In-Situ, Real Time Gas Composition Measurements for SOFC's using Laser Spectroscopy

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Abstract

The use of standard gas composition measurement techniques, such as gas chromatography, in large scale solid oxide fuel cells (SOFC's) operating at high temperatures can be both complex and time consuming. One of the main constraints is the necessity to condense out the water vapour present in the gas streams prior to measurement in the Gas Chromatograph (GC). True gas compositions can only be extracted through back-calculation, with each measurement taking in the order of minutes, and a number of measurement points needed to make the final measurement.

For system status monitoring such a time delay between condition changes and measurement is a serious disadvantage. One of the main concerns for systems running on natural gas is the risk of methane slippage through the internal reformer, which increases the risk of carbon formation on the SOFC anode, invariably leading to irreversible loss of performance. It is therefore highly advantageous to measure gas stream compositions within the SOFC system in real time, enabling a rapid response to composition deviation outside of acceptable limits. Gas chromatography can never be made to work as a real-time system status monitoring product solution.

A suitable, *in-situ*, solution for measurement is tuneable diode laser spectroscopy, TDLS. Using this technique it is possible to measure both the gas concentration and system pressure simultaneously for a number of different species, without condensing out the water vapour: reducing analysis time considerably and reducing errors associated with back calculation.

In this paper, data taken on an operational fuel cell system is presented for methane, and a comparison with results obtained using a GC is made.

1. Introduction

The advancement of laser spectroscopy for gas monitoring has been significant over the past twenty years, with the introduction of new laser and detector technology and techniques such as tuneable diode laser spectroscopy (TDLS). This work has been driven by a number of factors, including the increase in environmental legislative requirements and the need for faster, more accurate measurements [1].

The deficiencies of standard gas analysis techniques, such as gas chromatography are highlighted in high power output solid oxide fuel cells (SOFC's), where real-time gas composition measurements are highly advantageous for system status monitoring, especially in the detection of methane slippage. The water vapour present in an SOFC prevents immediate measurement using gas chromatography, and the evaporation of the water vapour implies that the true gas composition can only be obtained through back-calculation. The non-invasive nature of TDLS will allow measurements to be taken directly at the source, allowing real-time, true composition measurements of a number of species, including the water vapour.

We present a comparison of results taken on an operating fuel cell using both a TDLS system and a GC. It will be shown that the TDLS results are as accurate as the GC, and furthermore provide valuable information that cannot be obtained using standard gas composition measurements. This data has been used to successfully automate composition measurements on an operating SOFC.

2. Gas Analysis Theory

It is assumed that in a gas of concentration, c, the absorption of light of frequency, ν, follows the Beer-Lambert law

$$I_{out} = I_{in} e^{-\alpha_0(\nu)cl} \tag{1}$$

where I_{out} is the final laser intensity, I_{in} is the initial laser intensity, *l* is the length of the gas cell and $\alpha_0(\nu)$ is the absorption co-efficient, which is defined as the product of the transitional line-strength, *S(T)* and the line-shape, $\varphi(\nu)$

$$\alpha_0(\nu) = S(T)\varphi(\nu) \tag{2}$$

where $\varphi(\nu)$ has been normalised to 1. The line-shape is dependent on a number of broadening effects, with the two most important being Doppler broadening and collisional broadening, which are described by Gaussian and Lorentzian line-shapes respectively. This results in an overall line-shape that is a convolution of the Gaussian and the Lorentzian, described as a Voigt profile [2].

$$V(X,Y) = \frac{Y}{\pi} \int_{-\infty}^{\infty} dz \frac{e^{-z^2}}{Y^2 + (X-z)^2} \tag{3}$$

This work uses an approximation method to describe the Voigt, which has been derived by Martin and Puerta [3], in which four generalised Lorentzians are used in two variables.

The Gaussian full-width half-maximum (FWHM), used to describe Doppler broadening is given as

$$\Gamma_G = 7.1625 \times 10^{-7} \left(\frac{T}{M} \right)^{0.5} \tag{7}$$

where T (K) is the gas temperature and M is the molecular mass. The Lorentzian FWHM, used to describe collisional broadening term is given as

$$\Gamma_C = 2P_{tot} \sum_n \chi_n \gamma_L^n(T_0) \left(\frac{T_0}{T} \right)^m \tag{8}$$

where χ is the molar fraction of each species, n, $\gamma_L^n(T_0)$ is the collisional term for each species at a reference temperature, T_0 and m is the temperature dependence exponent for each species. The total collisional broadening effect is therefore dependent on the concentration of each species and also the temperature of the gas.

The line-strength is described in terms of a line-strength at a reference temperature, $S(T_0)$ by

$$S(T) = S(T_0) \left[\frac{Q(T_0)}{Q(T)} \right] \left[\frac{T_0}{T} \right] \exp \left[-\frac{hcE''}{k} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \left[1 - \exp \left(\frac{-hc\nu_0}{kT} \right) \right] \left[1 - \exp \left(\frac{hc\nu_0}{kT_0} \right) \right]^{-1} \tag{10}$$

where $Q(T)$ and $Q(T_0)$ are the partition functions at the gas temperature and the reference temperature respectively, h is Plank's constant, c is the speed of light, E'' is the lower state energy, k is Boltzmann's constant and ν_0 is the transition frequency.

A number of the necessary parameters are given in the HITRAN2008 database [4], at a reference temperature of 296K. However, the database does not provide collisional-broadening parameters for any gases other than air and the measurement gas, and is also known to be incomplete for high temperatures [5].

3. In-Line Gas Analyser

The in-line gas analysis cell is shown in figure 1. One end of the cell contains a sapphire ball lens of diameter 6.35mm and the other contains a 300mm focal length gradient index lens. Both ends are sealed with 353ND high temperature optical adhesive. An automated selection valve is used to take gas samples from numerous bleed-pipes located around the fuel cell. Gas from the valve is reduced in pressure to ~2bar and the water is condensed away prior to flowing through the gas cell and finally into a GC. The gas cell was placed as close to the GC as possible allowing an accurate comparison between the two techniques.
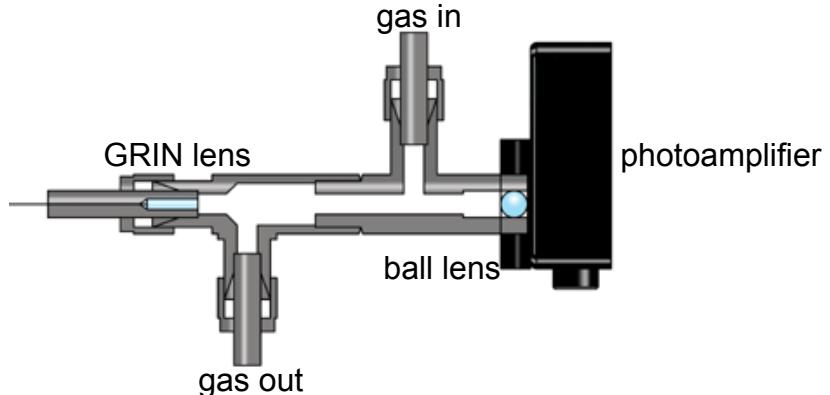
Figure 1: In-line gas analyser. Light enters through the GRIN lens, and is focused onto the photodiode using a sapphire ball lens. Gas passes through the cell via the inlet and outlet Swagelok piping.

A butterfly packaged distributed feedback laser diode, operating at 1650.8nm, is used for the detection of methane. The laser can be wavelength tuned using two methods; variation of the diode temperature and variation of the applied diode current. Usually, the centre wavelength of the diode is temperature tuned close to the spectral line of interest, and then repeatedly scanned over the line using current tuning. In this work the laser was controlled using an Optosci laser control unit.

Light from the gas cell is focused onto a Thorlabs PDA10CS-EC switchable gain InGaAs photoamplifier (PA) using the sapphire ball lens. The signal from the PA is fed into a Pico Technology 4424 digital oscilloscope, with a 20Ms/s sampling rate and a 12bit ADC resolution. A custom made PTFE threaded adaptor was used to connect the PA to the gas cell, in order to reduce thermal losses through the PA casing.

A thermocouple is located inside the gas cell, allowing the temperature to be logged using a Pico Technology TC-08 temperature logger. Remote access and control of the oscilloscope, the temperature logger and the laser driver is achieved using a laptop via an Ethernet connection. A Lantronix Ubox 2100 is used to adapt the USB protocol of all the devices for transmission over an Ethernet network.

Three sample lines from the SOFC were sampled; the reformer inlet, reformer outlet and the stack outlet. As the methane concentration from the stack outlet is negligible the stack outlet signal is used to normalise the reformer inlet and outlet methane signals.

The obtained spectra are wavelength referenced using a fibre ring resonator with a free-spectral range of 0.425GHz [6], and compared to a theoretical model, derived as described in section 2, using a golden section search (GSS) fitting procedure for pressure and the concentration.

4. Results

Each of the sample lines contains a mixture of gas species at various concentration levels, the main being nitrogen, methane, water, hydrogen, carbon dioxide and carbon monoxide. Equation 8 can be expanded as

$$\Gamma_C = 2P_{tot}\left[\left(\chi_{CH_4}\gamma_{CH_4}(296)\left(\frac{T_0}{T}\right)^{m_{CH_4}}\right)+\left(\chi_{bulk}\gamma_{bulk}(296)\left(\frac{T_0}{T}\right)^{m_{bulk}}\right)\right] \quad (11)$$

where gases other than the measured gas are combined into *bulk* parameters. The bulk broadening parameter was calculated using a known methane concentration measurement from the GC (11.8%), and a GSS fitting process on an experimental signal. This provided a broadening parameter which was 1.0245 times larger than the nitrogen-broadening parameter. It was not necessary to calculate the temperature dependence as it is only a significant variable if there are large temperature fluctuations in the gas cell.

A response time for the purging of the condenser unit and pipework from the multi-position selection valve to the GC was taken in order to ensure concentration calculations are accurate. This measurement is not possible with the GC as the purge time is much shorter than the GC calculation time. The TDLS system was able to make a concentration measurement every 20s, for a total of 500s, as the sample line was switched from the stack outlet to the reformer inlet. Figure 2 shows the increase in methane concentration as a function of time, fitted with a step-response of the form

$$C(t) = C_f\left(1 - e^{t/\tau}\right) \quad (12)$$

where *C(t)* is the concentration at time *t*, C_f is the final concentration and τ is the time constant, calculated to be 50s. For an absolute concentration measurement error to be less than 1% takes 250s, which is a value 5 times larger than the time-constant τ. This implies there should be at least 250s delay before a new measurement is taken once the selection valve has been operated.
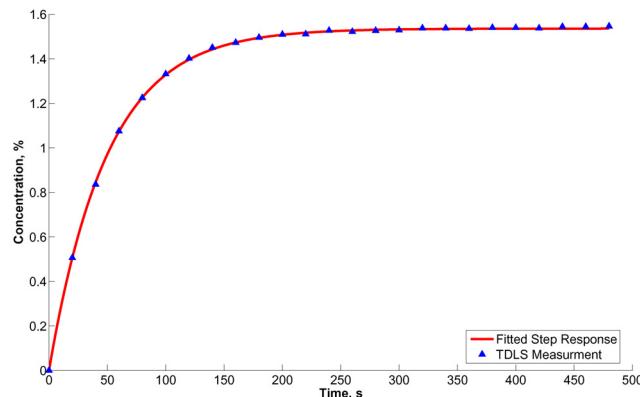

Figure 2: Time evolution of the methane concentration from one of the bleed lines after the selection valve has been changed.

Figure 3 shows concentration and pressure measurements at the reformer inlet when the stack is at half-load (a) and full load (b). The absolute error in the concentration was of the order of 1%, as compared with the GC, for both measurements. As pressure is measured at the same time as concentration, it is also noted that there is an increase in pressure in the SOFC as it is loaded with methane, indicated in the broadening of the absorption profile in figure 3(b).
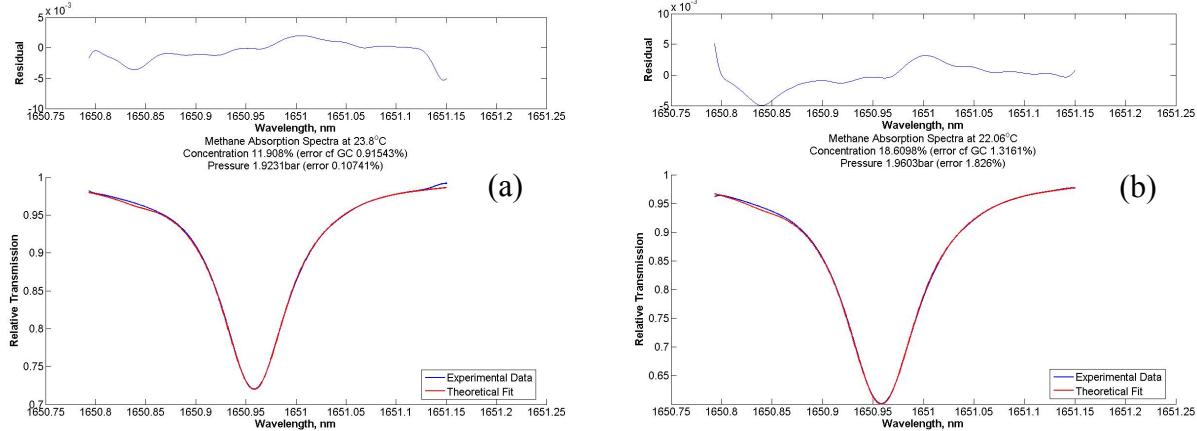

Figure 3: Methane spectra providing concentration and pressure measurements for the reformer inlet. Comparisons with the GC measurements show errors in the concentration and pressure of less than1.5%.

One of the important measurements is the reformer outlet, as discussed previously, in order to ascertain if there is methane slippage into the stack. Figure 4 shows a measurement of the reformer outlet when the stack was fully loaded. Although there is a large overall percentage error in the concentration measurement it is within the quoted errors for the GC. A point to note is that it may also be necessary to calculate a separate bulk broadening term for the reformer outlet, as the same value was used as for the reformer inlet.
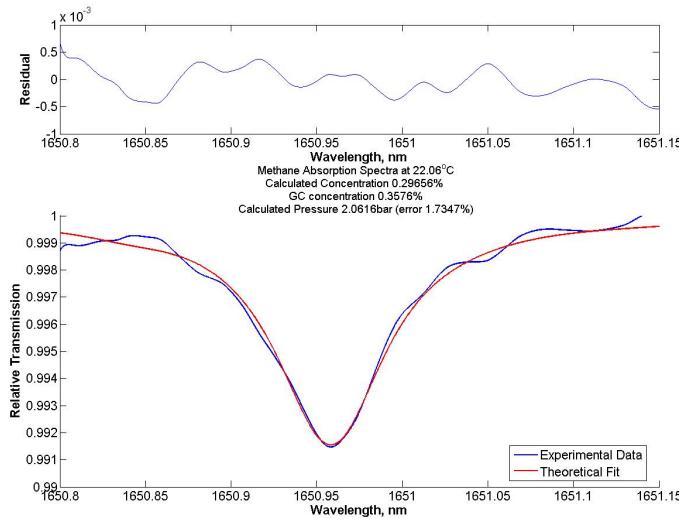

Figure 4: TDLS concentration and pressure measurement for the reformer outlet, and a comparison with the GC

4. Conclusion

TDLS has been shown to be as accurate as a GC for taking methane concentration measurements on a working, large-scale, SOFC. Furthermore, due to the faster response of the TDLS system it has been possible to accurately calculate the total purge time of gases from the selection valve to the gas analysis rig. This has provided useful information that has not previously been available and given concentration measurements down to 0.1%. Furthermore, this system has proven that it can be used as a fail-safe mechanism for methane slippage into the main stack with a response time of less than 2 minutes, with the limiting factor being the location of the gas cell, and not the data acquisition time.

In order to increase accuracy, and carry out measurements in a wet environment, the gas cell needs to be located in a high temperature zone. As the cell operates at temperatures up to 200°C, and pressure of 2.5bar, it is still necessary to reduce the gas pressure, and operate remotely from the SOFC stack itself. If these tests prove successful however, it will be possible to locate a TDLS system directly in a cooler zone within the SOFC system.

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