

Accepted Manuscript

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PII: S0925-4005(15)30104-0
DOI: <http://dx.doi.org/doi:10.1016/j.snb.2015.07.046>
Reference: SNB 18777

To appear in: *Sensors and Actuators B*

Received date: 20-3-2015
Revised date: 3-7-2015
Accepted date: 13-7-2015

Please cite this article as: A.M. Schultz, T.D. Brown, M.P. Buric, S. Lee, K. Gerdes, P.R. Ohodnicki Jr, High Temperature Fiber-Optic Evanescent Wave Hydrogen Sensors Using La-Doped SrTiO₃ for SOFC Applications, *Sensors and Actuators B: Chemical* (2015), <http://dx.doi.org/10.1016/j.snb.2015.07.046>

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High Temperature Fiber-Optic Evanescent Wave Hydrogen Sensors Using La-Doped SrTiO₃ for SOFC Applications

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Abstract

Advanced sensors are needed for development of next-generation fossil fuel power generation technologies and for enhancing efficiencies of existing power generation systems. Optical waveguide-based sensing technologies have become increasingly important for harsh environment energy applications. In this manuscript, we present sensing results for fiber-optic evanescent wave hydrogen sensors employing La-doped SrTiO₃ layers as the active sensing element. These sensors show a rapid, reproducible sensing response to hydrogen fuel gas streams at elevated temperatures (600-800 °C). The presence of hydrogen results in a reversible and reproducible decrease in near-infrared transmission through the sensor. Sensors were also tested directly in the anode assembly of an operating solid oxide fuel cell (SOFC) with the sensor response correlating with both H₂ concentration and SOFC cell potential. Keywords: Optical fiber sensor; Metal oxide; Hydrogen sensor; SrTiO₃; High temperature

1. Introduction

To increase the efficiency of state of the art energy generation technologies, advanced sensor development is needed. In many cases, sensors embedded at locations suitable for collecting the highest value information must be capable of withstanding extreme environments including high temperatures, high pressures, and corrosive, highly reducing, and highly oxidizing gas streams. As just one example, *in situ* monitoring of fuel gas compositions in solid oxide fuel cell (SOFC) anode streams within the anode and cathode flow fields would provide valuable information for future improvement of SOFC efficiency and lifetime. Hydrogen sensors in SOFC fuel streams must measure hydrogen compositions in the range of 1-100 vol% and must be stable in humid environments at operating temperatures of 600-800 °C. Sensors based on optical fiber platforms are well suited for harsh environment sensing applications and are safer than traditional resistive sensing technologies for combustible environments, owing to the absence of electrical current. Optical fiber-based sensors also remove the risk of electrical interference to or from the operating fuel cell. Advanced interrogation and/or device fabrication approaches combined with fiber-based sensors offer the possibility of remote, distributed sensing in which high value information is provided versus position inside the test environment. This sensing data is directly relevance

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to advanced energy systems in which a gradient in fuel gas stream composition, temperature, and/or pressure are inherent to the system and difficult to measure using current sensor technology.

Commercially deployed optical fiber sensors are increasingly used in the oil and gas industry, for example to enable temperature and pressure monitoring in well-bore environments.[1] High temperature H₂- and CO sensing using fiber-Bragg grating based optical fiber devices have been reported by a number of authors, although the refractive index modified grating structure required for a measurable signal tends to exhibit instabilities at temperatures of approximately 500 °C and greater.[2,3] More recently, several classes of optical-fiber sensors and associated functional sensor materials have been demonstrated in which the sensing layer showed a sufficiently large response that eliminates the need for fiber-Bragg grating based interrogation approaches previously utilized and which allows for potentially improved temperature stability of the device platform.[4–7] However, even for these previous works an instability of the selected functional sensor layer[5,6] and/or the silica-based optical fiber transmission in the visible range was observed, spurring additional research to demonstrate a device that is potentially suitable for H₂ sensing in SOFC and other power generation applications.

In this work, we demonstrate a new set of optical fiber based H₂ sensor devices that utilize high temperature stable undoped and La-doped SrTiO₃ as the active sensing elements. SrTiO₃, a cubic perovskite oxide, is a well-studied material exhibiting high temperature stability.[8,9] La acts as an A-site donor impurity at high temperature under reducing conditions, increasing the free carrier concentration.[8,10–12] The increase in free carrier concentration has been shown to result in a near-infrared (NIR) optical response in planar La-doped SrTiO₃ films,[7] similar to previously studied Al-doped ZnO[5,6] and Nb-doped TiO₂ films.[5]

2. Methods

Optical fiber sensors were fabricated by etching away the cladding of a 125 μm diameter F-doped silica cladding/100 μm diameter silica core optical fiber and coating the exposed region using a dip coating process following the same procedure described in our previous work.[4] Precursor solutions for La-doped films were prepared following a modified recipe from Liu et al.[13] 1.00 mmol Ti-isopropoxide and 1.00 mmol acetylacetone were combined with magnetic stirring. The resulting pale yellow mixture was allowed to stir for 5 min. A solution of 2 mmol citric acid in 1.000 mL deionized water was quickly added to the Ti-acac mixture. Any resulting precipitate quickly redissolved with stirring. After 5 min, a solution containing a total of 1 mmol in the desired ratio of Sr(NO₃)₂ and La(NO₃)₃•6H₂O in 1.000 mL deionized water was added to the solution. Finally, 0.500 mL glacial acetic

acid was added to promote wetting of the substrate. The resulting solutions served as stable stock solutions for all subsequent coatings. The exposed core sensing region was approximately 5 cm in length and the dip-coating was performed at a rate of approximately 5 cm/s. Coated fibers were calcined in laboratory air by heating to 950 °C over 10 h, holding at 950 °C for 3 h, and cooling to room temperature over 3 h. Optical fiber sensors were characterized after gas sensing tests with a Quanta FEG environmental scanning electron microscope in low vacuum mode using a large field detector, an accelerating voltage of 20 kV. Cross-sectional transmission electron microscopy (TEM) was also employed using a Tecnai F20 with an accelerating voltage of 200 kV in bright field mode. Cross-sectional TEM samples were prepared using an FEI Nova dual-beam focused ion beam (FIB) SEM with standard lift-out procedures.

Sensors were tested in varying hydrogen fuel atmospheres to characterize their sensing response. The sensor was placed in a tube furnace through which varying compositions of ultra-high purity (UHP) nitrogen and hydrogen were flowed using a custom automated gas distribution system. Total flow rate was held constant at 100 SCCM. During hydrogen flow, near infrared transmission through the fiber was recorded using a portable FTIR spectrometer (ARCOptix Rocket FTIR). The illumination source was a high power halogen lamp (Ocean Optics Jaz). Optical transmission was normalized to a starting reference value, according to Equation 1.

$$\% \text{Transmission} = \frac{T}{T_{ref}} * 100 \quad (1)$$

For *in situ* sensing in a fuel cell anode assembly, a fuel cell test station known as the SECA Test Stand was chosen as the reconfigurable test platform.[14] The sensor was mounted with the sensing portion centered in a shallow channel in the anode plate exposed to fuel streams. For total sensor transmission measurements, the illumination source was a superluminescent diode (Thorlabs S5FC1005S) with narrowband emission centered at 1560 nm. The detector was a solid state power meter (Thorlabs PM100D) directly coupled to the sensor. Power transmitted through the sensor was monitored during fuel cell heating, at the onset and termination of fuel gas flow, and while loading of the fuel cell at various current levels.

3. Results and Discussion:

3.1. Physical characterization of sensing element

After completion of sensing tests reported in the following sections, the structure and phase of the sensing element was characterized using cross sectional transmission electron microscopy (TEM). Cross-sectional TEM specimens were prepared using conventional focused ion beam (FIB) milling

techniques. Acquired microscopy data are presented in Figure 1. Figure 1(a) and (b) depict bright field microscope images of the undoped and 30% La-doped sensing elements respectively. Visible in both images are the protective Pt layer deposited prior to FIB milling, the active sensing layer, and the silica fiber substrate. In both cases, the films are 70-100 nm thick with significant porosity and grain sizes on the order of the film thickness. Phase information was confirmed via convergent beam electron diffraction (CBED) and high resolution TEM. Figure 1(c) depicts a CBED pattern for the undoped sample. The pattern is consistent with the expected pattern for a $\{001\}$ -type zone axis for SrTiO_3 , verifying the expected cubic perovskite phase. Figure 1(d) shows a high resolution TEM image of the doped sensing element, along with an FFT-calculated diffraction pattern (inset). D-spacings and angles for the image are consistent with expected results for the cubic perovskite $\{001\}$ zone axis. Figure 1(e) demonstrates the geometry of the sensor structure. The fiber cladding is etched away in the sensing region, and the exposed core is coated with the active La-doped SrTiO_3 sensing material.

3.2. Laboratory scale fuel gas tests

Laboratory scale sensing tests in response to varying fuel gas atmospheres were carried out on the fabricated sensors. The effect of doping level, temperature, and wavelength of interrogation were evaluated with respect to sensor performance. Each sensor (SrTiO_3 , $\text{Sr}_{0.9}\text{La}_{0.1}\text{TiO}_3$, and $\text{Sr}_{0.7}\text{La}_{0.3}\text{TiO}_3$) along with an uncoated control fiber was exposed to the same series of sensing tests. For each test, a series of varying hydrogen compositions (1-100 vol% H_2) were alternated with ultra-high purity nitrogen in 1 hour intervals. The entire gas cycle was performed at 600, 700, and 800 °C consecutively. Optical transmission through the fiber was monitored, and normalized to the value at the start of each cycle.

Figure 2 summarizes the effect of interrogation wavelength on the sensing response of a 10% La-doped SrTiO_3 sensor at 700 °C. Typical near infrared transmission spectra through the fiber at various gas compositions are displayed in Figure 2(a). Transmission at selected wavelengths, noted by vertical dashed lines in Figure 2(a), is plotted versus time in Figure 2(b). Also shown is the applied hydrogen composition (in a balance of UHP nitrogen) versus time. Figure 2(c) plots normalized transmission through the fiber during gas flow versus gas composition for each selected wavelength.

The sensor was exposed to varying compositions of hydrogen (1-100% by volume) in ultra-high purity nitrogen, controlled by an automated mass flow control system. Transmission through the fiber is normalized to that at 100% N_2 at the start of the sensing test. After each hydrogen exposure, the fiber was allowed to recover in a pure N_2 atmosphere. Across nearly the entire spectrum of interrogation depicted in Figure 2(a), hydrogen in the gas stream is correlated with a decrease in transmission through the fiber. The magnitude of the decrease is most significant at wavelengths between 1600 and 2200 nm, roughly

unaffected at wavelengths near 2400 nm, and greater than baseline at wavelengths of 2500-2600 nm. The magnitude of the transmission change increases with increasing hydrogen composition across the spectrum. Also visible in Figure 2(a) is a characteristic feature associated with an absorption band centered at ~2250 nm arising from the silica fiber itself, which has been reported in other recent work and was attributed to OH-defects within the silica glass network.[15]

Kinetics of response and recovery, which are illustrated in Figure 2(b), are similar for all wavelengths. Sensing response commences rapidly after hydrogen introduction to the gas stream. The initial rapid decrease in transmission takes place on the order of 10-20 seconds, followed by a more gradual leveling of the transmission signal. After hydrogen is removed from the gas stream, the transmission through the fiber returns to within 5% of the initial value for all wavelengths and hydrogen levels. Sensor recovery is characterized by a multi-step process, particularly for recovery from higher hydrogen concentrations. After the gas stream is returned to 100% nitrogen, an initial rapid increase in transmission is observed. The initial increase slows, followed by a second rapid increase back to the baseline value. The duration of the multi-step recovery increases with increasing hydrogen content in the gas stream. In Figure 2(b), the recovery after 1% and 2% hydrogen exhibits no perceptible multi-step behavior. For hydrogen exposures of 5% or greater, the clear multi-step recovery is observed, similar to an earlier observation for TiO_2 based sensors.[16,17] Introduction of O_2 into the gas stream following hydrogen exposure rapidly accelerates the recovery process. Additionally, the inclusion of a constant background of low concentrations of O_2 (e.g. 1-2% by volume) during the entire test causes a significant improvement in recovery kinetics without hindering onset of sensing and with only a slight reduction in overall sensing response. This effect of background O_2 on recovery kinetics was previously observed for TiO_2 -based sensors and is an area deserving further future study.[16,17]

The calibration curves presented in Figure 2(c) compile the results from the sensing test presented in Figure 2(b). When normalized transmission through the fiber is plotted versus the log of hydrogen composition, the sensing response is roughly linear. As stated previously, the largest magnitude of sensing response is observed for the shortest wavelengths. Additionally, the slope of the plots increases with decreasing wavelength. The shortest wavelength of interrogation shows the greatest response as well as the greatest sensitivity to varying hydrogen compositions. A relatively large response for wavelengths in the vicinity of 1550 nm is particularly noteworthy as a large array of telecommunications technologies exist to transmit, interrogate, manipulate, and detect light in this range thereby helping to further pave the way for low cost and commercially viable sensing devices.

Figure 3 presents results for fibers coated with various compositions of La-doped SrTiO_3 , as well as results for a control test with an uncoated fiber. Undoped, 10% La, and 30% La-doped samples were

tested. Figure 3(a) plots transmission through the fiber at 1550 nm for each of the four tests. Transmission is normalized to the value at the beginning of the sensing test under a pure nitrogen gas stream and plots have been rigidly shifted to increase figure readability. Transmission through the uncoated fiber was unchanged compared to the initial value for all hydrogen flows at 1550 nm, confirming that the signal observed in the coated fiber is due to the sensing layer, rather than an inherent sensing response from the fiber platform. The observations also indicate that the fiber platform has an acceptable level of stability under varying H₂ exposures in this wavelength range allowing for useful sensing responses to be derived from the functional sensing layer. For long-term stability in application relevant environments, it is possible that improvements to the platform stability may be required. For completeness, we note that some reversible H₂ responses were observed in the vicinity of characteristic OH-related absorption peaks at $\lambda \sim 1350$ nm and 2250 nm for the uncoated fiber platform at the highest temperatures investigated. Such responses may be related to reversible defect formation at elevated temperatures, which do not appear to interfere with measured fiber sensor responses in the vicinity of the wavelength region of interest (1550 nm).

At 700 °C, all compositions of La-doped SrTiO₃ showed a sensing response to the hydrogen analyte. The magnitude of the sensing response is increased with increasing La content in the films. The calibration curves plotted in Figure 3(b) show that this increase in sensing response is observed for all hydrogen levels in the gas stream. At low hydrogen levels, the sensing response of the 10% La-doped fiber is only slightly improved compared to the undoped sensor. At higher concentrations of hydrogen in the gas stream, the 10% sensor shows more improvement compared to the undoped sensor. Across all hydrogen concentrations, the 30% La-doped sensor has a larger sensing response. In a gas stream containing 100% hydrogen, the 30% La sensor shows a maximum sensing response approaching a 50% reduction in optical transmission through the fiber. The slopes of plots presented in Figure 3(b) suggest that while the sensing response for the undoped and 10% doped samples are roughly linear with respect to the log of the hydrogen composition, the 30% sample begins to show signs of saturation at the higher hydrogen concentrations. These subtle details of the observed sensing responses require further investigation to fully clarify the active sensing mechanism.

Figure 4 plots sensing test results for a sensor with 30% La content at three operating temperatures (600, 700, and 800 °C). The sensing response is lowest at 600 °C, and increases with increasing temperatures. At 600 °C, the recovery time is significantly longer than at higher temperatures. Throughout the test at 600 °C, the sensor does not recover to the initial value within the one hour recovery period before the next hydrogen exposure. At 700 and 800 °C, recovery is complete to within 5% of the initial transmission through the fiber well within the recovery period. At both higher temperatures, speed

of recovery is dependent on the hydrogen composition in the gas stream, with increased recovery times for higher hydrogen exposures. At 800 °C, recovery is slightly (~5 min) faster than for 700 °C at the highest hydrogen levels, while at lower hydrogen levels no difference in recovery time was observed with the experimental limits. This is potentially an effect of the multi-step recovery process, which increases in prominence at higher hydrogen levels.

Higher doping levels are associated with increased generation of free carriers in the material, leading to increases in free carrier absorption. When La-SrTiO₃ is initially calcined at high oxygen pressures, La dopants are reported to be compensated ionically in SrTiO₃, forming SrO enriched areas along with oxygen vacancies in the lattice.[8,18–21] Under reducing conditions, compensation shifts to electronic compensation, such that La impurities can now contribute to the free carrier concentration in the material through the introduction of free electrons into the conduction band. Additionally, oxygen vacancies exist in undoped SrTiO₃ in equilibrium with the external atmospheric oxygen partial pressure. At high temperatures, oxygen vacancies created through oxygen exchange with the external atmosphere are associated with additional free carriers in the material.[22] In this case, as hydrogen concentration is increased in the gas atmosphere, both sources of free carriers would result in an increased composition of free carriers in the sensor material and an increase in NIR free carrier absorption. Increased temperatures work to increase the equilibrium concentration of defects as well as the kinetics of defect diffusion through the material. These effects may explain both the increased response with increasing temperature as well as the improved recovery characteristics at higher temperatures. As sensor development continues, optimization of doping levels to target operation temperature could potentially help in fabricating sensors with a non-saturating high magnitude sensor response to high-hydrogen content fuel streams.

Compared to planar samples of La-doped SrTiO₃,[7] the detailed wavelength dependence of the response appears to be different for samples deposited on planar substrates interrogated in a transmittance geometry as compared to the fiber sensors discussed in this work. For the fiber sensors, the highest response in the wavelength range interrogated occurs at ~1500-1700 nm, while for planar films the highest response occurred at the longest wavelengths interrogated of ~2400-2600 nm. In the case of the planar films, only specular transmission through a thin (~50-100 nm) layer of material is examined using the experimental set-up reported previously.[7] The optical physics are considerably more complex for optical transmission through a large diameter multi-mode fiber such as those used to fabricate the sensors presented here. Instead of specular transmission through a 50-100 nm film, the light now interacts with a sensing element ~5 cm in length along the fiber as a guided wave within the optical fiber. These differences help illustrate the complexities of optical sensor development; the optical response of a particular sensor configuration is dependent on sensor geometry and method of interrogation, even when

responding to the same external stimuli. Further studies are underway to better understand the detailed wavelength dependences of the sensing responses observed for the optical fiber sensors under investigation here.

3.3. *In situ testing in SOFC anode stream*

A $\text{Sr}_{0.7}\text{La}_{0.3}\text{TiO}_3$ sensor was fabricated for in situ testing in a solid oxide fuel cell anode channel. Optical power, generated by a narrow band 1560 nm superluminescent diode source, transmitted through the sensor was monitored during fuel cell operation at 750 °C under various fuel stream compositions and current loading conditions. Figure 5 compiles results for these *in situ* fuel cell tests. Figure 5(a) plots the open circuit voltage of the cell along with the optical power through the sensor as a function of time. The anode gas atmosphere was manually adjusted at various points, noted in Figure 5. In general, introduction of a reducing gas stream is correlated with an increase in cell voltage. Conversely, an inert argon stream is correlated with a decrease in the cell voltage. Throughout the test, transmission through the fiber is inversely correlated with the cell potential. This agrees with expectations from the laboratory scale tests, where introduction of hydrogen caused a decrease in transmission through the sensor. The noted gas compositions listed in Figure 5 only refer to manual opening and closing of valves in the gas distribution system, which is designed for steady state operation and long-term testing of SOFC cells rather than gas sensor development and testing. Because of differences in gas distribution plumbing for the various gas specie, the exact gas atmosphere within the anode channel at any given point in time is imprecisely known except in the stead state. In particular, for the case of the introduction and elimination of dry H_2 , cell voltage does not follow the clear rapid change observed for 4% H_2 and wet H_2 at other points in the test cycle. However, the sensor signal still strongly correlates with the measured cell voltage. This suggests the sensor is capable of sufficiently rapid response to multi-component gas atmospheres despite the uncertainties inherent to the gas distribution system.

Figure 5(b) and (c) show the sensor signal and fuel cell voltage in response to changing current loads on the cell. For the duration of these tests, the anode stream was 100% dry H_2 . When alternating between open circuit (zero current) and 2.1 A, as shown in Figure 5(b), both the cell voltage and the power through the sensor show a square wave pattern. The power through the sensor inversely correlates with the cell voltage. Increased current load on the cell would be expected to correspond to increasing fuel consumption in the anode, decreasing the hydrogen composition measured by the sensor. From the lab scale tests, a decreased hydrogen composition is expected to correlate with an increase in transmission through the sensor, as seen in Figure 5(b). Figure 5(c) shows the cell voltage and optical power through the sensor as the current load on the cell is increased stepwise from open circuit to 3.0A. As hydrogen

consumption increases (drawn current increases), the cell voltage decreases and the transmission through the sensor increases. Similar to the on/off tests presented in (b), an increased current load is correlated with increased fuel utilization at the anode and a lower composition of hydrogen in the process stream. Increased transmission through the sensor is correlated to a lower concentration of hydrogen as would be expected based on laboratory scale tests.

The magnitude of the *in situ* sensing response appears to be lower compared to that which would be expected based upon the observations in controlled varying H₂ in UHP N₂ laboratory scale tests for the variations between Ar and pure H₂ gas flows in the SOFC assembly. The difference in the magnitude of sensor response will be a subject of future study and may possibly be related to a number of factors including (1) the details of the gas flow distribution system and gas composition for the SOFC assembly, (2) the detailed placement of the sensor element within the SOFC anode stream, and (3) inadequate recovery times within the SOFC assembly for the pure Ar gas stream exposures.

6. Conclusions

The hydrogen sensing performance of La doped SrTiO₃ coated fiber optic evanescent wave sensors was examined. The sensors show a rapid response to hydrogen gas streams ranging from 1-100 vol%. Full recovery in nitrogen within 1 hour was observed at temperatures greater than 700 °C. Increased La-doping levels improves sensitivity, though at very high levels leads to saturation of sensing signals. Sensing performance and recovery kinetics improve at higher temperatures. When tested in actual process streams in a fuel cell anode, the sensors show good correlation with cell voltage under varying fuel stream compositions and current loads. Prototype fiber optic sensors based on La-doped SrTiO₃ show promise for potential future applications for process improvements and efficiency enhancements in next-generation energy technologies.

Acknowledgements and Disclaimer

The authors acknowledge Dr. Gregory Hackett and Mr. Dave Ruehl for assistance and support in completing the SOFC experiments. This work was funded by the U.S. DOE Advanced Research/Crosscutting Technologies program at the National Energy Technology Laboratory. This research was supported in part by an appointment to the National Energy Technology Laboratory Research Participation Program, sponsored by the U.S. Department of Energy and administered by the Oak Ridge Institute for Science and Education.

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References

- [1] A.D. Kersey, *IEICE Transactions on Electronics* 83 (2000) 400.
- [2] X. Tang, K. Rummel, X. Lan, J. Deng, H. Xiao, J. Dong, *Anal. Chem.* 81 (2009) 7844.
- [3] X. Wei, T. Wei, J. Li, X. Lan, H. Xiao, Y.S. Lin, *Sens. Actuators B Chem.* 144 (2010) 260.
- [4] P.R. Ohodnicki, M.P. Buric, T.D. Brown, C. Matranga, C. Wang, J. Baltrus, M. Andio, *Nanoscale* 5 (2013) 9030.
- [5] P.R. Ohodnicki Jr., M. Andio, C. Wang, *J. Appl. Phys.* 116 (2014) 024309.
- [6] P.R. Ohodnicki, C. Wang, M. Andio, *Thin Solid Films* 539 (2013) 327.
- [7] A.M. Schultz, T.D. Brown, P.R. Ohodnicki, *J. Phys. Chem. C* 119 (2015) 6211.
- [8] R. Moos, K.H. Hardtl, *J. Am. Ceram. Soc.* 80 (1997) 2549.
- [9] B.F. Flandermeyer, A.K. Agarwal, H.U. Anderson, M.M. Nasrallah, *J. Mater. Sci.* 19 (1984) 2593.
- [10] P.R. Slater, D.P. Fagg, J.T.S. Irvine, *J. Mater. Chem.* 7 (1997) 2495.
- [11] U. Balachandran, N.G. Eror, *J. Electrochem. Soc.* 129 (1982) 1021.
- [12] O.A. Marina, N.L. Canfield, J.W. Stevenson, *Solid State Ionics* 149 (2002) 21.
- [13] J. Liu, R.W. Smith, W.-N. Mei, *Chem. Mater.* 19 (2007) 6020.
- [14] Y.S. Chou, J.W. Stevenson, Z.G. Yang, G.G. Xia, K.S. Weil, J.P. Choi, J.D. Templeton, K.P. Recknagle, M.A. Khaleel, P. Singh, (2008).
- [15] P.R. Ohodnicki, *J. Non-Cryst. Solids* (n.d.).
- [16] P.R. Ohodnicki, T.D. Brown Brown, *Nanomaterials and Energy* 3 (2014) 40.
- [17] P.R. Ohodnicki Jr., T.D. Brown, G.R. Holcomb, J. Tylczak, A.M. Schultz, J.P. Baltrus, *Sens. Actuators B Chem.* 202 (2014) 489.
- [18] R. Moos, A. Gnudi, K.H. Härdtl, *J. Appl. Phys.* 78 (1995) 5042.
- [19] R. Moos, T. Bischoff, W. Menesklou, K.H. Hardtl, *J. Mater. Sci.* 32 (1997) 4247.
- [20] U. Balachandran, N.G. Eror, *J. Electrochem. Soc.* 129 (1982) 1021.
- [21] T. Kolodiazny, A. Petric, *J. Electroceram.* 15 (2005) 5.
- [22] R. Meyer, R. Waser, *Sens. Actuators B Chem.* 101 (2004) 335.

Figure Captions

Figure 1: Transmission electron microscopy characterization of sensor element. (a-b) Bright-field TEM image of undoped SrTiO₃ and 30% La-doped SrTiO₃ sensing elements respectively. Sensors were coated with a protective Pt layer (visible in micrographs) prior to FIB milling. In both sensors, the active sensing layer is on the order of 70-100 nm thick. (c) Convergent beam electron diffraction image for undoped SrTiO₃ sensor showing a pattern consistent with a {001} type zone axis. (d) High resolution TEM image for the doped sensor with calculated diffraction pattern. The diffraction pattern can be indexed as a {001} zone for cubic SrTiO₃. (e) Schematic depicting evanescent wave based sensor element geometry. The fiber cladding is etched away, and the exposed core is coated with the active sensing material.

Figure 2: Summary of wavelength dependence of optical hydrogen sensing response for a 10% La-doped SrTiO₃ sensor at 700 °C. (a) Representative near-IR transmission spectra through the fiber in varying gas compositions. Transmission through the fiber is normalized to transmission at 100% N₂ atmosphere. Vertical dashed lines correspond to wavelengths plotted in Figure 2(b) and (c). Magnitude of the sensing response is largest at shorter wavelengths. The broad absorption peak centered at 2250 nm is characteristic of inherent hydroxyl features in the silica fiber platform, rather than the SrTiO₃ overlayer. (b) Full sensing test results for selected wavelengths. Varying hydrogen compositions (1-100%) in the atmosphere are associated with a decrease in transmission through the fiber. The magnitude of the decrease increases with increasing gas composition. Error bars represent the time dependent response observed at higher hydrogen compositions, where the sensing signal does not reach a constant value. (c) Calibration curves showing the sensing response related to gas composition for each selected wavelength. Sensing response increases monotonically with increasing hydrogen levels in the gas stream for all wavelengths.

Figure 3: Summary of the effect of La-doping level on the magnitude of the sensing response at 700 °C and 1550 nm. (a) Sensing test results for an etched, uncoated fiber, pure SrTiO₃-coated fiber, 10% La-doped SrTiO₃-coated fiber, and 30% La-doped SrTiO₃-coated fiber. Transmission through the fiber is plotted relative to transmission at the beginning of each sensing test, and plots are rigidly shifted to improve figure readability. The uncoated fiber shows no sensing response. Each of the coated fibers shows a significant response to the hydrogen gas flows, with the magnitude of the sensing response increasing with increasing doping levels and hydrogen content in the gas stream. (b) Calibration curve showing magnitude of sensing response versus gas composition. Each sensor shows a monotonically increasing response to hydrogen composition, with a maximum response approaching a 50% decrease in transmission for the 30% doped sample at 100% H₂.

Figure 4: Summary of the effect of temperature on the magnitude of the sensing response for a 30% La-doped sample at 1550 nm. (a) Sensing test results at 600, 700, and 800 °C. Transmission through the fiber is plotted relative to transmission at the beginning of each sensing test, and plots are rigidly shifted to improve figure readability. At 600 °C, the sensing response does not return to the initial baseline within the 1 hour period of pure N₂ flow, while at 700 and 800 °C, transmission through the fiber returns to the initial level after each hydrogen flow. (b) Calibration curve showing magnitude of sensing response versus gas composition. Increasing temperature results in increasing sensing response, approaching 50% for 800 °C at 100% H₂.

Figure 5: Results for *in situ* fuel cell anode stream tests. (a) Fuel cell voltage and optical power through the sensor (a) at open circuit under varying fuel stream compositions, (b) with a constant fuel stream and application and termination of a current load on the cell, and (c) with a step function increase in current load on the cell. The gas stream for current variation tests was 100% dry H₂. In all figures, the sensor signal inversely correlates with the measured cell voltage.