 0.2 $\Omega \cdot$ cm$^2$ and showed little shift during the successive gas exposures. The high frequency arc is attributed to the impedance of the charge transfer processed occurring at the electrolyte/electrode interface and at the Ni/YSZ interface. The low frequency arc is associated with the bulk capacitance and the chemical processes including adsorption, surface migration, bulk migration, and other mechanistic steps. It is illustrated that the polarization resistance (the total arc width) increased with time during exposure to PH$_3$-containing moist hydrogen fuel gas. When exposed to 10 ppm PH$_3$ with 6 vol% H$_2$O, the polarization resistance increased 34% in 41 h. The corresponding ohmic resistance increased 50%, which indicated the cell degradation due to PH$_3$ effects. On the other hand, the cell resistance showed little increase under 10 ppm of PH$_3$ in dry conditions, as shown in Fig. 5. Hence, the poisoning effect of PH$_3$ was sincerely associated with the content of steam in the fuel gas: the more moist content, the faster the polarization resistance increases. Figure 7 shows the corresponding IV-curves and power densities under different conditions, which are consistent with the cell degradation indicated in the Figs. 5 and 6.

It has been reported that the exposure to phosphorous leads to irreversible degradation of the anode in the coal syngas.$^3$–$^7$ However, there are few studies focused on the relationship between the phosphorus compounds and steam in fuel. In this case, it appears that Ni-cermet-based SOFCs anode is less susceptible to degradation due to PH$_3$ in the absence of steam. These experimental data agree with the conclusions drawn by Krishnan et al.$^5$–$^6$ that PH$_3$ can be converted to HPO$_2$ (g) in the presence of steam between 700$^\circ$C and 900$^\circ$C, which had a deleterious effect on the SOFC performance.

Conclusions

A modified Sagnac interferometry method and infrared thermometry are utilized to monitor the anode surface temperature of a button cell under operating conditions.

Fig. 5. Variation of SOFC power density under different testing conditions at $i = 0.7$ A/cm$^2$. SOFC, solid oxide fuel cells.

Fig. 6. Impedance plots for SOFC operating under the open circuit voltage condition (OCV) at 800$^\circ$C. SOFC, solid oxide fuel cells.
The tests are conducted under hydrogen and simulated coal syngas with different applied current densities. An increase in temperature of about 4.5°C was observed on the anode surface temperature as the current density was increased from 0 to 0.8 A/cm², while the increase in anode surface temperature was higher under simulated coal syngas (7.6°C) for the same current density due to the entropic heating from different fuel gas oxidation. The addition of 10 ppm of PH₃ does not significantly change the cell temperature field in the short-term test, and long-term tests are under progress. PH₃ poisoning tests, conducted with the exposure of 10 ppm of PH₃ in hydrogen with/without steam, indicate that the Ni-tern-based SOFC anode is more susceptible to degradation due to PH₃ in the presence of steam than under dry conditions.

**Acknowledgements**

This work is conducted under U.S. DOE (Department of Energy) EPSCoR Program. Dr. Tim Fitzsimmons is the DOE Technical Monitor. Dr. R. Bajura is the Administrative Manager and Dr. I. Celik is the Technical Manager and the Principal Investigator of this project.

**References**


