Proton exchange membrane (PEM) fuel cells generate electricity directly from chemical energy by electrochemical oxidation of hydrogen (fuel) at the PEM-catalyst-layer interface. Nafion, the most commonly used membrane material, is known to exhibit a proton conductivity change by an order of magnitude due to variation in relative humidity between 35 and 85%. Therefore, proper internal water management is necessary for efficient operation of a PEM fuel cell. The final product of hydrogen-fed PEM fuel cells is H2O; thus, the transport of this produced water can strongly affect cell performance. However, only the inlet humidity of the anode and cathode side gas channels can be directly controlled. The presence of an excess amount of water vapor at the inlet may result in flooding of the PEM fuel cell due to condensation at the cathode side, while an insufficient humidification may result in membrane drying due to evaporation into the reactant stream and electro-osmotic drag from the anode to the cathode. Both of these conditions are known to severely degrade the performance of PEM fuel cells.

The temperature distribution within PEM fuel cells also influences the overall performance. For the aforementioned reasons, rapid in situ measurements of temperature and water vapor partial pressure are important for the improvement of fuel cell operation and design optimization. In this paper, we report an improved, non-intrusive optical technique for determining in situ water vapor partial pressure and gas temperature simultaneously in gas channels of a prototypical PEM fuel cell during operation on both the cathode and anode sides. This improvement not only permits a detailed understanding of PEM fuel cell operation but also in situ monitoring for control purposes.

The most common and simplest characterization of PEM fuel cells is the determination of its electrical performance in the form of a polarization curve. Simplified models of fuel cells have been based on comparison with such data. Other global measurement techniques have evolved that enable monitoring of flooding or drying conditions by recording the pressure drop in the channel cathodes and the increase in cell resistance, respectively. Research has been done on a separate examination of anode kinetics, anode mass transport, cathode kinetics, cathode mass transport, and membrane conductivity based on ac impedance spectroscopy, determination of the ohmic resistance of a membrane electrode assembly (MEA), and the mass-transport coefficient of the electrodes by an MEA resistance and electrode diffusion technique. These global measurement approaches yield only the values of the parameters integrated over the entire fuel cell.

Several techniques have been developed that permit the diagnosis of local fuel cell parameters. These techniques include physical probe measurements using gas chromatography, commercial portable humidity-temperature meters, liquid water measurements via neutron scattering, membrane hydration via X-ray scattering, catalyst composition via X-ray absorption, Fourier transform infrared (FTIR) spectroscopy, and membrane water content and acidity measurements. These techniques are restricted to either measurement by extractive sampling with limited temporal response, such as in gas chromatography and FTIR spectroscopy, or using sophisticated facilities that are only accessible at a few sites, such as neutron scattering and X-ray absorption.

Recently, Basu et al. devised an in situ intrusive measurement technique for monitoring water vapor partial pressure and temperature in one of the cathode flow channels of a serpentine channel PEM fuel cell. This was the first demonstration of tunable diode laser absorption spectroscopy (TDLAS) in a PEM fuel cell. The data were obtained for temperature and water vapor partial pressures in the flow channels only on the cathode side using a direct absorption technique. The direct absorption spectroscopy necessitated knowledge of a background signal, where some approximations were necessary to obtain the absorption profiles. The data obtained for water partial pressure had a typical error of ±5% and the temperature had an error of ±2.5°C. More recently, Fuji et al. studied the steady-state spatial concentration distribution of water vapor and oxygen in a custom made single channel fuel cell with an active area of 3 cm² and a channel length of 100 mm with transparent endplates using TDLAS. They measured a peak absorption value and compared their results to tabulated line intensities from the HITRAN database to determine concentration. Separate calibrations were not used for anode and cathode measurements, which may result in errors due to the different collisional environments. Hinds et al. recently measured the local temperatures and relative humidity by a bandgap temperature sensor and a capacitance polymer sensing element embedded in an external recess adjacent to the measurement channels. They reported a time scale of 100 s for the channel to reach steady-state water concentrations. However, this measurement may include additional delays due to required diffusion from the main channel to the measurement recess. The summary of the different in situ water and temperature measurement techniques in polymer electrolyte fuel cells available to date is given in Table I. As mentioned earlier, each technique has its advantages and disadvantages in terms of their applicability for commercial cells, time response of measurements, and spatial resolution. The measurement technique presented in this paper is a variation in the previously demonstrated TDLAS approach utilized by our group.
large variety of gases can be measured

- Large size of sensor, low time resolution
- Not quantitative, special apparatus, not applicable for commercial cells
- Large size of sensor, low time resolution
- Expensive apparatus, not feasible in commercial cells, data are qualitative
- Limited to low humidity and nonflooding regimes
- Large size of sensor, low time resolution
- Low time resolution, somewhat intrusive
- Expensive apparatus, not feasible in commercial cells, data are qualitative

**Experimental**

*Sensor working principle and calibration.—* TDLAS with wavelength modulation (WM) was used to measure water vapor partial pressure and gas temperature in the bipolar plate gas channels on the cathode (mixed with air) and anode (mixed with hydrogen) sides of the cell. The water vapor transition at 1469.637 nm was carefully chosen by Basu et al. to optimize sensitivity to temperature changes over the range relevant to PEM fuel cell operation. The same spectral line was measured here, but the approach to the spectral measurements, simulations, and curve fitting was modified. The experiments consisted of two parts: (i) experimentation in a reference absorption cell with an optical path length of 24.3 cm to determine the spectral parameters, characteristic of this particular water vapor transition in the presence of air or hydrogen, and (ii) experimentation in the fuel cell gas channels (at the inlet and outlet sides) for unknown temperatures and gas compositions at different operating conditions.

A NEL distributed feedback (DFB) diode laser (center wavelength = 1470 nm) was used for the experiments. The laser was controlled by a Thorlabs thermolectric temperature controller (TEC2000) and a Thorlabs laser diode current controller (LDC500). The temperature controller was kept at a fixed control value at which wavelength measurements were done using an optical spectrum analyzer. The wavelength of the laser was modulated by varying the voltage input to the laser diode current controller. A triangular wave superimposed with a sine wave was sent to the laser diode controller. The modulation of the laser was created using a sine wave with a frequency of 320 Hz superimposed on a triangular ramp with a frequency of 1 Hz (Fig. 1, left). The laser wavelength and intensity were a function of the injected current; thus the laser wavelength scans following the modulation signal. The magnitude of the triangular ramp was chosen to scan the wavelength slowly across a spectral absorption line of an absorbing gas (water in this case), and the faster but lower amplitude sinusoidal modulation provided for small wavelength modulations as the wavelength scanned.

The laser radiation was projected through a flow channel and interacted with the gas media. The resultant absorbed beam was intercepted by a photodiode (PD) detector. The voltage generated from the photodiode was measured by a data acquisition system and computer. The measurement system was timed and controlled by a National Instruments Labview data acquisition program, which created both the modulation signal for the laser and monitored the PD signal. The signal collected from the PD was multiplied in software by separate sine waves of the same and twice the frequency as that of the sinusoidal ramp voltage sent to the voltage input of the laser diode current controller. The resultant two signals were filtered by a fifth order digital Bessel filter to remove fluctuations at frequencies higher than the cutoff frequency (20 Hz), which removed the sinusoidal modulation frequency itself. The first signal yielded the first harmonic of the absorption profile, the so-called 1f curve, and was proportional to the slope of the triangular ramp and the first derivative of the absorption profile. The second signal yielded the second...
harmonic or 2f curve (Fig. 1, middle), which was related to the second derivative of the absorption profile. When the ratio of the 2f to 1f signal was taken, it yielded a quantity in which the incident laser intensity and the system signal gain effects were removed, making instantaneous background signal collection unnecessary.

The absorption of the laser beam passing through a gas medium is given by the Beer–Lambert law as

$$I = I_0 \exp(-\int_0^L \alpha \, dl)$$  \hspace{1cm} (1)

where \(I_0\) is the incident laser intensity, \(I\) is the measured intensity after absorption, and \(\alpha\) (cm\(^{-1}\)) is the absorption coefficient dependent on the wavelength, partial pressure, and temperature. The integration is taken over the total path length \(L\) of the absorbing medium. The absorption coefficient \(\alpha\) can be computed as

$$\alpha = 2 \times P_i \times S(T, v_0) \times \sqrt{\frac{\ln(2)}{\pi}} \times V(X, Y)$$  \hspace{1cm} (2)

where \(P_i\) is the partial pressure of the absorbing gas, \(S(T, v_0)\) is the line strength in cm\(^{-1}\) atm\(^{-1}\) (related to the transition dipole moment), and \(V(X, Y)\) is the Voigt function describing the convolution of Gaussian and Lorentzian line broadening. For the Voigt function, \(X = 2\langle v - v_0\rangle/\alpha_0\langle v\rangle \ln 2\) and \(Y = \alpha_0\langle v\rangle \ln 2\), where \(\alpha_0(T)\) is the Doppler half-width, \(\alpha_0(P_i, T)\) is the Lorentzian half-width, \(v_0\) is the transition line center wavenumber in cm\(^{-1}\), and \(v\) is the wavenumber of the incident laser. The Doppler half-width (\(\alpha_0\)) is related to temperature by

$$\alpha_0 = 7.162 \times 10^3 v_0 \sqrt{\frac{\Sigma_{n=1}^{N} \frac{\partial}{\partial T}}{M \ln 2}}$$  \hspace{1cm} (3)

where \(M\) is the molecular weight of the absorbing species and \(T\) is the gas temperature in Kelvin.

Simulations of the 2f/1f signal were generated for known water concentration and temperature conditions by multiplying the transmission coefficient \((I/I_0)\) in Eq. 1 with a measured PD signal from a reference cell without any water absorption. This approach accounted for any small background signals in the experimental setup as discussed by Rieker et al.\(^\text{23}\). For computing the absorption coefficient, the Voigt profile was generated using the Humlicek algorithm\(^\text{24}\) that was programmed in Labview. The 2f/1f profiles were then generated from this simulated absorption signal using the same software lock-in algorithms as those used in the experiments. The resultant simulated profiles were matched with those obtained from the experiments using a Levenberg–Marquardt algorithm, and the known conditions used in the generation of the simulated 2f/1f spectrum were used to determine the experimental conditions in the fuel cell. This process was similar to that used in direct absorption, where no sinusoidal modulation was used; however, the use of modulation and the 2f/1f algorithm enhanced sensitivity to absorption and decreased sensitivity to background variations in signal.

For the experiments conducted in the reference cell, the data fitting was done to find the parameters \(S(T, v_0)\) and \(\alpha_0(P_i, T)\) at each water vapor partial pressure \((P_i)\) and temperature \((T)\), in effect calibrating the simulation technique used for later measurements in a fuel cell. The frequency modulation depth was carefully chosen to be around 2.2 (varying from 1.8 to 2.6) times the half-width at half-maximum of the water transition, as suggested by Reid and Labrie.\(^\text{25}\). The two parameters \(S(T, v_0)\) and \(\alpha_0(P_i, T)\) obtained at different \(P_i\) and \(T\) in the reference cell were simultaneously used to predict the unknown temperatures and partial pressures in the fuel cell by a two-parameter fit. A bilinear fit was performed to find the intermediate data points. Unlike Basu et al.,\(^\text{10}\) no approximations were made regarding the shape of the absorption profile.

The strong transition lines of water around 1470 nm are caused by rovibrational energy transitions. The line absorption strength is a function of the ground state energy and the gas partition function that is also a function of temperature. The widths of these transitions are affected by both Doppler broadening (molecular motion) and collisional broadening. Water–water self-collisions were very effective compared to other collisions; thus, higher water partial pressures increase the collisional broadening term, \(\alpha_2\). Collisions with different coexisting gas molecules also affect the broadening in smaller ways, resulting in slightly different Lorentzian half-widths as a function of gas concentrations. At the same temperatures and water vapor partial pressures, different broadening widths are therefore expected for water vapor–air and water vapor–hydrogen mixtures. Thus, separate calibrations were required for measurements on the anode and cathode sides of the fuel cell.

The measurements in the reference cell were performed to find the unknown water vapor spectral transition parameters, Lorentzian half-width [\(\alpha_1(P_i, T)\)], and line intensity [\(S(T)\)] at different water vapor partial pressures \((P_i)\) and temperatures \((T)\) in a mixture with either air or hydrogen. The data collected in the reference cell satisfied a linear trend for the Lorentzian half-width as a function of partial pressure at different fixed temperatures, as shown in Fig. 2.

The line transition intensity parameter is a function of the system partition function, transition energy, and temperature. All these parameters can be expressed as a function of temperature alone. Thus the presence of a different surrounding gas did not influence this parameter. As obtained experimentally, the line intensity had unchanged values for both experiments with hydrogen–water and air–water mixtures, as shown in Fig. 3.

Diode laser timing for dynamic measurements.—The triangular wave used for scanning the wavelength across the water transition...
had uneven sides to accommodate more data points on the rising edge, which was used for measurements, and fewer on the falling edge, which was only used to return the laser to its starting current. For steady-state measurements in a fuel cell, the rising edge had 75,000 sample points and the falling edge had 25,000 sample points. The frequency of the triangular ramp including the rise and fall was 1 Hz. The frequency of the sine wave added to the ramp was 320 Hz; thus 240 complete sinusoids were used for the measurement of the 1f and 2f signals. To increase the data acquisition speed for transient measurements in the fuel cell, only 10,000 data points were used in the triangular ramp due to limitations in the buffer memory in the data acquisition board. This decreased water partial pressure accuracy by about 0.06%. For collection of data simultaneously in four channels, the ramp frequency was limited to 5 Hz. The frequency of the sine waves in the transient measurements was 3.2 kHz. Thus, the time resolution of collected transient data was 0.2 s. This was sufficient to resolve the transient time scales in a fuel cell operating in a dynamic cycle. The data collected were processed by a software lock-in amplifier to compute the 2f/1f waveforms as discussed previously.

Experiments in the PEM fuel cell.— An optically accessible fuel cell was used as in our previous work to deliver a diode laser beam through select flow channels in the bipolar plate. The DFB laser was coupled to a collimator that was inserted directly into the edge of the bipolar plate. The bipolar plate had a counter-flow serpentine channel geometry comprising 15 straight segments of which the 2nd and 14th channels from the air and hydrogen inlets at the cathode and anode sides were milled out to the end so that the diode laser beam could be transmitted along the channel length. Each flow channel length was 7 cm with channel cross-sectional dimensions of 1.5 × 2.0 mm, as shown in Fig. 4. The rib widths were made larger (2.9 mm) than the channel widths. For making measurements simultaneously in the two anode and two cathode channels, the fiber coupled output of the laser was divided into four fiber outputs via three 2:2 bifurcated optical fiber couplers connected to four collimators fixed at one end of each optically accessible channel. Each laser beam, after crossing the flow channels, emerged out of an antireflective IR transparent wedged glass window fixed at the opposite ends of the fuel cell channels and was collected by four different photodiodes PD 1–4. The optical path length was 9.79 cm.

The experiments in the PEM fuel cell were carried out in the apparatus, as schematically shown in Fig. 5. The fuel cell was controlled by a Scribner Associates 890C fuel cell load control box with the aid of a controller computer. A five-layer MEA manufactured by Electrochem was used in the PEM fuel cell. The membrane in the MEA was DuPont Nafion 212. The carbon fiber paper GDL of 250 μm thickness was manufactured by Toray. The temperature of the fuel cell was controlled by two Watlow silicone heating pads attached externally to the gold coated aluminum end plates and monitored with a single thermocouple drilled into the graphite bipolar plates. The fuel cell was operated in a vertical orientation with the outlets at the bottom.

Results and Discussion

Experiments were carried out at steady-state and transient conditions corresponding to different fuel cell inlet humidities and operating temperatures. In the following sections, the experimental results are discussed first for the steady and then for the transient cycle experiments. The cell temperature was maintained at 70 and 80°C with several different inlet humidity levels for the anode and cathode sides.
The maximum current density was 400 mA/cm². The flow rate was kept constant at 0.25 slpm for the anode and 0.50 slpm for the cathode. This corresponds to a stoichiometry range of 1.5–2.5. The primary goal of this study was to demonstrate the capabilities of this measurement system, particularly its utility for obtaining transient data.

The error in the experimental data can be estimated from the calibration experiments, which showed a ±2.5% error in partial pressure of water vapor and ±3°C error in temperatures. These uncertainties arose due to the optical noise that could not be completely eliminated and the fluctuations in temperatures throughout the calibration experimental setup. The line intensities obtained from calibration also show scatter (Fig. 3) and result in further inaccuracies in temperature. Especially at the higher humidity levels, the condensation of liquid water in the optical path causes noise in the transmitted power leading to poor data quality. The transient data collected involved faster modulation of the diode laser current leading to some instability in the laser wavelength as compared to the steady-state measurements. This variation resulted in a higher sensitivity to transmission variations vs wavelength in the optical path; thus uncertainties were higher for the dynamic measurements.

Steady-state experiments.—Steady-state measurements were taken at experimental conditions, as described in Table II. Figure 6 shows the measurements of cell voltage and water vapor concentrations at the four measurement locations. At open-circuit voltage (OCV) conditions for equal inlet humidities (cases A and C), there is no change in water partial pressure from the inlet to the outlet. However, for other cases with nonequal water concentrations (cases A, B, and D–G), diffusion across the membrane is apparent at OCV as a difference in the inlet and outlet gas concentrations.

The steady-state measurements indicate that there is a monotonic rise in the partial pressure of water with increasing current density corresponding to the electrochemical reaction at the cathode side. For the inlet side, the water partial pressure does not change as significantly because the measurements are taken in only the second serpentine channel and the water concentration is impacted more strongly by the inflow conditions. However, at the outlet channel, the integrated effects of water production and transport through the cell are measured. The rise in cathode outlet water is not linear with current density as there is some back-diffusion of water toward the anode side particularly near the outlet where the concentration gradient is largest.

At higher humidity levels at the anode, the outlet concentration is less than the inlet concentration despite the consumption of hydrogen. For example, in case E, which represents 80% anode inlet humidity and 18% cathode inlet humidity, there is a substantial reduction in the anode side gas channel humidity from the inlet due to anode dry-out. The deficit in the humidity levels from the inlet to the outlet decreases as the current density is increased as a result of increased back-diffusion. For the measurements at 80°C (cases F and G) the trends are comparable to those at lower temperatures. For example, the nature of the anode dry-out at condition G is comparable to E except for a larger magnitude due to increased water diffusivity of the membrane at 80°C.

For cases where the anode inlet is more humid than the cathode inlet gas stream (cases B and D–G), the increase in the amount of water vapor at the cathode with increasing current density is more than the corresponding increase for equal humidity conditions on both sides of the fuel cell (cases A and C). This is believed to be due to additional diffusion of water from the anode side gas stream to the cathode side near the inlet and reduced back-diffusion near the outlet. For case A, a steep rise in the anode humidity was noticed for 350 mA/cm² due to possible flooding. The water back diffused to the anode side, resulting in saturation of both the anode and cathode outlet streams. The temperatures, as shown in Fig. 7 for an example condition (case A), did not vary more than 8°C during the steady operation for any case. For this reason, the measured temperatures are not shown for the other cases.

**Dynamic cycling experiments.—** Water vapor partial pressure and temperature measurements were also performed during the dynamic cycling of the PEM fuel cell corresponding to steady-state experimental cases C and E with a stair-step pattern of load currents, as shown in Figs. 8 and 9 and listed in Table III. The inlet and outlet conditions are labeled a and b, respectively. The time resolution of data acquisition for each sampled point was 0.2 s. Figures 8 and 9 shows that the time scales for the cell to reach steady state were on the order of 20 s. These transient features were well resolved using this sensor. The transient measurements result in a steady-state value of the concentrations, which agree with the measured steady-state water vapor partial pressures shown in Fig. 6.

There are distinctly observed dips in the water vapor concentration obtained at the anode channel outlet just when a sudden increase in the current is initiated. These dips result from the sudden rise of current that induces an increase in electro-osmotic water drag from the anode to the cathode side. The immediate source of water for the electro-osmotic flux is the water content of the membrane that decreases the membrane water content toward the anode and increases absorption of water by the membrane on the anode side. This causes a concentration drop in the anode outlet, which reflects the integrated water uptake by the membrane on the anode side. As the electrochemical reaction proceeds, the water produced in the cathode diffuses back to the anode, resulting in the water concentration recovery at the anode. The minima of the membrane hydration level are thus reflected in the minima of the anode outlet water concentration levels. The larger the sudden increased demand of water for the electro-osmotic flux after load change, the higher the amount of anode water carry-over to the cathode. Hence the dip in anode water content is larger and it takes longer for the anode to recover the water concentration level at the exit. This is demonstrated in Fig. 10a, which shows four consecutive current density dynamic cycles with increasing step changes. As the current step size increases, an increasing dip in the anode exit water partial pressure.

![Figure 5. (Color online) Schematic of the experimental setup.](image-url)
sure level is observed just following the step change. This is also supported by the fact that there is a distinct voltage undershoot just after the step change, revealing a greater amount of internal resistance in the proton transport mechanism before the water content recovery. The dip is much more significant for a step increase from the OCV condition to a load as compared to a step from a given load to a higher load as a result of the greater availability of the water in the membrane under loading. The time scales for reaching the minimum in this dip are around 2.4–3.7 s after the load change. The cathode outlet does not show this short time scale dip and instead approaches steady-state conditions asymptotically with time scales on the order of 20 s that vary only slightly with load step size (Fig. 10b). These time scales can be ascribed to several transport phenomena. Some of these processes are relatively fast and hence their contributions can be neglected. These fast processes include the following.

1. Electro-osmotic drag. Because this is connected directly to proton conduction, this transport phenomenon occurs on the same time scale as charging or discharging of the electrochemical double layer. The double layer occurs in a nanometer scale thin layer adjacent to the electrode surface.
cent to the reaction interface and acts as a capacitor during transients. The water transport time scale is associated with this phenomenon on the order of microseconds.\textsuperscript{30}

2. Diffusion from the gas channels to the membrane through the gas diffusion layer (GDL). Water enters from the gas channels into the GDL through binary diffusion of either water vapor–air or water vapor–hydrogen. The time scale of such a diffusive process is\textsuperscript{31,32}

$$\tau_{\text{GDL}} = \frac{\delta_{\text{GDL}}}{D_{\text{GDL}}} \sim 1-5 \text{ ms}$$ \hfill [4]

where $\delta$ is the GDL thickness and $D$ is the diffusivity. This GDL diffusion time is on the order of milliseconds.

Several transport processes occur on the order of seconds and are relevant to the observed dynamics. These processes include the following.

3. Membrane hydration via chemical reaction. Due to reactions and resulting increased water concentration on the cathode side, the membrane absorbs water as it approaches its steady-state water content distribution. The time constant for membrane hydration is given by\textsuperscript{30,31}

$$\tau_{\text{m,H}} = \frac{(\rho_{\text{m}}\Delta \lambda)/\text{EW}}{1/2F} \sim 15-25 \text{ s}$$ \hfill [5]

where $\rho$ and EW are the density and equivalent molecular weight of the membrane, respectively. The water content $\lambda$ is the number of water molecules per sulfonic acid group within the membrane and $\Delta \lambda$ is the change in water content during the step change. $\delta_{\text{m}}$ is the membrane thickness and $I$ is the current density. For the range of conditions examined here, this time constant is on the order of 15–25 s and is consistent with the longest time scales observed in the experiments.

4. Diffusion across the membrane. As water is taken up by the
membrane on the cathode side, it back diffuses due to concentration gradients with a time scale given by

$$\tau_{m,D} = \frac{D_m}{\lambda^2} \approx 2 \text{s}$$

where the diffusivity is computed for conditions of $T = 70^\circ\text{C}$ and $\lambda = 3$. This time scale is faster than the rate at which the membrane takes in water due to chemical reactions (time scale 3); thus, it can be expected that the distribution of water within the membrane is in quasi-steady-state during water uptake.

5. Advection in the gas channels. Because the sensor measures only the gas concentration in the bipolar plate flow passages, the time required for gas flow from the inlet to the outlet affects the sensor response to changes in membrane water content. For the anode flow rates of 0.25 slpm and a total flow passage volume of 3.15 cm$^3$, the time scale for this advective transport is 0.76 s, which is close to the order of the anode outlet water vapor dip.

Although not believed to be important for our experiments, other two phase water transport phenomena could be important at other operating conditions.

<table>
<thead>
<tr>
<th>Case no.</th>
<th>Steady-state case</th>
<th>$t = 0–20$ s</th>
<th>$t = 20–50$ s</th>
<th>$t = 50–70$ s</th>
<th>$t = 70–90$ s</th>
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</thead>
<tbody>
<tr>
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<td>E</td>
<td>0</td>
<td>100</td>
<td>150</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>E</td>
<td>0</td>
<td>150</td>
<td>200</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>E</td>
<td>0</td>
<td>200</td>
<td>250</td>
<td>0</td>
</tr>
<tr>
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<td>250</td>
<td>300</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>C</td>
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<tr>
<td>6</td>
<td>C</td>
<td>0</td>
<td>200</td>
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<td>0</td>
</tr>
</tbody>
</table>

Figure 9. (Color online) Current density, voltage, and partial pressure of water at anode and cathode (a) inlets and (b) outlets. All measurement conditions correspond to case C, described in Table II. The different numbered dynamic load cycles for each plot are described in Table III.

Figure 10. (Color online) Measured water partial pressures at (a) anode and (b) cathode outlets with varying load cycles, case E. The dotted line in (a) shows a decreasing trend in the local anode partial pressure minimum with increasing current density step size. The solid line shows the partial pressure baseline at OCV.
6. Liquid water removal from the GDL. In cases where significant liquid water is present on the GDL surface, transport through the GDL can be restricted. Liquid water transport has longer time scales than the gas phase due to the additional process of separating the liquid droplets from the GDL surface. Temperature equilibration. Meng numerically showed the importance of temperature distribution inside the membrane. The temperature variations are closely connected to liquid water saturation. The two-phase interfaces within the GDL increase the time scales for reaching steady state to a great extent. In the presented cases, humidity levels were low such that liquid water presence was infrequently observed.

This comparison of time scales suggests that the time required for the anode outlet partial pressure dip to reach a minimum is due to two competing processes: (i) electro-osmotic drag moves water toward the cathode within the membrane and increases the rate of water absorption at the anode. As the time for advection increases, the gases reaching the sensor have interacted with the drier membrane for a longer period and thus the outlet concentration decreases at a rate related to the advective time scale of about 3/4 s. (ii) Water production due to the electrochemical reaction at the cathode provides for increased back-diffusion that begins to affect the anode on the order of 2 s (the back-diffusion time scale) but takes about 20 s to equilibrate limited by the rate of water production. The minima of the dip in outlet water partial pressure are thus a superposition of these two opposite trends in water flux at the anode.

Another study was completed to assess the significance of the operating inlet humidity conditions at the anode. The anode outlet concentration was normalized with the steady-state concentration at OCV for dynamic loading cases 1 and 5, as shown in Fig. 11. The magnitude of the relative dip in anode outlet water partial pressure was greater for the drier inlet anode condition C (case 5) than for condition E (case 1). For drier gas flows, a relatively larger fraction of the provided humidity is required to temporarily hydrate the membrane during the transient cycle, and the overall performance is poorer for the drier anode inlet. The increased amount of the voltage undershoot for the drier case C as compared to case E is consistent with this observation.

Conclusions

The use of a robust, accurate, and fast in situ sensor is demonstrated for detection of water vapor partial pressure and temperature simultaneously at the anode and cathode channels of a PEM fuel cell by TDLAS utilizing WM. The use of the ratio of the second and first harmonics (2f/1f) of the spectroscopic absorption profile by the aid of a software lock-in amplifier eliminated the need for measuring a background signal in the absence of absorbing gases. A detailed curve fit analysis by a Levenberg–Marquardt algorithm resulted in errors less than ±2.5% in concentrations and ±5 °C in temperature. The measurement technique was shown to be capable of accurately measuring the water vapor partial pressure and channel gas temperature under steady and transient operating conditions. The steady-state and dynamic operating conditions indicate that anode dry-out, water uptake via chemical reactions, and gas advection play major roles in the dynamics of fuel cell performance to changes in load. Transient dips in anode outlet water concentration were observed, which reflect the unsteady drying of the membrane on the anode side via increased electro-osmotic drag following a step change in external load and the time necessary to rehydrate the membrane. This diagnostic tool allows more detailed characterization of localized PEM fuel cell operation and dynamics.

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References


Figure 11. (Color online) Comparison of water partial pressure dynamics at the anode outlet for cases C and E, as described in Table II.