A calorimetric analysis of a polymer electrolyte fuel cell and the production of H$_2$O$_2$ at the cathode

Odne Burheim, Preben J. S. Vie, Steffen Møller-Holst, Jon Pharoah and Signe Kjelstrup*

ABSTRACT

A calorimeter has been constructed and used to measure the total heat production of a single polymer electrolyte fuel cell that is operated on hydrogen and oxygen at 50 °C and 1 bar. The cell had a SolviCore Catalyst Coated Backing and Nafion membranes 112,115 and 117. We report that the total heat production plus the power production corresponds to the enthalpy of formation of water for cell potentials above 0.55 V. For cell potentials less than 0.55 V, we measured a linear decrease in the reaction enthalpy with decreasing cell potential. This effect was obtained independently of membrane thickness and current density. We propose therefore that the main power loss at low cell potentials and the inflection point in the polarisation curve is due to hydrogen peroxide formation at the cathode. The total heat production was decomposed into reversible and irreversible effects (non-ohmic and ohmic). The result was evaluated using Tafel plots. We show that it is possible to determine the overpotential of an electrode also from its thermal signature.

Nomenclature

<table>
<thead>
<tr>
<th>Greek Letters</th>
<th>Latin Letters</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>$a$</td>
</tr>
<tr>
<td>$H$</td>
<td>$b$</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>$J$</td>
</tr>
<tr>
<td></td>
<td>$j_o$</td>
</tr>
<tr>
<td></td>
<td>$P$</td>
</tr>
<tr>
<td></td>
<td>$X$</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
1. INTRODUCTION

The energy that is dissipated as heat in fuel cells is interesting for several reasons. It provides information that is important for design of auxiliary systems; in particular the cooling systems. Knowledge of the dissipated energy can also help explain the causes of these losses [1]. These issues are now getting increased attention [2][3], and has motivated us to build a calorimeter and measure the thermal signature of the low temperature polymer electrolyte fuel cell. This paper reports on the construction, test and use of a new calorimeter, as announced earlier [4].

We present a first set of direct calorimetric measurements on a single polymer electrolyte fuel cell, PEMFC, aimed to give direct information of the thermal effects in the cell. To our knowledge, no measurements have so far been reported to access directly the heat produced by fuel cells. The thermal signature was however measured in Li-batteries where possibilities of overheating are large upon discharging as well as charging of the battery [4][5][6][7][8]. The heat production was measured by placing the battery inside a calorimeter [7], [8]. In the present work, the calorimeter has been tailored to fit around a single cell. The cell has a cylindrical membrane-electrode assembly, and is studied at stationary state. In addition to the heat production, we measure also the simultaneous electric current, the total electric resistance of the cell, and the cell potential.

The cell power can be found from the polarisation curve. By measuring also the heat production, one may add the two values and find the total energy production as a function of current density. If the reactant and product states are the same during the operation, the sum is a constant, as is well known [8]. The characteristic shape of the polarisation curve can be related to the dissipation of energy or the entropy production in the cell. The rapid non-linear fall at relatively low current densities in this curve has thus been attributed to the overpotential, mainly of the oxygen electrode. The linear variation in the potential, $E$, with current density at intermediated values of the current density is called the ohmic regime. In this regime, the ohmic dissipation explains the variation in the curve. The fall beyond this regime at very high current densities (low cell potentials) has often been attributed to mass transfer limitations [9]. In a simplified calculation of the entropy production, Kjelstrup and Røsjorde [1] found that the non-linear variation in the membrane resistance with water content was essential for the rapid decline. We shall see in this work, that yet another explanation is possible, because the sum of the power production and the heat production can not be explained by the enthalpy of formation of water in the low potential region. Another aim of the work is to find the overpotential, not only from the polarisation curve, but also from its thermal signature. This can be found, as we shall see below, by subtracting the reversible heat and the Joule heat from the total heat production.
In the present set of experiments, a standard membrane (Nafion 112, 115 or 117) and gas diffusion layers, coated with micro porous layers and catalyst (SolviCore Batch-Number: # 205-07-1) were chosen, in order to establish results that can be used as reference for later experiments. The cell reaction of the polymer electrolyte fuel cell at the operating conditions in question here (50 °C and 1 bar) can be written as:

\[
2H_2(g) + O_2(g) \iff 2 H_2O(l)
\]  

(a)

Water leaves the cell in the liquid state at these conditions. The electro-osmotic transport of water from the anode to the cathode side, gives a contribution to the cell potential in the mV range [10]. This contribution shall be neglected.

Kinoshita et al. [11] proposed that reduction of oxygen gas proceeds via two parallel pathways, see also Okada and Kaneko [12]. The most important is a direct 4-electron pathway with \( E^0 = 1.22 \) V vs. the standard hydrogen electrode,

\[
O_2(g) + 4 H^+ + 4 e \iff 2 H_2O(l)
\]  

(b)

The four-electron step was supported by Kuhn et al. [13]. The alternative, undesirable path is a two step pathway via peroxide. The first step has \( E^0 = 0.67 \) V vs. the standard hydrogen electrode:

\[
O_2(g) + 2 H^+ + 2 e \iff H_2O_2(l)
\]  

(c)

while the next step e) has \( E^0 = 1.77 \) V vs. the standard hydrogen electrode;

\[
H_2O_2(l) + 2 H^+ + 2 e \iff 2 H_2O(l)
\]  

(d)

In view of the high half cell potential, an alternative decomposition of peroxide into water and oxygen is likely:

\[
H_2O_2(l) \iff 2 H_2O(l) + O_2(g)
\]  

(e)

Whether the oxygen reduction proceeds via path (b) or paths (c+d) or (c+e) is still a matter of debate among electrochemists [11]. Water formation is thermodynamically favoured, but peroxide production may take place for kinetic reasons. Because hydrogen peroxide formation only requires two electrons transferred it can be kinetically favoured over water formation, requiring four electrons.

Paths (b) and (c+d) involve the same beginning and end states, defined by the enthalpy of formation of water. Path (c+e), however, is not parallel to step (b) in the sense that this path gives a different end state from the two first paths. The sum of the heat and power production in the cell is therefore expected to change if there is a crossover from path (c+e) to the other paths. The Tafel slopes for path (b) or (c+d) have been reported as 2.3 \( RT / F \), i.e. \( \alpha = 0.43 \) [12].

Yamanaka has shown that a polymer electrolyte fuel cell can produce hydrogen peroxide [14]. The cathode of his cell was fed oxygen in the water phase while the anode was in contact with hydrogen gas. Maximum concentrations of peroxide (up to 7 wt%) were obtained under short circuit conditions with heat treated, carbon-containing catalysts in NaOH. Although the yield of water from oxygen reduction is normally more than 98% on Pt, peroxide production was shown to occur below 0.3 V vs. the standard hydrogen electrode [12]. In an evaluation of the cell’s heat and power production, peroxide formation at low potentials is therefore a
possibility. We report measurements that allow us to evaluate this from the perspective of combined calorimetric and potential measurements.

We shall thus report on the total heat production and the simultaneous power production in this cell and evaluate the combination. We shall find the separate contributions to the heat production as mentioned above, using the ohmic resistance, the cell potential and the electric current in the cell under operation. This allows us to answer the following questions: Which reaction mechanism is supported by the experimental data? Which overpotential can be calculated from the total heat production, and how does this calculation compare to the standard determination of the overpotential? Answers to these questions may add insight into the cause of the overpotential. They may also be important, not only for fuel cell modelling, but also for analysis of electrochemical cells where heat effects are important, like Li-batteries.

We shall first see that we have been able to establish a reliable measuring technique, and that we can use this technique to evaluate the electrode reactions. We shall next see that is possible to find the overpotential also via its thermal signature, with fair precision. The outline of the paper is as follows. We give first an overall thermodynamic analysis of the single polymer electrolyte fuel cell, when placed in a calorimeter at steady state (section 2). We describe next a first generation calorimeter used to measure the described effects (section 3), and the experimental procedure used (section 4). The results are then presented and discussed in section 5.

2. THEORY

Consider first the open cell at temperature $T$ under reversible conditions. There is a change in internal energy, $\Delta U$, when heat is added to the cell and work is done by the cell. The pressure, $p$, is constant, and $\Delta V$ is the volume change by the reaction. The electric work per mole of charges passing the cell is $nFE_{rev}$. The first law of thermodynamics gives

$$
\Delta H = \Delta U - p\Delta V = q_{rev} - nE_{rev}F
$$

Here $F$ is Faraday's constant and $n$ is the number of electrons transferred in the cell reaction. The heat delivered to the cell under reversible conditions is $q_{rev}$, and from the definition of entropy we have

$$
q_{rev} = T\Delta S
$$

where $S$ is the entropy and $\Delta$ refers to the cell reaction. The heat change in the surroundings at reversible conditions equals

$$
q_{sur} = -q_{rev} = -T\Delta S
$$

This makes the entropy change in the reversible fuel cell plus its nearest surroundings equal to zero, in agreement with the second law. In this particular fuel cell, $\Delta S$ is negative and relatively large, since water is formed in the liquid state and gas molecules disappear, cf. Eq.(a). Therefore, the reversible heat effect in the surroundings is positive. Other electrochemical cells may have a cell reaction with a positive entropy change. Such cells can convert heat directly to electric work by taking heat from the surroundings, see [4] and [5].

By introducing eq. (2) and the definition of Gibbs energy, $G$, into Eq. (1) we obtain the Nernst equation:
For reversible conditions, $E_{\text{rev}} = -\Delta G/nF$. The theoretical value of $E_{\text{rev}}$ is 1.21 V at $T = 298$ K when water is in the liquid state and the reactants are at 1 bar [6]. The negative reaction entropy contributes by -0.27 V and $E_{\text{TN}} = \Delta H/nF$ by 1.48 V at $T = 298$ K. So already for very small current densities, the heat production in the cell is substantial. Away from reversible conditions, where there is a net current, the heat production and the entropy production increases [1], [4].

The polarisation curve, where the potential $E_{\text{cell}}$ is plotted as a function of the current density, $j$, is used to describe the cell’s performance. The current density is the electric current per unit area. As the current density increases, the heat production increases relatively more. We shall use conditions that give small diffusion limitations in the electrodes. The potential of a cell in operation, $E_{\text{cell}}$, is then the reversible potential minus the ohmic potential drop, $Rj$, minus the sum of the overpotentials at the cathode and the anode, $\eta$ [8]. Here $R$ is the ohmic resistance of the total cell.

$$E_{\text{cell}} = E_{\text{rev}} - Rj - \eta$$  \hspace{1cm} (5)

The ohmic potential drop and the overpotential give irreversible heat production (entropy production). These well known thermodynamic relations for an electrochemical cell are illustrated in Fig. 1. The overpotential can be described by the Butler-Volmer equation for small current densities and by the Tafel equation for larger ones. The overpotential is zero when $j=0$. When $j \to 0$, we obtain the Nernst equation (4).

---

**Figure 1.** Thermodynamic properties of an electrochemical cell. The thermoneutral potential in kJ/mol is represented by $-\Delta H$. Part of this energy is needed to compensate the entropy change $\Delta S$ at temperature $T$, leaving us with $-\Delta G$, available for electric work at reversible conditions, $E_{\text{rev}}$. The electric potential under operation is $E_{\text{cell}}$. Parts of $E_{\text{rev}}$ (in V) are used to compensate the overpotential ($\eta$) and the Ohmic potential drop ($jR$).

The power production of the cell (in W per unit of membrane area) is
P = E_{cell} j = \left( \frac{\Delta H - T \Delta S}{nF} \right) j - \eta j - j^2 R \quad (6)

The total heat production by the fuel cell becomes:

Q = - \frac{T \Delta S}{nF} j + \eta j + R j^2 \quad (7)

The sum of the power production and the heat production (in J per unit of membrane area) is therefore:

P + Q = - \frac{\Delta H}{nF} j = P + q_{sur} \frac{\eta}{F} j \quad (8)

The sum is called the thermo-neutral power of the cell. It is a hypothetical power.

The heat effects that make \( q_{sur} \) different from \(-q_{rev} \) in Eq.(3) are due to the overpotential and the Joule heat under the current approximations. These heat effects in Eq. (7) are the entropy production [1], [4]. The heat production of the irreversible system is larger than of the reversible one, which it should be, according to the second law. The Joule heat term varies quadratically with the current density, as \( R j^2 \). The non-ohmic heat effect, the last term on the right hand side of Eq.(7), is a heat source which varies non-linearly in \( j \) because the overpotential is a strong function of \( \ln j \).

The overpotentials of the electrodes are here both represented by one symbol \( \eta \). This is possible if they have the same mathematical form. We can assume that the overpotential of the hydrogen electrode is small, and that the overpotential then represents the oxygen electrode overpotential. Above 0.3 V for the single reaction, the overpotential follows the Tafel equation

\[ \eta = \frac{(RT)}{\alpha F} \ln \frac{j}{j_0} \quad (9) \]

or

\[ \eta = a + b \ln j \quad (10) \]

where \( a = - \frac{(RT)}{\alpha F} \ln j_0 \) and \( b = \frac{RT}{\alpha F} \). Here \( j_0 \) is the exchange current density of the cathode, and \( \alpha \) is the transfer factor for the overall reaction of the electrode, while \( a \) and \( b \) are coefficients from a linear fit of data. When we introduce this expression for the overpotential into (6), the power becomes a non-linear function of the current density.

The purpose of this work is twofold. We want to determine the sum of \( P \) and \( Q \) in Eq.(8), and compare this value to \( \Delta Hj/nF \) for the normal cell reaction (a). We also want to calculate the overpotential using Eq.(7) from the total heat production by the fuel cell in the surroundings, \( Q \), the entropy change of the cell, and the measured total resistance and electric current density. We shall see that we can recover \( \Delta Hj/nF \) for reaction (a), but only for cell potentials above 0.55 V. For lower cell potentials, we find a systematic deviation from this value. This supports that the product states are different from those given by Eq. (b) or (c+d). In the regime where the experimental value for \( \Delta Hj/nF \) corresponds to the result of these paths, the Tafel plot from the thermal signature and from the polarisation curve become the same within the accuracies of the calculations.
3. APPARATUS

We report an isothermal calorimeter designed to measure the heat production of a fuel cell. The calorimeter is equipped to measure also the cell potential drop, and the cell electric resistance. The calorimeter was constructed as a cylinder with insulated walls, and with heat transport in the axial directions. A cross section through the axis of the cylinder is sketched in Fig. 2. The cylinder was insulated on the outside by a layer of expanded polyester (not shown).

Three materials were chosen for the construction. They were PEEK (Poly Ether Ether Ketone), copper and steel (ss316). PEEK was chosen as housing material (see Fig.2), because it is a good thermal and electrical insulator, and easy to machine. It was also the mechanically strongest polymer available. Due to high thermal conductivity, copper was used in the end plates and in two internal heaters (see Fig.2) where uniform temperature was required. Stainless steel was used in the polarisation plates next to the membrane-electrode-assembly, MEA, and in the tubes between the heaters and the end plates, where intermediate thermal conductivity was needed. The calorimeter was made symmetric in two pieces, sandwiching the fuel cell and its radial gas seals. It can thus be used to distinguish between heat leaving the cell on the cathode side and on the anode side. The material dimensions were determined using the computational software COMSOL 3.3. By modelling the heat flows from a central source in a suitably constructed grid, we found a suitable length for the steel cylinders between the central heaters and the end plates.

The stainless steel polarisation plate was 11 mm thick. A serpentine flow field (depth, land and channel width equal to 1 mm) was carved into the side next to the fuel cell. Hydrogen and oxygen were fed into the channels via inlets next to the polar plates, see arrows for each gas inlet in Fig. 2. Exhaust gases left the calorimeter through the central axis, as shown in the figure.

The heaters consisted of two copper disks, four and six mm thick, and a resistive heating wire, 10 Ω. The heating wire was laid into a channel which was carved into the thicker copper plate. The channel was two mm deep and two mm broad. By inserting two small K-type thermocouples into holes (diameter 0.7 mm) in the thin disk, we measured and controlled the temperatures of the doubly layered copper heaters. The planar copper surface facing the fuel cell was sealed from the PEEK housing by an O-ring, in a 0.5 mm deep channel in the PEEK. The sealing avoided gas leakage along the walls between the PEEK and the steel cylinder.

The purpose of the steel cylinders were to thermally insulate the copper end plate from the double layered heating plate, so that a significant temperature gradient would sustain throughout experiments at all cell operating conditions and at the same time collect the electric current.

Copper plates were used at the end of the steel cylinders. These end plates were cooled to constant temperature by circulating cold water through copper pipes, soldered onto the plate.

The apparatus allowed us to measure the local temperature at several positions. Potential differences were also measured. The fuel cell potential was measured between the gas flow channel plates. All thermodynamic data in Eqs. (7, 8) therefore refer to the polar plate positions. All parameters were surveyed and logged by a LabView setup. This includes the load (Agilent 6060B), the power supply (Agilent EE3633A), the High Frequency Ohm meter (HFO) (Agilent 4338B) and the gas flow meters (Burkert, CMOSens™). In fact, the LabView setup controlled all parts of the operating system except the heaters in the two copper heaters, the cooling water and the humidification. These were controlled by Eurotherm PID-controllers, a refrigerated water bath and by bubbling feed gases through thermostatted water.
Figure 2. A sketch of the cylindrical calorimeter, cutting through the axis of the cylinder. Potential differences, $E_1$ and $E_2$, and the fuel cell potential, $E_{\text{cell}}$, were continuously measured, along with the four temperatures, $T_{j,i}$. A denotes anode, C denotes cathode, i means inside and o means outside. The two inner temperatures were read to control the heaters. Gases were fed to the cell though the sides (see arrows), and were leaving the cell along the central axis, after passing the gas flow channels.

The fuel cell was put between the mirror symmetric heaters. The fuel cell consisted of a Nafion 112, 115 or 117 membrane sandwiched between pre-made sheets consisting of catalyst layer, micro porous layer and porous transport layer (these three sections were assembled to the SolviCore Catalyst Coated Backing, Batch Number # 205-07-1). The active area was 10.2 cm$^2$. The catalyst and catalyst backing were always the same.

The feed gases were humidified by bubbling them through water at 313 K. The humidifiers consisted of a cylindrical closed water bath, where the gases were bubbled through a porous plug close to the bottom. The humidifiers, containing magnetic stirrers, stood upon a plate which controlled the temperature inside the humidifiers. The stoichiometric flow rates where 1.5 for the hydrogen and 3 for the oxygen. The gases were pure thereby eliminating possible mass transfer limitations to the cell membrane.

4. PROCEDURE

4.1 Measurement

Each experiment started by conditioning the cell. This was done by alternating the cell potential, $E_{\text{cell}}$, between 0.70 and 0.20 V, keeping the voltage ten minutes at each level, until the current responses were reproducible. The procedure was repeated after the experiment to make sure that the cell performance was the same after as before the experiment.
Polarisation curves were next obtained, keeping a constant cell potential, $E_{\text{cell}}$, for one hour at every potential, changing the value in steps of 50 mV from 0.2 V up to OCP. At all currents, the power to the heaters were measured, $Q_{\text{heaters},j}$. The first ten minutes of every step was discarded as the PID controllers required time to adapt to new conditions. To monitor possible ohmic heating in the housing, the potential drops were logged across these regions as well. These potential differences are denoted $E_1$ and $E_2$ in Fig. 2, and represents, along with the total electric current, the resistances $R_1$ and $R_2$, respectively. The cell resistance is obtained by subtracting these resistances from the overall resistance measured with the Agilent high frequency ohmmeter.

The total heat production by the fuel cell was found as the heat production, $Q_{\text{heaters},j=0}$, in excess of the heat produced by the heating elements, $Q_{\text{heaters},j}$, corrected for the cooling of the cell by the feed gases, $Q_{\text{gas}}$, and the ohmic heating in the cell house. Whenever the fuel cell is giving off very little heat, the values of $Q_{\text{heaters},j=0}$ and $Q_{\text{heaters},j}$ are similar, and the accuracy in the determination of the difference goes down.

$$Q = Q_{\text{heaters},j=0} - Q_{\text{heaters},j} - Q_{\text{gas}} - Q_{\text{house ohmic}}$$

(11)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta G^0$ / kJ mol$^{-1}$</th>
<th>$E^0$ / V</th>
<th>$\Delta H^0$ / kJ mol$^{-1}$</th>
<th>$E_{\text{TN}}$ / V</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons H_2O(l)$</td>
<td>-237</td>
<td>1.23</td>
<td>-286</td>
<td>1.48</td>
</tr>
<tr>
<td>$H_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons H_2O(g)$</td>
<td>-229</td>
<td>1.19</td>
<td>-242</td>
<td>1.25</td>
</tr>
<tr>
<td>$H_2(g) + O_2(g) \rightleftharpoons H_2O_2(l)$</td>
<td>-120</td>
<td>0.62</td>
<td>-188</td>
<td>0.97</td>
</tr>
</tbody>
</table>

### 4.2 Data reduction procedure

Some of thermodynamic data used in the calculation are shown in Table 1. The entropy change in the cell is equal to:

$$\Delta S = \Delta S^0 + R \ln \frac{a_w}{(p_{O_2} / p^0)^{1/4} (p_{H_2} / p^0)^{1/2}}$$

(12)

The water activity $a_w$ is unity in pure liquid water. The total gas pressure on both sides is 1 bar. The partial pressures of oxygen and hydrogen are slightly lower than 1 bar, due to the presence of water vapour on both sides. This has a negligible effect on the entropy change (less than 1 % at 323 K), however, leaving us with the standard value.

Integrating from 298 K to the temperature of operation, 323.0 K, the entropy of reaction becomes -164 J K$^{-1}$ mol$^{-1}$, the enthalpy of reaction is -284 kJ mol$^{-1}$H$_2$O, the Gibbs energy change of the reaction is -231 kJ mol$^{-1}$, and the reversible cell potential is 1.20 V. The products $T\Delta S/nF$ and $\Delta H/nF$ are -0.27 and 1.47 V, respectively at 323 K.

The fuel cell electric power output, $P = E_{\text{cell}}j$, was calculated from measured cell voltage, $E_{\text{cell}}$, and the corresponding current density, $j = I/A$, where $I$ is the electric current (in C/s), and $A$ is the area of the fuel cell.
membrane. The total energy production, the thermoneutral power, $\Delta H (j/F)$, was calculated by introducing values of $P$ and $Q$ into Eq. (8).

5. RESULTS AND DISCUSSION

We present and discuss the measured contributions to total energy production in a fuel cell. We demonstrate that the total energy production is reduced at low cell potentials and that the power output from the fuel cell starts to decline simultaneously, and argue that these two trends are related to hydrogen peroxide production. We give also the overpotential of the cell obtained from the thermal signature, and conclude that it compares well to the value obtained from the potential measurements.

5.1. The reaction enthalpy

Typical results for heat and power measurements are shown in Fig. 3 for a cell with a Nafion 112 membrane at 323 K and 1 bar. The heat production is shown by square points as a function of current density. The cell power is shown by circular points. The sum of the two gives the total energy production from the fuel cell. We find that the energy production is directly proportional to $j$ until the current density reaches 0.9 A cm$^{-2}$ in Fig. 3. The theoretical value of the thermoneutral potential for production of liquid water, multiplied by the current density, is presented by the stippled line for comparison. We see a perfect agreement with the value for water production up to the given current density. After that, the total energy production falls below the one expected for water as a product.

In order to elucidate this situation further, we plotted the experimental result for the thermoneutral potential (the derivative of the total energy conversion in Fig. 3 (triangular points)) as a function of the cell potential in Fig. 4. This figure also gives the measured thermoneutral potential from cells using Nafion 115 and 117 membranes. The straight stippled line gives the theoretical value of the thermoneutral potential of formation of liquid water at 323 K, 1.47 V. It is equal to the slope of the stippled line in Fig. 3. A very good agreement between experimental and theoretical values is found for cell potentials above 0.55 V. The measurements show larger scatter in the measured thermoneutral potential at lower than at higher current densities. We compare very similar numbers, i.e. $Q_{j=0}$ vs. $Q_{j=0}$ in this region and fluctuations in the PID controllers enhance the error further. The scatter is randomly distributed, however (see also Figs. 5a and 5b). Below a cell potential of 0.55 V, the thermoneutral potential decreases, approximately linearly with the cell potential (Fig.4). The measurement was repeated several times with different membranes in order to make sure that the drop in the thermoneutral potential was not a random error caused by a poor thermal control of the calorimeter, as we believed at first.

We may speculate on the origin of this decline. The exhaust gases are kept at 50 °C at the polarisation plate and have this temperature when they are passing the heaters. The gases are fed at a rate proportional to the cell current and with constant humidity, and will thus leave at the same condition. The proportion between water vapor and liquid water is therefore expected to be constant in the experiment. The difference in enthalpy of formation for liquid and gaseous water is equal to the vaporization enthalpy for liquid water. Because water vapor in the product would condense at the gas flow plate, the measured heat from the process will thus relate to reaction 1 in Table 1 in any cases. It is therefore unlikely that the decline in the curve is due to production of water vapor instead of liquid water, which gives a smaller enthalpy of reaction. Given this, we must explain the lowering of the thermoneutral voltage in Fig. 4 by another product. Reaction (c) offers hydrogen peroxide as a possible product. The voltage at which it is produced, 0.55 V, supports the idea that hydrogen peroxide leaves the cell as a product.
In order to further test the hypothesis that hydrogen peroxide is formed, we conducted the same experiments with thicker membranes, Nafion 115 and 117, using the same PTL, MPL electrode materials. Fuel cells with these membranes have a higher resistance, and do therefore produce a smaller current at the same cell potential. The measured resistance for the cells where approximately 0.21, 0.41 and 0.71 ohm cm\(^2\), using Nafion 112, 115 and 117 respectively. Vie and Kjelstrup [16] reported 0.31 ohm cm\(^2\) for the total cell resistance at 70 °C using Nafion 112. We see that the thermoneutral potential varies essentially in the same way for all membranes. This supports the idea, that the cell potential, rather than the current density is essential for the decline in the thermoneutral potential. A further illustration of this is shown in Table 2. The table shows the current density for the three cells in Fig. 4 when the cell potential is 0.3 V. A factor 2 variation in current density is seen. The thermoneutral potential is the same within the uncertainties, however. We conclude that formation of hydrogen peroxide may explain the deviation from the straight stippled line in Fig. 4.

![Figure 3. The total heat production (squares), the electrical energy production (circles), and the total energy production (triangles) as a function of current density in an oxygen/hydrogen fuel cell at 323 K and with Nafion 112 membrane.](image-url)
Figure 4. Thermoneutral potential, (circles) as functions of the cell potential, $E_{cell}$, in a fuel cell operated at 323 K, 1 atm and with oxygen. Results are shown for three Nafion membranes.

Table 2. Corresponding values of cell potential, current density and thermoneutral potential recorded at 323 K using oxygen and hydrogen at 1 bar with various cell membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>$E_{cell}$ / V</th>
<th>$j$ / A cm$^{-2}$</th>
<th>$E_{TN}$ / V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion 112</td>
<td>0.30</td>
<td>1.19 ± 0.10</td>
<td>1.37 ± 0.01</td>
</tr>
<tr>
<td>Nafion 115</td>
<td>0.31</td>
<td>0.950 ± 0.001</td>
<td>1.38 ± 0.01</td>
</tr>
<tr>
<td>Nafion 117</td>
<td>0.31</td>
<td>0.602</td>
<td>1.40 ± 0.02</td>
</tr>
</tbody>
</table>

Because energies are additive, the total enthalpy change for reactions 1 and 3 in Table 1 can be written:

$$\Delta H_{tot} = x_{H_2O_2} \Delta H_{H_2O_2} + x_{H_2O} \Delta H_{H_2O} \iff x_{H_2O} = \frac{E_{TN} - E_{H_2O_2}^{TN}}{E_{H_2O}^{TN} - E_{H_2O_2}^{TN}}$$

where $x_i$ is the mole fraction of peroxide and water, respectively. The product water mole fraction, $x_{H_2O}$, corresponds to the current efficiency in water production and can be calculated from Eq. (13), i.e. at 323K thermoneutral potentials of 1.47, 1.43 and 1.39 correspond to mole fractions of water ($x_{H_2O}$), i.e. current efficiencies, of 1.0, 0.92 and 0.84 respectively. This means that our fuel cell produces more than 16 mol % hydrogen peroxide at the lowest cell potential. The peroxide may be diluted by the water transported along with the protons from the anode, so that the end product has a smaller concentration. The mole fraction calculated for water is equal to the current efficiency for water production, and its value is in agreement with other observations [14], [17], [18], [19].

The reduction in current efficiency for water production in the present cell can be compared to the anode processes in the chlorine-alkaline electrolysis cell. This is the largest electrochemical industrial process in the world and is therefore very well studied [20]. Oxygen evolution is thermodynamically favoured over chlorine evolution, while chlorine evolution has greater current exchange density and approximately half the Tafel slope of oxygen evolution. Therefore, when the overpotential increases to a significant level, the chlorine current efficiency dominates. A similar behaviour seems to be the case for hydrogen peroxide production vs. water production at low fuel cell potentials [14], [17], [18], [19].

5.2 The cell power and the polarisation curve

The results of Fig. 4 are further documented in Figs. 5a and 5b, for Nafion 112 and 115, respectively. Both Figs. 5a-b show a decline in the measured thermoneutral potential at high current densities, i.e. for cell potentials below 0.55 V. The polarisation curves and the power density as functions of the current density are also given in these figures. The start of the decline in the thermoneutral power coincides with the peak in the power density and the inflection point in the polarisation curve. The regions for reduced thermoneutral potential are painted gray in Figs. 5a and 5b in order to emphasise the relation between the thermoneutral potential reduction, the peak in the power curve and the inflection point in the polarisation curve. The stippled lines in Figs. 5a and b is meant to illustrate an idealised situation. Linearization of the polarisation curves for potentials between 0.55 – 0.85 V (where the ohmic behaviour is dominating) is used to demonstrate how the power curves would behave if the polarisation curve did not inflect (both stippled). The point where the power
curve peaks and starts to deviate from the idealized (stippled) behaviour systematically related to the reduction of the thermoneutral potential, and thus to the cell potential. Production of hydrogen peroxide leads to a reduction in the electric work, as the reaction Gibbs energy is lowered by approximately a factor two, see Table 1. A decline in the power production, as well as the polarisation curve inflection point, at high current densities is often connected to mass transfer problems, see e.g. [16]. In the present case, where pure humidified gases are fed stoichiometrically, this should not be an issue. If, however, mass transfer limitations occurred for the electrodes, this phenomena should reveal itself at a given current density (mass transfer related) rather than at a given potential (mechanism related). This further supports that the observed decline in the power density and the inflection point on the polarisation curve is related to formation of hydrogen peroxide.

Hydrogen peroxide production is a partial reduction of oxygen, favoured by simpler kinetics, few catalytic sites and high reaction rates, as each oxygen atom only has to exchange two electrons [21]. The catalyst and catalyst backing used here were of a commercial pre-made type. The polarisation curve and the power curve depend on the catalyst and its backing. Peroxide production is unwanted, as it affects the fuel cell life time and leads to detrimental loss in the current efficiency. Knowledge about its production is thus essential for fuel cell construction and operation. The present technique is suited to reveal ill performance.

Figures 5a and b. Thermoneutral voltage (squares), polarisation curve (triangles) and electric power (circles) as functions of current density in a fuel cell operated at 323 K, 1 atm, with oxygen and hydrogen and either Nafion 112 or 115 membranes – a and b respectively.

5.3. The overpotential from the polarisation curve and the thermal signature

The data discussed above were further reduced to give the overpotential of the oxygen electrode.

Figure 6 gives the familiar polarisation curve (triangles); the measured cell potential as a function of current density. It is reassuring to see that the polarisation curve extrapolates to a value just below 1 V as is commonly observed in fuel cells. The constant upper limit is again the total energy production, discussed above. We shall now limit the analysis to current densities, where the electrode reaction proceeds via the four electron step, or via two two-electron steps, since we are after the overpotential for a well defined cell reaction.
Figure 6. The polarisation curve (triangles), the ohmic potential drop (crosses), the measured and theoretical thermo neutral voltages at 323 K (1.47 V) for a fuel cell at 1 bar and 323 K with a Nafion 112 membrane.

The overpotential of the oxygen electrodes was therefore calculated from Eq. (11) using data from Fig. 6 and plotted in Fig. 7. The plot as a function of ln $j$ is done for fuel cell potentials above 0.55 V, as this is the region where we can expect Tafel behaviour for a reaction between two defined states. The contribution from the anode overpotential is normally small [11], and we have assumed that the results reflect the cathode overpotential only. The three terms from which the overpotentials stem, $R_j$, $TΔS/nF$ and $Q/j$ are also shown in the figure. The fit to the plot of $η$ versus ln $j$, gave a straight line, Eq. 15. The cell resistance was 0.45 ohm cm$^2$.

For comparison, the overpotential was also calculated directly from the cell potential and the ohmic potential drop, which is the classical approach. The result is given by Eq. 16. The overpotentials, $η_{thermal}$ and $η_{classic}$, have dimension V and the current density is in A cm$^{-2}$. The two values agree within the accuracy given, though the classical approach gives a better precision in the determination. This is again due to the scattered results caused by the PID controllers, as can be seen from Fig. 7.

$$
η_{thermal} \left( j/A \text{ cm}^{-2} \right)/V = (0.472 \pm 0.007) + (0.063 \pm 0.005)\ln j, \quad j_o = (5.36 \pm 0.02) \cdot 10^{-4}, \quad α = 0.45 \pm 0.04 \quad (15)
$$

$$
η_{classic} \left( j/A \text{ cm}^{-2} \right)/V = (0.447 \pm 0.002) + (0.0577 \pm 0.0016)\ln j, \quad j_o = (4.24 \pm 0.01) \cdot 10^{-4}, \quad α = 0.483 \pm 0.015 \quad (16)
$$

The transfer factor was calculated to 0.45 from the thermal signature and 0.483 from the classical approach. The transfer factors can be compared with the value given by Okada and Kaneo [12]. They reported Tafel slopes for path (b) or (c+d) equal to $2.3 \, \frac{RT}{F}$, or $α = 0.43$ [12].

The intercepts on the y-axis gave exchange current densities of 9.8 and $3.5 \times 10^{-4}$ A cm$^{-2}$ referred to membrane area, from the two approaches respectively. We did not determine the area of the catalyst, so it is not possible to give absolute exchange current densities.
5. CONCLUSIONS

One aim of the present work has been to document that the thermal signature of the fuel cell is useful. For this purpose we have constructed a calorimeter that is tailor-made to find the heat production corresponding to a fuel cell power. We report some first results of calorimetric measurements in combination with standard electrochemical measurements, and show that new information can be obtained.

A first set of in situ calorimetric measurements has thus been presented for the single polymer electrolyte fuel cell. We also report a non-ohmic heat production, compatible with Tafel’s equation, an exchange current density of $5.4 \times 10^{-4} \text{ A/cm}^2$ (referred to the membrane area) and a transfer factor of 0.45. We have demonstrated for the first time that the electrode overpotential in a cell can be determined via a characteristic heat production.

We have seen that the combined measurements indicate that hydrogen peroxide takes place when the cell voltage falls below 0.55 V. We have demonstrated that this effect is partly imposes the location of the peak in the power density curve and the inflection point in the polarisation curve. At a cell potential of 0.3 V, the current efficiency for production of water may be as small as 85 %. If this is the sole reason for a deviation observed in the energy production, it represents a more important loss in electric power at high current densities than diffusion limitations do.

ACKNOWLEDGMENTS

The authors acknowledge the Norwegian Research Council for financial support, the RENERGI program, grant number 164466/S30. SolviCore is acknowledged for providing fuel cell parts.
REFERENCES