Short communication

Tuneable diode laser gas analyser for methane measurements on a large scale solid oxide fuel cell

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ARTICLE INFO

ABSTRACT

A new in-line, real time gas analyser is described that uses tuneable diode laser spectroscopy (TDLS) for the measurement of methane in solid oxide fuel cells. The sensor has been tested on an operating solid oxide fuel cell (SOFC) in order to prove the fast response and accuracy of the technology as compared to a gas chromatograph. The advantages of using a TDLS system for process control in a large-scale, distributed power SOFC unit are described. In future work, the addition of new laser sources and wavelength modulation will allow the simultaneous measurement of methane, water vapour, carbon-dioxide and carbon-monoxide concentrations.

1. Introduction

Solid oxide fuel cells (SOFCs) are currently being developed as an alternative to large-scale, centralised power plants, due to their higher efficiency and lower pollutant levels [1]. However, the high operational temperature [2] and pressure [3] of the proposed industrial distributed power SOFC units provide a number of challenges for real-time gas composition measurements needed for process control. One such example is the monitoring of methane slippage from the steam reformer into the SOFC, which would ensure that carbonation could not occur within the SOFC causing reduced operational efficiency or even system failure [4].

Gas chromatography is currently the standard process for gas composition measurements for both process control and for fundamental research on large-scale SOFC devices. However, there are a number of disadvantages to using gas chromatographs (GC), including: the inability to operate at high temperatures and pressures; the necessity to remove the steam prior to measurement; the long time-scale for each measurement and the overall cost. In order to ensure the low temperature, low pressure, dry operational conditions are met, a selected gas sample line from the SOFC is reduced in pressure, the sample gas is cooled and the water is removed in a condenser unit. The resulting GC measurements therefore only provide analysis on the remaining gas constituents and further analysis time is necessary to back-calculate the gas concentrations in the

SOFC. Here we present a more advantageous, real-time, gas composition measurement technique, known as tuneable diode laser spectroscopy (TDLS) [5]. The low cost of near-infrared (IR) laser sources and photo-detectors, through the progression of the optical communications industry, also makes TDLS technology competitive in terms of overall cost [6]. Here we present a comparison of methane concentration measurements, taken from a number of sample lines on an operational SOFC, using a TDLS system and a GC. This work highlights the advantages of real-time operation, by showing the time evolution of methane concentration for an emergency shut-down of the SOFC using the TDLS technique, which is impossible to achieve with a GC. Prior to these results, the TDLS gas sensor is described.

2. Prototype gas-analyser

A schematic of the experimental apparatus is shown in Fig. 1. A distributed feedback laser (DFB) diode is used for the detection of methane. The laser is controlled using an Optosci Ltd. Integral Precision Laser Driver and Thermo Electric Cooler (TEC) Controller, allowing both current and temperature tuning of the output wavelength. Thermal wavelength tuning is used to locate and fix the wavelength close to a suitable absorption feature of methane, in this case the R(4) ro-vibrational transition at $\sim$1650.96 nm. A 5 Hz current ramp is used to scan the laser wavelength across the entire absorption feature. Light from the laser is coupled into single-mode (SM) optical fibre and then passes through a 50:50 splitter. The first arm of the splitter sends $\sim$50% of the light to the in-line gas measurement cell via a length of SM fibre, and the second arm

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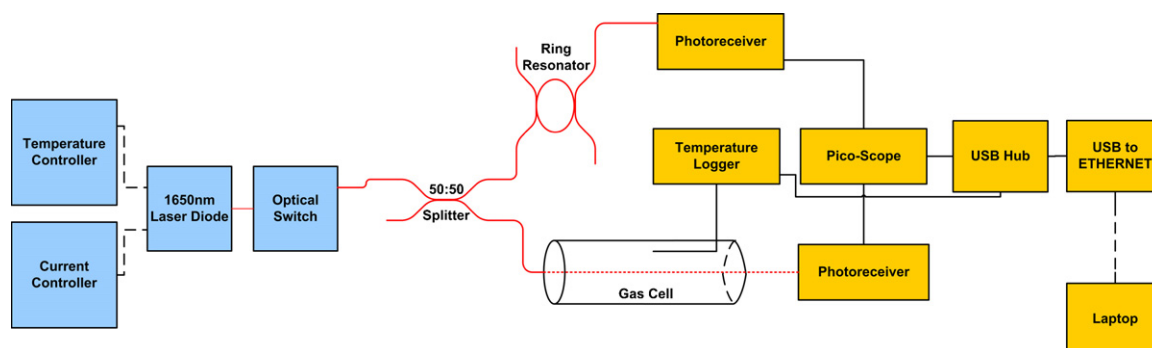*E-mail address:* michael.lengden@eee.strath.ac.uk (M. Lengden).

Fig. 1. Experimental schematic.

sends ~50% of the light to a fibre ring resonator for wavelength referencing [7].

The in-line gas cell, shown in Fig. 2, is 63.5 mm in length and is constructed from 316 stainless steel Swagelok components suitable for 1/4 in. pipework. Light enters the gas cell via a fibre coupled collimation lens, resulting in a collimated beam of light passing through the cell and interacting with the gas. A 3.175 mm radius sapphire ball lens, mounted on to the opposite end of the in-line cell, is used to focus the collimated beam onto a Thorlabs PDA10CS-EC amplified, switchable gain InGaAs photodetector (PD). Both the collimator and the ball lens are sealed in place with EPO-TEK 353ND high temperature optical adhesive to make the whole cell air-tight. Gas from a selected sample line is reduced in pressure and cooled to room temperature, before flowing through the TDLS measurement cell and finally entering the GC.

The signal from the PD is fed into a Pico Technology 4424 digital oscilloscope, with a $20\,\text{Ms}\,\text{s}^{-1}$ sampling rate and a 12bit ADC resolution, which results in a methane gas absorption profile. Remote access and control of the oscilloscope and the laser driver is achieved using a laptop via an Ethernet connection.

In order to accurately measure gas concentration and pressure using the TDLS device, it is necessary to compare the experimentally obtained gas absorption profiles with theoretically derived profiles. The parameters in the theoretical model are generally taken from databases, such as the 'high-resolution transmission molecular absorption database' (HITRAN2008) [8], and are therefore known and fixed. By varying the values of concentration and pressure in the model it is possible to obtain an accurate fit to an experimental signal using a least-squares fitting routine.

3. 'On-line' methane measurements

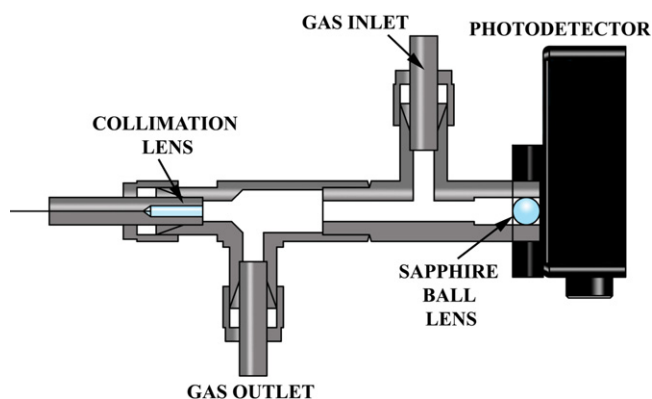Gas samples were taken from various points within a 15 kW fuel cell located at Rolls-Royce Fuel Cell Systems Ltd, and each sample flowed into a gas analysis cabinet through 1/8 in. 316 stainless steel piping. An automated multi-position valve, located inside the cabinet, was used to select one of the various sample lines containing methane concentrations ranging from 0 to 85%, for measurement by TDLS and the GC.

The pressure of the selected line was reduced from ~8 bar$_{\text{gauge}}$ to ~1 bar$_{\text{gauge}}$, measured using an analogue pressure gauge. It must be noted that during these tests the pressure was only measured for the anode ejector sample line. The gas sample then passed through a condenser unit, in order to remove any water vapour. The in-line gas analyser was positioned after the condenser unit but prior to a GC, allowing signal comparison between the two composition measurement techniques. Signals from a sample line containing 0% methane concentration were used to normalise the obtained gas absorption profiles from all other sample lines.

In order to obtain accurate concentration and pressure measurements using the TDLS gas sensor, all parameters in the model are fixed, except for concentration, and a comparison is made between theoretical profiles and experimental signals, as described in Section 2. This procedure is repeated for various incremental values of pressure and takes approximately 5–30 s, depending on the processing power of the PC. The concentration and pressure parameters in the best fit are used as the final measured values, and an example fit for an experimental absorption profile is shown in Fig. 3. This absorption profile was taken for the steam reformer outlet and gave a final concentration measurement of 0.603%, compared to value of 0.58% measured by the GC. As discussed previously, an accurate methane measurement at the output from the steam
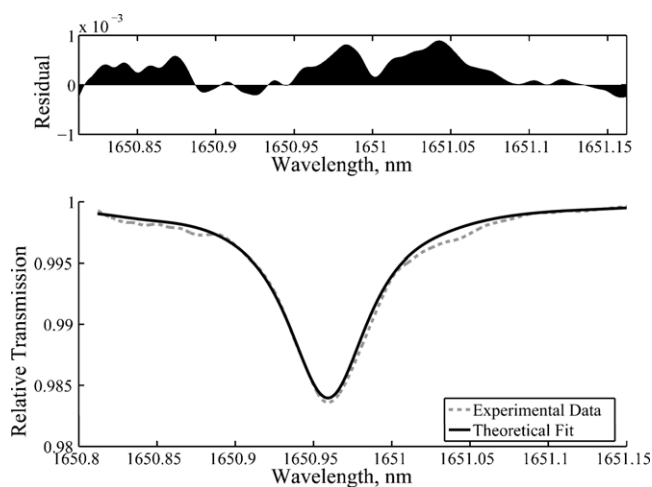

Fig. 2. In-line gas sensor, constructed from 316 Stainless Steel Swagelok fittings.

Fig. 3. Measurement of R(4) ro-vibrational transition of methane taken at the steam reformer outlet using the TDLS gas sensor, showing a comparison of the experimental signal and the theoretical absorption profile derived from the least-squares fitting procedure.

Table 1
Comparison of methane concentration measurements using TDLS and a gas chromatograph.

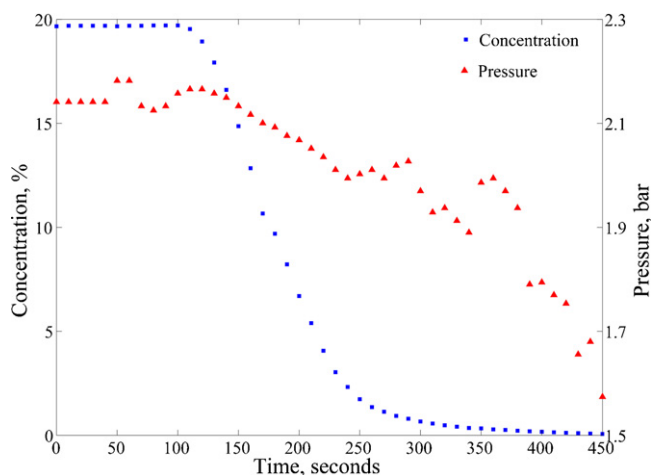| Position	P_{TDLS} (BAR_{GAUGE})	C_{TDLS} (%)	C_{GC} (%)	%Error
Anode ejector	1.97	14.93	14.9	0.2
Reformer inlet	1.79	84.90	84.5	0.47
Steam reformer exit	1.84	0.603	0.58	3.97
Stack 1	1.82	0.247	0.26	5
Stack 2	1.7	0.108	0.13	17
Stack 3	1.65	0.148	0.17	12.9
Stack 4	1.57	0.106	0.13	18
Stack 5	1.57	0.162	0.19	14.7

Fig. 4. Evolution of the methane concentration and system pressure during the emergency shut off of the SOFC. The initial increase in pressure is caused by the introduction of a hydrogen:nitrogen mixture into the system.

reformer is essential, in order to ensure methane slippage into the fuel cell does not occur, and the TDLS system measurement is shown to be as accurate as the GC. Furthermore, the overall calculation time of the TDLS gas sensor for this measurement was approximately 10 s, compared to a measurement time of up to 10 min using the GC.

Methane measurements were taken for all the sample lines using both the in-line gas sensor and the GC, to ensure the TDLS gas sensor system was operating correctly and providing accurate methane measurements for a range of concentrations, and the results are shown in Table 1. The variation between the results from the two measurement techniques are also shown in Table 1, and is seen to be significantly larger as the methane concentration decreases. However, it must be noted that the concentration error in the GC is ±0.03% absolute, for methane measurements below 5%. For example, if the measured methane concentration was 0.5%, the actual concentration value could be between 0.47% and 0.53%, which gives an overall variation of ~12%. As the absolute concentration values measured using the TDLS sensor only vary by ~0.03%

of the measured GC concentration, even at low concentrations, the TDLS system remains within the error range of the GC. Table 1 also provides values for the sample line pressure, calculated using TDLS, showing that there is a large measured pressure variation between sample lines.

Fig. 4 shows the evolution of the methane concentration and pressure of the anode ejector during an SOFC emergency shut-off. The measurements were taken at 10 s increments for a total of 450 s. For the first 2 min after the shut-off, the concentration level remains constant, however, the pressure is seen to increase. This pressure increase is due to the sudden introduction of a hydrogen:nitrogen mixture into the system to prevent anode oxidation. As the methane concentration begins to fall so does the pressure, as new conditions are established in the sample line. This proves that measurements can be made using the TDLS system to provide critical information on fuel cell performance in real-time, reducing overall operational costs.

4. Conclusion

An in-line gas sensor has been designed and used to measure methane concentrations on an operational 15 kW solid oxide fuel cell. This sensor has been shown to work accurately for methane concentration measurements down to 0.5% with measurement times of ~10 s. This data has provided new information and assisted in gas composition measurement automation at Rolls-Royce Fuel Cell Systems Ltd.

It is now important to locate the analyser on an operating SOFC system in a suitable environment to allow water and methane measurements to be carried out simultaneously using TDLS, i.e. at the upstream end of the gas sample lines. This will also eliminate the necessity for back-calculations in order to find the true gas concentrations within the fuel cell. Furthermore, the inclusion of water in the system may provide more accurate temperature measurements through the implementation of techniques such as ratio thermometry [9].

References

[1] A.S. Nesaraj, J. Sci. Ind. Res. 69 (2010) 169–176.
[2] A.B. Stambouli, E. Traversa, Renew. Sust. Energy Rev. 6 (2002) 433–455.
[3] S.E. Veyo, L.A. Shockling, J.T. Dederer, J.E. Gillett, W.L. Lundberg, J. Eng. Gas Turb. Power 124 (2002) 845–849.
[4] N.Q. Minh, J. Am. Ceram. Soc. 76 (3) (1993) 563–588.
[5] E.D. Hinkley, Appl. Phys. Lett. 16 (9) (May 1970) 351–354.
[6] P. Werle, Spectrochim. Acta Part A 54 (1998) 197–236.
[7] W. Johnstone, A.J. McGettrick, K. Duffin, A. Cheung, G. Stewart, IEEE Sens. J. 8 (2008) 1079–1088.
[8] L.S. Rothman, I.E. Gordon, A. Barbe, D. Chris Benner, P.F. Bernath, M. Birk, V. Boudon, L.R. Brown, A. Campargue, J.-P. Champion, K. Chance, L.H. Coudert, V. Dana, V.M. Devi, S. Fally, J.-M. Flaud, R.R. Gamache, A. Goldman, D. Jacquemart, I. Kleiner, N. Lacome, W.J. Lafferty, J.-Y. Mandin, S.T. Massie, S.N. Mikhailenko, C.E. Miller, N. Moazzen-Ahmadi, O.V. Naumenko, A.V. Nikitin, J. Orphal, V.I. Perevalov, A. Perrin, A. Predoi-Cross, C.P. Rinsland, M. Rotger, M. Simeckova, M.A.H. Smith, K. Sung, S.A. Tashkun, J. Tennyson, R.A. Toth, A.C. Vandaele, J. Vander Auwera, J. Quant. Spectrosc. Ra. 110 (2009) 533–572.
[9] X. Zhou, X. Liu, J.B. Jeffries, R.K. Hanson, Meas. Sci. Technol. 14 (2003) 1459–1468.