

In-Situ Temperature Measurement on Cathode GDL in a PEMFC Using an Optical Fiber Temperature Sensor

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Thermal management has been known to play a key role in all aspects of proton exchange membrane fuel cell (PEMFC) performance including transport of gaseous and liquid species. However, it remains a difficult topic to study due to a lack of experimental techniques as they are limited by the PEMFC internal environment and geometry. In this work a non-invasive optical temperature sensor, based on the principles of phosphor thermometry, is presented to measure the in situ temperature on the surface of a gas diffusion layer (GDL) in a PEMFC. Unlike most common experimental temperature measurement methods, the sensor was shown to have no detectable influence on PEMFC performance or local mass transport. The sensor was found to have a relatively high degree of accuracy with a mean temperature difference of 0.110°C with a high accuracy RTD and response time of 0.5 seconds. Temperature data from an experimental fuel cell is presented showing the utility of the sensor during static and transient operation. Results also suggest a strong coupling between local temperature and liquid water saturation.

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Temperature and temperature distribution affect nearly all chemical kinetics and mass transport mechanism which takes place in a Proton Exchange Membrane Fuel Cell (PEMFC). Not only are the oxidation and reduction reaction rates at the anode and cathode dependent upon local temperature, but properties such as membrane conductivity along with gas and water diffusivity are highly dependent upon temperature as well. Furthermore, over recent years the influence of thermally driven mass transport mechanisms on PEMFC performance has become evident. Thermo-osmosis and Phase Change Induced (PCI) transport have been shown to not only be evident, but can also greatly influence PEMFC performance and behavior with regards to liquid water transport.¹⁻⁴ While these thermally coupled mass transport mechanisms have been shown to be prominent in PEMFCs they are difficult to study experimentally due to limited experimental methods of measuring temperature and water content. Currently, numerical models are most commonly used to study such phenomena. However validating these models is often difficult due to a lack of experimental data.

One of the, if not the most common method used for studying in-situ temperature and temperature distribution in PEMFCs involve the use of thermoelectric sensors, such as thermocouples or Resistive Temperature Devices (RTDs), which are embedded in between adjacent fuel cell components. Due to the comparable geometry of fuel cell components and the sensors themselves these methods often, and almost always, interfere with the mechanical structure and properties of the cell components and interfaces thereby affecting the mechanisms which are being studied. Thermoelectric sensors also must be electrically insulated in a fuel cell environment which often requires the sensor to be, at least somewhat, thermally insulated as well reducing effective response time.

Lee et al. performed a study with a PEMFC by embedding microsized thermocouples in different layers of a PEMFC in order to study through-plane temperature distribution.⁵ However, the cell needed to be significantly modified by containing two layers of membrane material and two gas diffusion layers on the anode and cathode side of the cell. The diameter of the thermocouple beads also had comparable geometry to the thickness of the membrane and fuel cell components which resulted in a changed and abnormal performance of the cell.

Work performed by David et al.⁶ involved embedding several Bragg optical fiber sensors in a PEMFC to measure temperature along the in-plane direction of the cell. While the sensors did not need to be insulated and didn't require modification to the fuel cell GDL or catalyst layers, they required significant modification to the flow channel plates of the PEMFC and only had the capability of measuring an average temperature across the active part of the fiber sensor. It should also be noted that these Bragg fiber sensors had the added feature of being able to measure local humidity in the cell as well, a key feature for experimentally establishing relationships between temperature distribution and water mass transport. However, these humidity sensors were shown to have a relatively long response time, possibly significantly longer than the transient response time of internal temperature.

To overcome the shortcomings of many previous sensor designs an optical fiber temperature sensor based on the principles of phosphor thermometry was developed by McIntyre et al.^{7,8} The work involved the use of fiber optic probes which were embedded laterally in the flow channels of PEMFC. While these optical sensors are electrically nonconductive and did provide accurate temperature readings there was no information about the invasiveness of these sensors or how they might disrupt the fuel cells performance once installed.

The sensor design presented in this work is based on the principles of phosphor thermometry as well which employs the use of thermally sensitive inorganic compounds with phosphoresce when exposed to light. Previous work using this method, while relatively accurate, greatly affected fuel cell performance and behavior, especially water transport with regards to flooding.^{9,10} The design presented in this paper overcomes these issues and is shown to provide negligible or no disruption of fuel cell performance and is believed to not affect local mass transport.

Methodology

Phosphor thermometry is a well-established method that possesses several qualities which make it an ideal choice for temperature measurement in PEMFCs. The sensor design is centered on the concept of measuring the temperature of a phosphor material in physical contact, and therefore in thermal equilibrium, with the components or materials to be measured. Phosphors are inorganic compounds which typically are doped with transition metals or rare earth compounds and have a white or light hue color. They possess the qualities of electromagnetic immunity, are electrically non-conductive, and are highly chemically inert.^{11,12}

The specific method of temperature measurement used for this work is the "lifetime-decay" method of phosphor thermometry. The lifetime-decay method is based on the temperature dependent phosphorescent decay mechanism that phosphors exhibit. The method is performed by exciting the phosphor material with an external light source, then observing the phosphorescence of the phosphor material when the excitation source is removed. When the excitation source

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is reduced or removed, light of a greater wavelength of the excitation source is emitted at a decaying rate that is dependent upon the phosphors temperature. By measuring this rate of decay of emitted light, the temperature of the phosphor, and therefore the component in thermal equilibrium with the phosphor, can be measured. The sensor design used in this work involves exciting the phosphor with a periodic excitation light source at a high enough frequency such that the light emission from the phosphor takes the form of a semi-sinusoidal waveform. When the excitation and emission light signals are compared with respect to time, the phosphor emission will have a time lag or change in phase from the excitation source. The magnitude of this phase lag is proportional to the temperature of the phosphor at a fixed frequency. The dc-decoupled response signal from the phosphor, v_f , can be described mathematically as

$$\boldsymbol{v}_f = \boldsymbol{v}_a \sin(\omega t - \boldsymbol{\phi})$$
[1]

where ϕ , is the phase lag, ω , is the radian frequency, v_a , is the amplitude of phosphorescence response, and t, is the elapsed time. The pse lag or the difference in phase between the excitation modulated signal and the response signal of the phosphor is dependent upon the frequency of the modulated signal and is referred to as the phosphorescence lifetime, τ . The phosphorescence lifeme of the phosphor, that is the rate at which the emitted light decays, is temperature dependent and can be found by using Equation 2 by measuring the phase lag and frequency of the excitation source.^{13,14}

$$\tau = \frac{tan\phi}{\omega}$$
[2]

This concept is illustrated graphically in Figure 1, showing the modulated excitation and phosphor emission waveforms captured using an oscilloscope.

The relationship between temperature and the phosphorescence lifetime of the phosphor is most often non-linear and is determined experimentally. Furthermore, this relationship is also dependent upon dopant concentration and has also been shown to be dependent upon the form of the phosphor material as well. Therefore, calibration must be conducted in each application the phosphor material is used.¹⁵

Design and Construction

Sensor design.- The design of the optical sensor developed in this work is specifically designed to operate within the flow channels of a PEMFC by remotely measuring the temperature on the surface of the gas diffusion layer. This is accomplished by using Cr doped Y₃Al₅O₁₂ (Cr:YAG) as the phosphor in a fine powdered form that

Phosphor

Emission

Excitation

Signal

1

Non-Dimensional Amplitude

0

0.000

is directly applied to the surface of the cathode GDL. To provide an optical path to the phosphor a bifurcated optical fiber design is used.

For the optical pathway from the excitation source to the phosphor material, a 500 μ m diameter plastic optical fiber is used. The excitation source consists of a high power 405 nm LED that is coupled to the optical fiber using an aspheric lens. To provide an optical path from the phosphor to the photodetector a 1000 µm diameter optical fiber is used which interfaces with the photodetector using an aspheric lens and 697 nm band-pass optical filter to block light from the excitation source. The photodetector is an avalanche photodiode operated in reverse bias mode using a low noise 90 V DC power supply. The photodiode is interfaced to a transimpedence amplifier with a high feedback resistance to provide a usable voltage signal. The voltage signal from the transimpedence amplifier is amplified using a high gain instrument amplifier to raise the signal voltage to a usable amplitude. The signal is then filtered using an 8th order Butterworth filter.

In order for this method to achieve practical accuracy, the output signal from the photodetector must have a sufficient signal to noise ratio which is highly dependent upon the phosphor loading or the amount of phosphor that is in view of the optical fiber. A phosphor loading of approximately 10 mg cm⁻² in direct view of the optical fiber was experimentally determined to be sufficient for maintaining temperature measurement accuracy and repeatability.

The phase lag between the excitation source and phosphor emission was measured using a Stanford Research Systems SR830 Lock-in Amplifier (also known as a Phase-Sensitive Detector). The SR830 allows for a phase measurement resolution of 0.01° and a frequency resolution of 0.01 Hz and can measure the phase angle between the excitation and emission source with relatively high accuracy. A microcontroller is used to generate the modulation frequency of the system and provide the reference signal for the lock-in amplifier. The entire system is controlled using a second microcontroller which also communicates with a PC via USB for interfacing with the system and for data acquisition. A simplified block diagram of the entire system and its related components is illustrated in Figure 2.

The temperature is determined by measuring the phase lag of the phosphorescent response, ϕ , from the lock-in amplifier and the freguency at which the excitation source is modulated, ω , which is determined by the user. Using Equation 2, the phosphorescence lifetime, τ , is calculated from these two values. To determine temperature, an experimentally determined calibration curve relating the phosphorescence lifetime and temperature is used.

Sensor implementation .- To demonstrate the utility of this method, a single sensor was implemented in the cathode gas flow channels of a laboratory grade 5 cm² PEMFC. The fuel cell flow plate was a single serpentine design with channels measuring 1 mm in width and 1 mm in height with 1 mm wide lands. The Cr:YAG phosphor



0.010

0.005

φ

0.015



Figure 2. System diagram of optical temperature sensor system and related components.

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0.020



Figure 3. Placement of optical fibers installed in flow channel plate (Left) and Cr:YAG phosphor material applied to the outer surface of the cathode GDL (Right).

was applied to the surface of the GDL in the form of a fine powder by simply applying a small amount to the surface and pressing the GDL at 3 MPa at room temperature. Excess material was rinsed off with deionized water. The amount of phosphor material applied to the GDL was approximately 0.5 mg covering a \sim 2 mm diameter area giving a phosphor loading of approximately 15.9 mg cm⁻².

The optical fibers, serving as the light guides, were embedded in the flow channel plate in immediate proximity to each other perpendicular to the surface of the gas flow channel and were placed in such a manner that they did not interfere or disrupt the flow of gas and liquid water moving through the channel. Images of the optical fiber implementation and phosphor coated GDL are shown in Figure 3.

Experimental Methods

Calibration.- The sensor was calibrated by comparing the effective lifetime decay rate of the phosphor over a range of operating temperatures of a high accuracy RTD in close proximity. The RTD used as a temperature standard was a YSI 4600 Precision RTD Thermometer, with an accuracy of $\pm 0.12^{\circ}$ C. The RTD probe was placed underneath a GDL with the applied phosphor in a Maccor MTC-010 temperature controlled chamber. A graphite plate which contained the optical fibers was placed over the phosphor coated section of the GDL to simulate the actual placement in the experimental fuel cell. The entire assembly was placed in the thermal chamber where the temperature was ramped bidirectionally in increments of 5°C. Each temperature increment had a dwell time of 20 minutes to allow the assembly to reach a uniform temperature, after which temperature data was recorded. The phosphorescence lifetime of the phosphor and the temperature of the RTD were then plotted and compared to determine a calibration curve. The results of this testing is shown in Figure 4.

Using the data shown in Figure 4, a least-squares best fit second order polynomial was obtained with a RMSE value of 0.9999. It should be noted that the time constant value, τ , does not represent the actual phosphorescence lifetime of the phosphor but is rather an



Figure 4. Calibration curve for optical temperature sensor.



Figure 5. Comparison of measured optical sensor to RTD sensor used as temperature standard.

arbitrary value determined by the system. This approach was used to simplify the measurement process due to several factors including analog to digital conversion between the lock-in amplifier and the microcontroller along with shifting of the phase angle due to filtering.

The temperature of the RTD and the reported temperature of the sensor were compared and plotted in Figure 5. The difference between the optical sensor and RTD throughout the calibrated temperature range was found to be 0.110° C on average with a standard deviation of 0.112° C.

Experimental test cell.— Experimental testing was performed using a membrane electrode assembly that consisted of a NRE-211 Nafion membrane with platinum loadings of 0.5 mg Pt/cm² on the anode and cathode catalyst layers. The GDL material used was Avcarb GDS2120 with microporous layer (MPL) on both sides of the cell. Both flow channel plates were a single serpentine design with 1×1 mm channels and 1 mm lands constructed from POCO AXF-5Q graphite. Both anode and cathode sides of the cell have water flow plates for maintaining constant temperature on each side of the cell. The water flowing through the cooling plates was controlled using two Thermo Scientific AC-150 immersion circulators.

To determine the invasiveness of the temperature sensor, the polarization curve of the fuel cell was determined before and after the cell was modified with the optical sensor. The resulting polarization curves are shown in Figure 6. As can be seen from the polarization curves in Figure 6, the performance of the fuel cell with and without the phosphor material and sensor are nearly identical with no appreciable change in performance. This would suggest that the phosphor



Figure 6. Polarization curve of the experimental fuel cell showing the effects of cell behavior with and without sensor and phosphor material.



Figure 7. Average steady state in situ temperature of experimental PEMFC under different current loadings.

material added to the GDL has little to no influence on local transport phenomenon or the behavior of the fuel cell in general.

Results and Discussion

Experimental testing was performed to demonstrate the performance of the optical sensor under both steady state and transient conditions. Initial steady state testing was performed by measuring temperature over time as the fuel cell output current was gradually increased. For this testing the cell was operated at current densities from 0 to 1.2 A/cm^2 in increments of 0.25 A/cm^2 . The cell was operated at each increment for a period of two minutes to allow for thermal equilibrium to be reached. The temperature sensor recorded temperature in 5 second intervals over the entire period of the test. Both the temperature and the voltage were averaged over 1 minute periods after the cell reached a steady state and plotted with respect to current density.

As can be seen from Figure 7, the temperature profile on the cathode side of the cell increases with current density as would be expected. The temperature profile is complimentary to the polarization curve indicating that as the reaction rate and losses in the fuel cell increase, the rate of heat generation with respect to current density increases as well. It can be seen that at a current density of 0.4 A/cm^2 the cell experienced a temperature rise of approximately 0.8°C compared to operating at open circuit voltage. This temperature rise is of similar magnitude to those reported by Lee et al.⁵ and David et al.⁶ under similar operating conditions and sensor locations.

Further testing was performed to determine the applicability of the sensor to transient analysis. For this testing the experimental cell was operated at open circuit voltage for a period of approximately 10 minutes to allow the cell to reach equilibrium with the sensor recording temperature at 1 second intervals. After this 10 minute period a current load of 1 A/cm² was placed on the cell and the temperature observed for a period of 7 minutes followed by a brief 2 minutes cool-down period. The results of this testing are shown in Figure 8. The measured temperature follows the cell current loading very closely demonstrating the small amount of thermal capacitance that is present to the internal PEMFC components relative to the heat generation and removal rates. It can also be seen that the optical temperature sensor provides an adequate response time and is capable of capturing rapid transient temperature changes in the fuel cell. It should be noted that while the measurement interval for this test was 1 second, the sensor is capable of recording temperature every 0.5 seconds.

Further transient testing was performed by recording temperature data at 5 second intervals for the cell during shutdown. During this test, the cell was operated at 1 A/cm^2 until a steady temperature was reached, and then turned off (no load) with all heaters and humidifiers



Figure 8. Transient in situ temperature of experimental PEMFC with a single pulsed current load.

deactivated. Anode and cathode gases continued to flow in order to detect any influence of water removal or condensation. The results of this test are shown in Figure 9. The recorded internal temperature of the cell shows a steady exponential decrease in temperature over time up to approximately 1700 seconds. However, after this time period large random spikes in temperature were observed once the cell began to cool down below 45°C. This is assumed to be due to liquid water formation or water droplets moving in between the optical fiber and phosphor as the cell cooled. It should be noted that while liquid water between or on the optical fiber and phosphor may cause the response signal, v_f , to become attenuated, the magnitude of this attenuation is not large enough to have any significant impact on sensor accuracy or operation.

To better determine if these artifacts in temperature were the result of liquid water, the cell was operated under a high humidity of 95% RH and low humidity of 25% RH at a current density of 0.5 A/cm² in order to create conditions where liquid water would and would not be present. The temperature profile from the sensor was then monitored for such artifacts expecting little to no activity at lower humidity and higher activity at high humidity. Samples of the collected measurements are shown in Figure 10. The transient temperatures from high and low humidity operation clearly show differing thermal behavior inside of the fuel cell. Operation at a relative humidity 25% yields a relatively steady and constant temperature over time. However, operation at a relative humidity of 95% shows a thermal behavior that is very sporadic with large fluctuations in temperature which suggest liquid water local to the sensor for causing large abrupt changes in temperature. It should be noted that the temperature spikes or artifacts



Figure 9. Transient in situ temperature of experimental PEMFC during cell shutdown.



Figure 10. Sample temperature data for experimental fuel cell operation at high and low humidities.

always result in an increase in temperature and never a decrease. The reason for this behavior is still being investigated but is believed to be due to the water droplet inhibiting convective heat removal from the GDL at the location of the sensor or possibly the liquid water in the fuel cell being warmer than surrounding components due to latent heat from condensation.

Conclusions

A novel method of measuring in situ temperatures on the surface of GDLs in a PEM fuel cell has been developed. The method is based on the life-time-decay method of phosphor thermometry which exploits the thermo-luminescent properties of phosphors which have ideal characteristics for diagnostic testing and study in PEM fuel cells. The sensor developed in this work has been shown to provide useful information about the internal thermal characteristics that are present in PEM fuel cells with reasonable accuracy and response time with a mean temperature difference of 0.11°C from a high accuracy RTD and resolution up to 0.5 seconds. The sensor has also been shown to be non-invasive by displaying no measurable influence on internal transport mechanisms or disrupted performance of the cell.

Through testing for steady and transient conditions, along with high and low humidity conditions, it is suggested that liquid water formation has a notable impact on local temperature. Large and rapid changes in measured temperature are assumed to be due to liquid water formation and transport in the flow channels of the fuel cell. This further suggests that thermally dependent transport mechanisms may have a significant influence on liquid water transport in the GDL and flow channel portions of PEMFC's. These ideas will be further explored in future work.

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