



Novel in situ measurements of relative humidity in a polymer electrolyte membrane fuel cell

G. Hinds*, M. Stevens, J. Wilkinson, M. de Podesta, S. Bell

National Physical Laboratory, Teddington, Middlesex, TW11 0LW, United Kingdom

ARTICLE INFO

Article history:

Received 19 May 2008

Received in revised form

10 September 2008

Accepted 28 September 2008

Available online 10 October 2008

Keywords:

PEMFC

Relative humidity

Temperature

Measurement

Water

ABSTRACT

Miniature temperature/humidity sensors are incorporated into the graphite flowplates of a single cell polymer electrolyte membrane fuel cell (PEMFC) in order to measure the humidity profile along the serpentine channels of both anode and cathode in real time. The sensors show robust performance and importantly are able to recover after saturation. The key observation is a significant increase in relative humidity along the anode gas channel due to back diffusion of water from cathode to anode. Such measurements may be used to determine the water balance in the cell under a range of operating conditions to facilitate model validation and system optimisation.

Crown Copyright © 2008 Published by Elsevier B.V. All rights reserved.

1. Introduction

The polymer electrolyte membrane fuel cell (PEMFC) is a potential replacement or hybrid partner for gas turbine, internal combustion engine and battery technologies. The advantages of PEMFCs are high efficiency, low emissions, silent operation and relatively fast start-up times but commercialisation of the technology is currently hampered by high material and processing costs, limited durability and the lack of a refuelling infrastructure. It is anticipated that improvements in efficiency and durability will be facilitated by system optimisation based on improved models of PEMFC performance. In situ measurement of critical parameters is required both for model validation and to develop further understanding of the physical processes taking place in the fuel cell.

The distribution of water in a PEMFC is critical to its operation. The sulphonic acid side chains of the Nafion membrane must be hydrated in order to facilitate conduction of protons from anode to cathode. The active layers at both anode and cathode usually contain ionomer, which must also be hydrated. For this purpose the inlet gases are usually humidified, although there is a balance to be maintained as too much water will flood the pores and retard transport of reactant gas to the active sites. This problem is exacerbated at the cathode, where water is produced in the electrochemical reaction. Water may also be transported across the membrane by

electro-osmotic drag (anode to cathode) or back-diffusion (cathode to anode). An understanding of the distribution of water throughout the fuel cell is clearly very important for design and performance optimisation.

A range of experimental techniques has been applied to the study of water distribution in the gas channels of PEMFCs. Mench et al. [1] used gas chromatography (GC) to measure the water vapour content in the anode and cathode gas channels. They showed very little difference in relative humidity between anode and cathode for a relatively thin membrane ($\sim 50 \mu\text{m}$), demonstrating that the rate of back-diffusion is comparable to that of electro-osmotic drag. However, the drawback of the GC technique is that the measurements can only be made about every 2 min. Partridge et al. [2] demonstrated that mass spectrometry could be used to measure relative humidity by sampling gas from a PEMFC stack through fine glass capillaries. Chen et al. [3] used neutron radiography to detect liquid water in the gas channels of a single cell PEMFC of active area 100 cm^2 . Unfortunately, in order to differentiate between water content in the cathode and the anode, the cathode and anode channels were shifted by one channel width, which meant that they did not overlap over the majority of the active area. Basu et al. [4] explored the use of absorption spectroscopy with a fibre optic coupled diode laser sensor in a single cell PEMFC. Nishikawa et al. [5] measured the relative humidity in the cathode flow channel of a single cell PEMFC of active area 289 cm^2 by extracting the gas through a stainless steel tube to a humidity sensor of diameter 4 mm located outside the cell. An increase in relative humidity from inlet (30%) to outlet (70%) was observed

* Corresponding author. Tel.: +44 20 8943 7147.

E-mail address: gareth.hinds@npl.co.uk (G. Hinds).

with a humidifier temperature of 40 °C and a cell temperature of 80 °C.

While these techniques provide useful information about the variation in water content in the gas channels, they lack a simultaneous measurement of temperature at the point of interest in order to enable accurate calculation of the dew-point temperature. Lee et al. [6] recently used a dual temperature/humidity probe to measure the relative humidity in a micro-fuel cell but no information on the spatial variation of relative humidity was obtained. The aim of the present work was to obtain in situ measurements of temperature and relative humidity in real time using a series of miniature sensors embedded in both cathode and anode flowplates. While it would be preferable to obtain measurements of temperature and humidity within the active area, there are severe constraints with regard to sensor location and perturbation of fuel cell operation. Nevertheless, the measurements obtained from the gas channels may be used to establish boundary conditions when modelling the active layer.

2. Experimental

2.1. Fuel cell

A single cell PEMFC of active area 7 cm × 7 cm was used for all measurements. The membrane electrode assembly (MEA) consisted of two identical Johnson Matthey Pt/C electrodes (Pt loading 0.44 g cm⁻²) on a Nafion 115 membrane (thickness 127 μm). Both anode and cathode flowplates were machined from impregnated graphite with a flow field consisting of six parallel serpentine channels in partial counter-flow mode. A Hydrogenics Test Systems FCATS-G50 test stand (Vancouver, Canada) was used to control the experiments. The cell temperature was maintained by cartridge heaters embedded in the stainless steel fixing plates. The environmental conditions held constant during the tests are listed in Table 1.

The temperature of both anode and cathode humidifiers and the current drawn from the cell were varied during the tests. The gas flow rates used correspond to a stoichiometry of 2 for the highest current density applied (0.5 A cm⁻²). The fuel cell was oriented horizontally to avoid build up of condensed water in the recesses containing the temperature/humidity sensors and the MEA was positioned with the cathode facing downwards to facilitate draining of any liquid water. Current interrupt measurements were made to correlate the relative humidity measurements with membrane resistance. The steady state cell potential was also measured under each set of conditions.

2.2. Temperature/humidity sensors

The sensors used in the tests were Sensirion SHT75 single chip temperature/humidity sensors. These miniature sensors comprise a bandgap temperature sensor and a capacitive polymer sensing element for relative humidity. The manufacturers' specifications for these sensors are ±1.2 °C at 80 °C and ±1.8%rh in the range 10–90%rh. Both sensors are coupled to a 14-bit analogue to digital

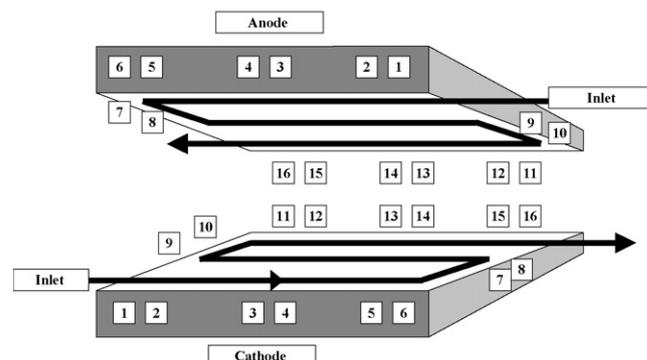
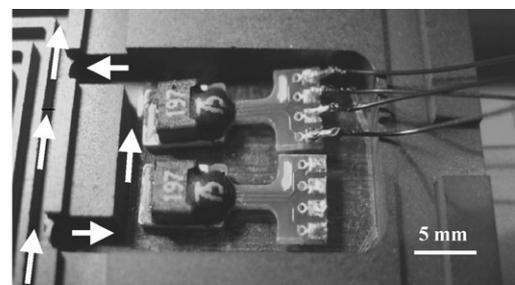


Fig. 1. (a) Recess in graphite flowplate showing location of the sensors relative to the gas channel on the left. (b) Schematic showing the relative positions of the sensors on the cathode and anode flowplates. The sensors are numbered in sequence and characterised by their distance from the inlet as measured along the gas flow channels. The schematic has been simplified for clarity; the actual cell comprises six parallel channels with five passes. Note that the partial counter-flow arrangement places sensors 1 and 2 in the anode flowplate above sensors 5 and 6 in the cathode flowplate.

converter and a serial interface circuit, giving high signal quality, fast response time and insensitivity to external disturbances. The sensors were embedded in recesses in the graphite flowplates along the edge of the serpentine channels, as shown in Fig. 1a, allowing direct measurement of the temperature and humidity of the gas without significantly impeding the flow. Two sensors were inserted into each recess in case of failure of one of the sensors. After the sensors had been fixed in place, the recesses were filled with silicone rubber to minimise dead volume. A schematic showing the relative positions of the sensors on the cathode and anode flowplates is shown in Fig. 1b. Here the detailed arrangement of the serpentine channels has been simplified for clarity. Due to the layout of the six parallel channels, the sensors close to the inlet are sampling Channel 1, while those close to the outlet are sampling Channel 6. However, both channels are sampled approximately halfway through the cell, providing a check on any effect of the presence of the sensors on the downstream behaviour in the channel.

Each flow-plate contained 16 SHT75 sensors located in pairs at measurement positions around the edge of the plate. For calibration, the plates were placed in a Montford temperature and humidity-controlled chamber at approximately 80 °C. The temperature was measured using calibrated platinum resistance thermometers placed close to the plates, and the humidity was measured in the dew point range from 50 °C to 80 °C (saturation) by sampling gas from near the plates using a calibrated MBW DP3-D optical dew-point hygrometer. A table of corrections was compiled for each of the 32 sensors and applied to the data after collection. After calibration we estimate the uncertainty of measurement to be almost as good as the reproducibility of the sensors, i.e. ±0.2 °C at 80 °C and ±1%rh in the range 50–90%rh. The sensors were calibrated in air at atmospheric pressure, while in the cells the measurements are made at 2 barg operating pressure

Table 1
Environmental conditions held constant during the tests.

Cell temperature (°C)	80
Cathode inlet gas temperature (°C)	90
Anode inlet gas temperature (°C)	90
Air flow rate (L min ⁻¹)	0.813
H ₂ flow rate (L min ⁻¹)	0.340
Cathode pressure (barg)	2
Anode pressure (barg)	2

and the anode sensors operate in a hydrogen rich atmosphere. Calculations and initial measurements indicate the corrections to the results will be small, but these corrections have not yet been made.

The conversion from relative humidity (RH) to dew point, T_d , was calculated from the measured relative humidity and temperature values using an expression based on the Sonntag approximation [7] for saturation vapour pressure

$$T_d = 13.715y + 0.84262y^2 + 0.019048y^3 + 0.00078158y^4 \quad (1)$$

$$\text{where } y = \ln\left(\frac{\alpha}{6.1213}\right) \quad (2)$$

$$\text{and } \alpha = \frac{(RH/100)\exp(-6097/T) + 21.24 - 0.02711T + ((1.674 \times 10^{-5})/T^2) + 2.434 \ln T}{611.2} \quad (3)$$

where RH is in %rh and T in kelvin.

2.3. Test procedure

Adequate control of temperature throughout the test system is essential when making relative humidity measurements. Heated gas lines were used to maintain the temperature of the inlet gas

above the dew point as it passed from the humidifier to the fuel cell. The temperature of the gas just before the inlet was monitored using a thermocouple and controlled at 90 °C, i.e. 10 °C above the cell temperature. This is common practice in sample handling for humid gases and ensures that condensation of water vapour does not occur before the gas reaches the flowplate. In each test, gas flow was only initiated after the fuel cell plates and heated gas lines had reached their set temperatures. Next the system was pressurised using a back-pressure regulator at the cell exhaust and finally the humidifiers were brought to temperature. This sequence of events was necessary to avoid condensation in the cell before commencing the test.

In these tests, measurements of relative humidity along both anode and cathode channels were made as a function of current density for a range of humidifier temperatures (50–80 °C). The system was allowed to reach steady-state before each measurement (typically ~15 min).

3. Results and discussion

A plot of temperature as a function of distance along the cathode and anode gas channels for a humidifier temperature of 50 °C is shown in Fig. 2. At open circuit (Fig. 2a) there is a temperature gradient of approximately 2 °C along each gas channel, with the upper plate (the anode) being systematically approximately 0.5 °C

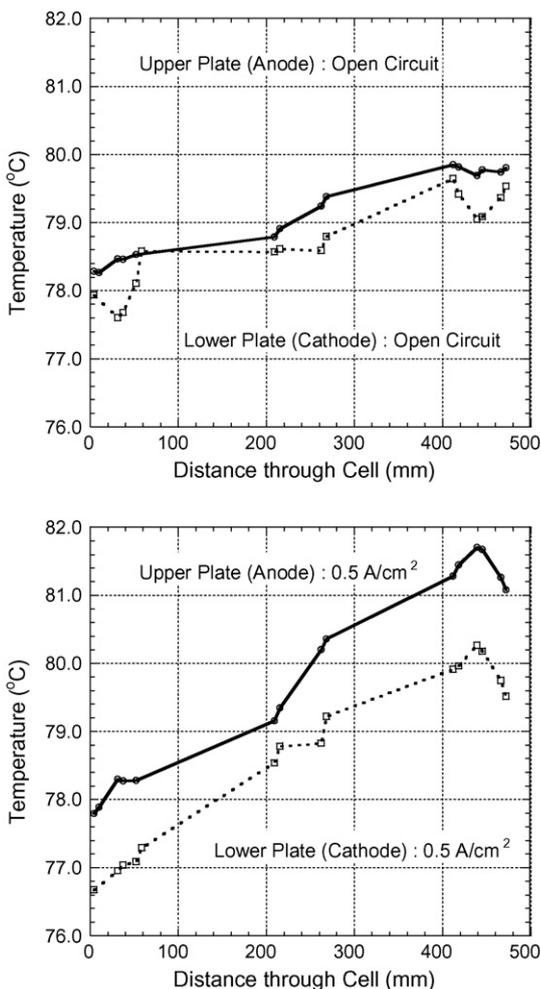


Fig. 2. Temperature versus position along both gas flow channels at (a) open circuit, and (b) a current density of 0.5 A cm⁻² for a humidifier temperature of 50 °C. For these graphs the order of data has been changed so that sensors which lie above each other (see Fig. 1b) are plotted as being the same distance along the gas flow path.

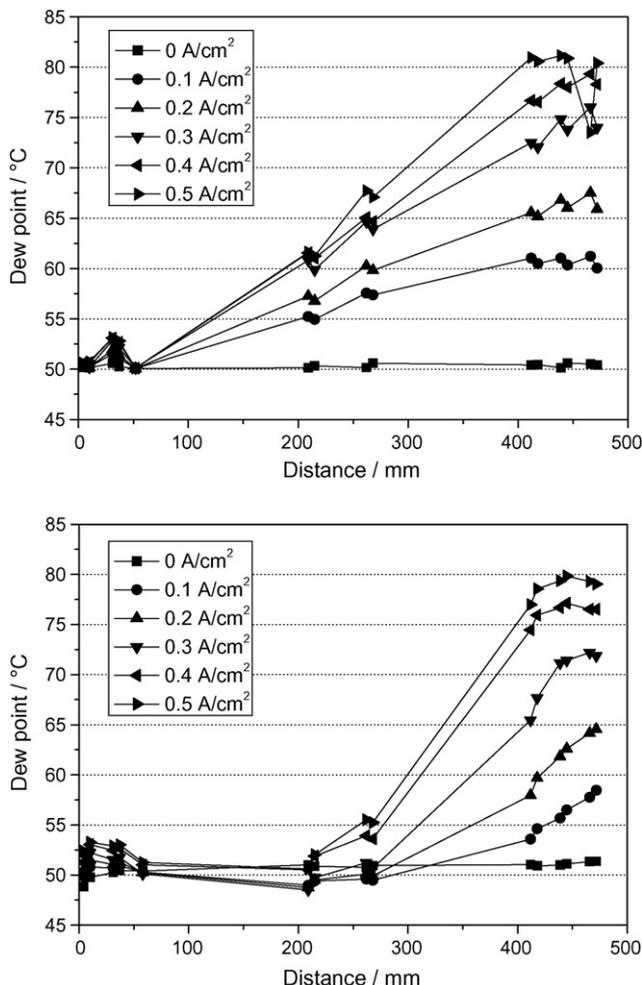


Fig. 3. Dew-point temperature as a function of position along the (a) cathode and (b) anode gas channels with a humidifier temperature of 50 °C.

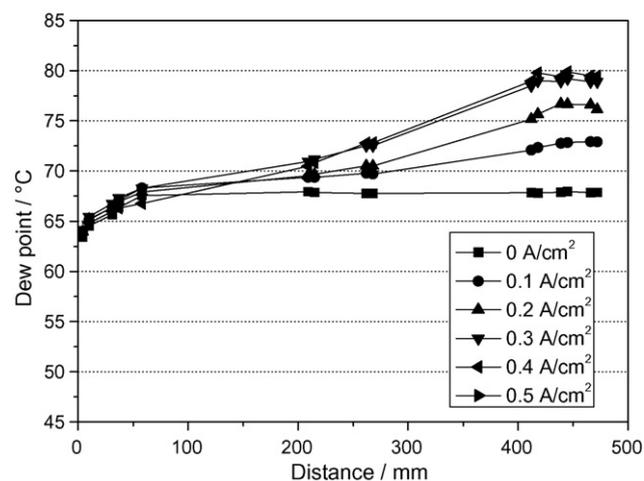
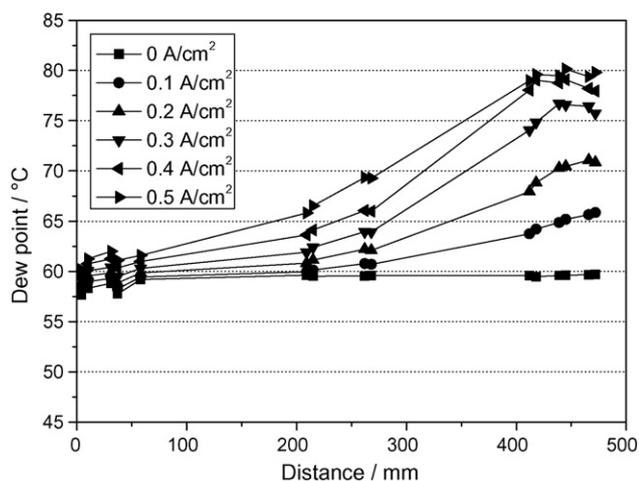
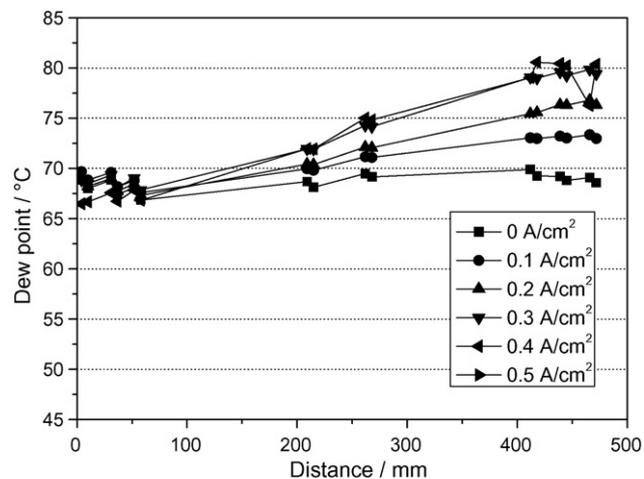
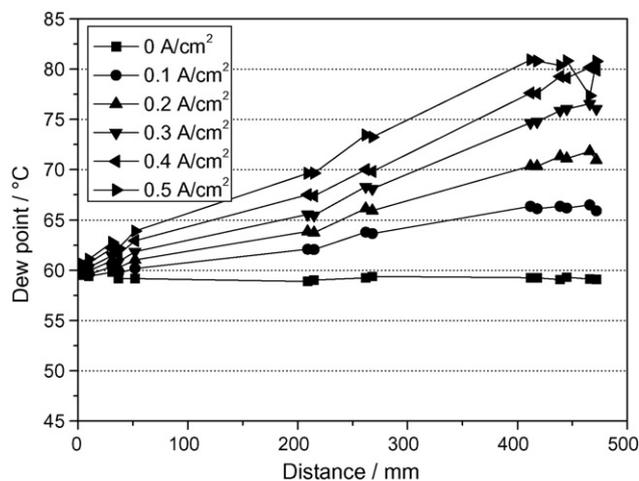


Fig. 4. Dew-point temperature as a function of position along the (a) cathode and (b) anode gas channels with a humidifier temperature of 60 °C.

Fig. 5. Dew-point temperature as a function of position along the (a) cathode and (b) anode gas channels with a humidifier temperature of 70 °C.

warmer. Fig. 2b shows the equivalent data for a current density of 0.5 A cm⁻². The temperature gradient in each channel has increased to more than 3 °C and the difference in temperature between the plates has risen to approximately 1 °C. This is most likely due to additional heat generated in the cell reaction and by ohmic losses being dissipated through the gas channels. The fact that the temperature of the anode flowplate is higher than that of the cathode is slightly surprising, but it may be related to more efficient heat transfer in the cathode gas channel due to the higher flow rate and also the different thermal properties of air and hydrogen.

A plot of dew point as a function of distance along the cathode gas channel for a humidifier temperature of 50 °C is shown in Fig. 3a. At open circuit the dew point remains relatively constant at 50 °C throughout the channel. When current is drawn from the cell, the relative humidity in the cathode channel increases from inlet to outlet due to generation of water in the electrochemical reaction. Saturation (where the dew point reaches the cell temperature) occurs about 100 mm before the outlet at a current density of 0.5 A cm⁻². The corresponding plot for the anode gas channel is shown in Fig. 3b. The key observation is the appearance of water due to back diffusion from the cathode after about 200 mm. Fig. 3 indicates the complexity of moisture generation and transport within the cell. The cathode shows a nearly linear increase in humidity – as measured by dew point – as the gas moves through the cell, consistent with more or less uniform generation of electricity throughout the cell. However, the anode shows complex behaviour. There is

an initial change in humidity which is correlated with the cathode humidity, indicating that water can diffuse across the membrane in both directions. In the anode channel, the gas stays relatively dry for about half of its transit through the cell, before wetting rapidly and approaching saturation at the exit. The reason for this non-linear behaviour is not clear, but it may be connected with the very dry operation of the cell.

The unexpected pattern of moisture readings at the start of flow channels is being investigated further, but is probably related to slight differences in pre-saturation temperature and the partial counter-flow arrangement of the flow-plates (Fig. 1b). For example, the cathode data in Fig. 3a show an unexpected 'dry' reading from sensors 5 and 6 located in the same measurement area 55 mm along the gas channels. This is directly below the gas inlet to the anode which contains dryer gas. Fig. 3b shows that indeed the anode sensors 1 and 2 do show initial rises in dew point, probably due to diffusion through the membrane from the cathode. The extent of this diffusion is likely to depend on membrane temperature and humidity.

Robust performance of the sensors was observed up to saturation. Following saturation, sensor output was often lost due to condensed water building up on the sensing element. However, evaporation of this water by lowering the dew point of the gas was shown to reactivate the sensors with no deterioration of performance or loss of functionality. Notice that the use of two sensors at each measurement position allows us to check our

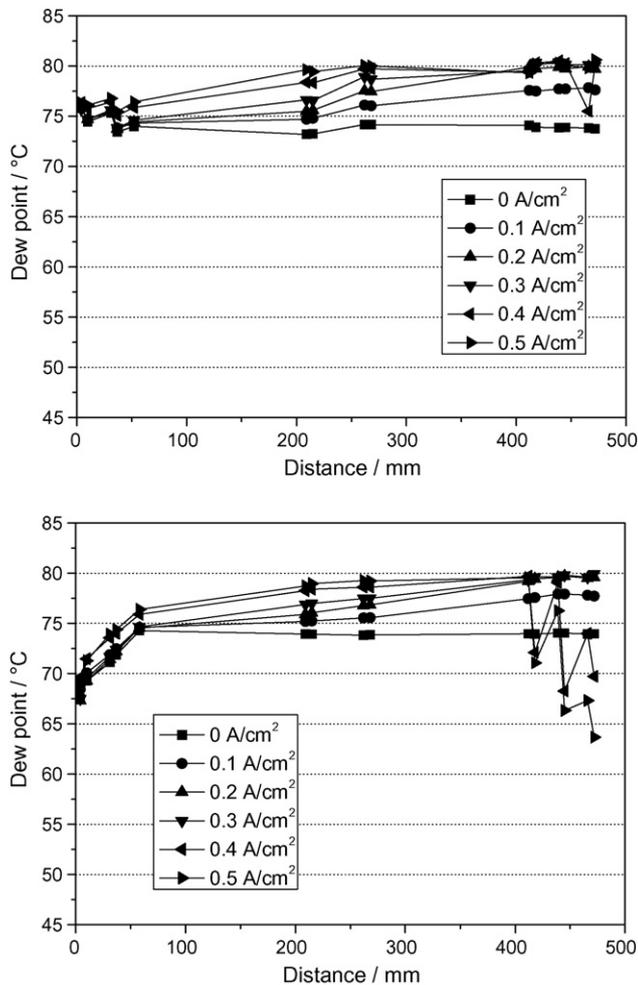


Fig. 6. Dew-point temperature as a function of position along the (a) cathode and (b) anode gas channels with a humidifier temperature of 80 °C.

estimate of the uncertainty of measurement, and indicates that the sensors have a reproducibility of approximately $\pm 0.5^\circ\text{C}$ dew point and 0.1°C in temperature. Additionally, the sensors located approximately 210 mm along gas flow channel 1 give data which are consistent with the sensors located 260 mm along gas flow channel 6. Since the gas in channel 1 has passed three previous measurement locations and that in channel 6 has passed no measurement locations, we conclude that the sensor positioning, and the use of recesses to accommodate the sensors, has not materially affected the temperature or moisture balance in the cell.

The effect of varying humidifier temperature is demonstrated in Figs. 4–6. At the higher humidifier temperatures a more uniform distribution of relative humidity is observed. Note that as the humidifier temperature is increased, the efficiency of both humidifiers decreases, demonstrating the importance of dew point calibration of fuel cell humidifiers.

A typical transient response of a sensor following a step change in current density is shown in Fig. 7. Note the rapid response of the sensor to the increased humidity level at time $t=0$. The time to reach steady state is comparable to that for the cell potential, reflecting the time required for the water distribution in the cell to re-stabilise (of the order of 100 s). This demonstrates that the sensors are providing valuable information on the dynamics of the water transport and could be employed for feedback control.

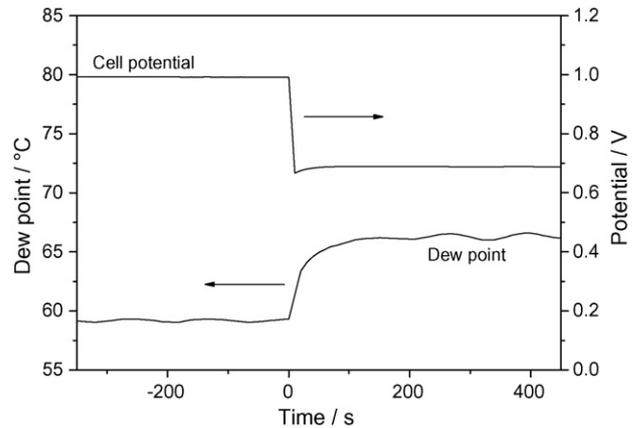


Fig. 7. Typical transient response of an individual sensor following a step change in current density from 0 to 0.1 A cm^{-2} at time $t=0$. The sensor was located near the outlet on the anode gas channel. The evolution of cell potential with time is shown for comparison.

The steady-state cell potential and current interrupt data under each set of conditions are summarised in Fig. 8. As expected for the region where no mass transport limitation applies, the performance of the cell at a fixed current density increases with increasing rela-

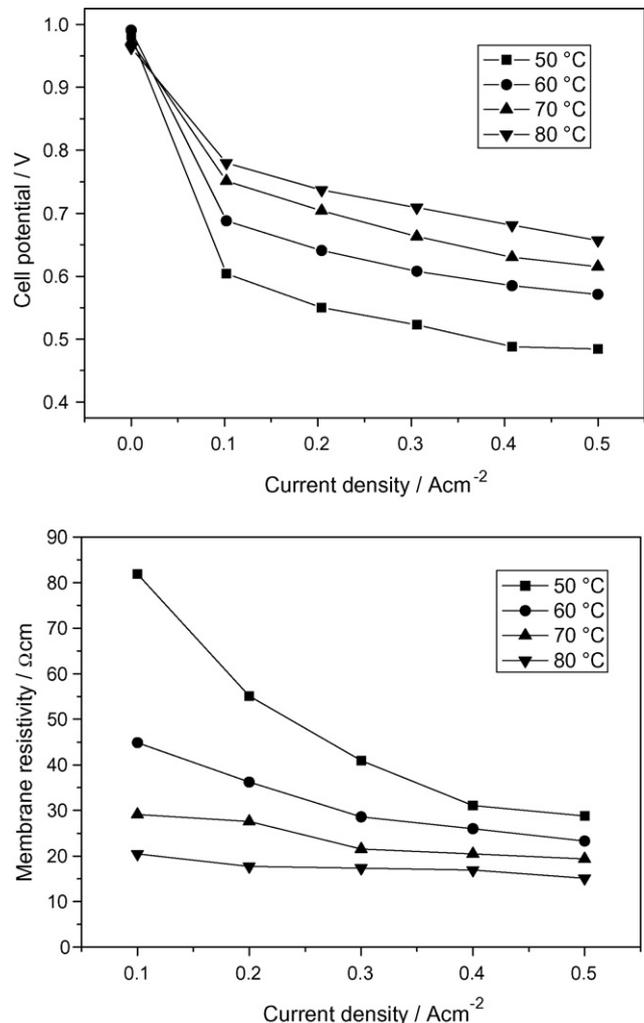


Fig. 8. (a) Cell potential and (b) membrane resistivity as a function of current density and humidifier temperature.

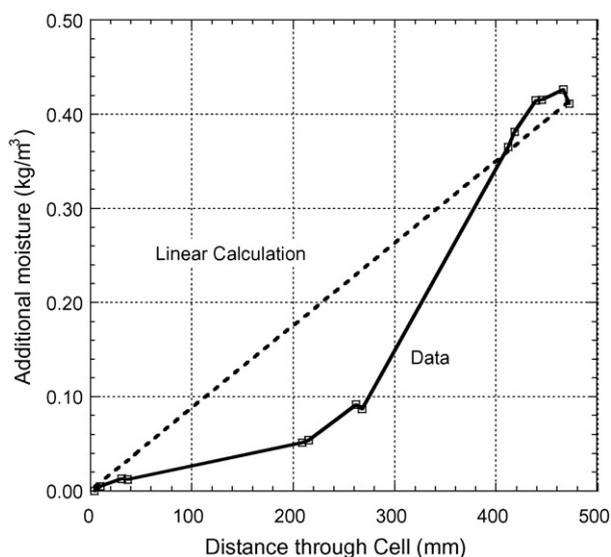


Fig. 9. Total additional moisture measured in both anode and cathode shown as a function of position through the cell. The current density was 0.4 A cm^{-2} and the data are compared with a straight line showing the expected behaviour if the moisture is generated uniformly throughout the cell. The humidifier temperature is 50°C .

tive humidity (Fig. 8a). It would be expected that at higher current densities flooding of gas pores in the cathode active layer would lead to a reduction in performance at higher humidifier temperatures. The current interrupt measurements correlate well with the humidity measurements, showing a decrease in membrane resistivity with increasing humidifier temperature. The effect is more marked at low current densities, reflecting the lower amount of water generated in the cell reaction. The membrane resistivity in the most humid condition is consistent with measured Nafion 115 resistivity values at high water content [8].

By converting the humidity measurements from dew-point temperature to an absolute measurement of moisture content in kilograms of water per cubic metre of air, we can compare the results in Figs. 3–6 with the total amount of moisture that we would expect to be generated from the electrochemical reaction. Partial counter-flow patterns in the two flowplates make a straightforward comparison difficult. However, we can check our results by adding together the total amount of *additional* moisture detected in *both* anode and cathode flow channels. Fig. 9 shows the total additional moisture detected as a function of position along the flow path for a total cell current density of 0.4 A cm^{-2} and a humidifier temperature of 50°C . These data represent the integral of the electrochemically generated moisture through the cell. The data are in good agreement with the theoretical final value of 0.414 kg m^{-3} . If we assume that the current is generated uniformly through the cell, then we might have expected the additional moisture to vary linearly through the cell, but this is clearly not the case. The agreement between measured and calculated moisture levels is less good at higher humidifier temperatures; here the measured values are slightly less than the calculated values since the sensors do not detect condensed water.

The advantage of this experimental set-up is that the temperature and relative humidity are measured at the same location. In previous work [5], the gas was extracted from the cell to make the relative humidity measurement, leading to uncertainty in the temperature at the point of interest within the cell. This is significant since small changes in temperature, of the order of those observed in the flow channels ($1\text{--}3^\circ\text{C}$), lead to significant variations in dew point. The use of sensors in both anode and cathode gas channels allows spatial resolution of back diffusion of water through the membrane for the first time. The use of a relatively thick membrane is ideal for this purpose. It is envisaged that this technique will be used to validate models of water distribution and transport in PEMFC membranes and to support fuel cell design and optimisation.

4. Conclusions

In situ measurement of temperature and relative humidity in real time along both anode and cathode gas channels has been demonstrated for the first time in a PEMFC.

The striking feature of the measurements is the significant increase in relative humidity along the anode gas channel due to back diffusion from the cathode.

Measurements of total additional moisture generated in the cell reaction agree well with the theoretical value at a humidifier temperature of 50°C . Agreement is less good at higher humidifier temperatures since condensed water is not detected by the sensors.

In situ measurement of relative humidity is critical in providing input data for model validation to support fuel cell design and optimisation.

Acknowledgements

This work was carried out under the Measurement for Emerging Technologies Programme, a joint venture between the United Kingdom Department of Innovation Universities & Skills and an Industrial Group comprising C Tech Innovation, CMR Fuel Cells, Ceres Power, Dart Sensors, Gary Acres, Ineos Enterprises, Imperial College, Intelligent Energy, Johnson Matthey, Rolls Royce Fuel Cell Systems and Solartron Analytical. The authors are grateful to Sarah Ball and Jonathan Sharman of Johnson Matthey Technology Centre for supply of fuel cell components.

References

- [1] M.M. Mench, Q.L. Dong, C.Y. Wang, J. Power Sources 124 (2003) 90–98.
- [2] W.P. Partridge, T.J. Toops, J.B. Green, T.R. Armstrong, J. Power Sources 160 (2006) 454–461.
- [3] Y.S. Chen, H. Peng, D.S. Hussey, D.L. Jacobson, D.T. Tran, T. Abdel-Baset, M. Bier-nacki, J. Power Sources 170 (2007) 376–386.
- [4] S. Basu, H. Xu, M.W. Renfro, B.M. Cetegen, J. Fuel Cell Sci. Tech. 3 (2006) 1–7.
- [5] H. Nishikawa, R. Kurihara, S. Sukemori, T. Sugawara, H. Kobayashi, S. Abe, T. Aoki, Y. Ogami, A. Matsunaga, J. Power Sources 155 (2006) 213–218.
- [6] C.Y. Lee, W.J. Hsieh, G.W. Wu, J. Power Sources 181 (2008) 237–243.
- [7] D. Sonntag, Z. Meteorol. 40 (1990) 340.
- [8] S. Slade, S.A. Campbell, T.R. Ralph, F.C. Walsh, J. Electrochem. Soc. 149 (2002) A1556–A1564.