Calorimetric study of the PEMFC

O. Burheim[1], P. J. S. Vie[2], S. Møller-Holst[3], J. Pharoah[1, 4] & S. Kjelstrup[1]

[1] NTNU, Dept. of Chemistry, [2] IFE, Kjeller, [3] SINTEF Materials [4] On leave from Queen's RMC FCRC

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 a Nafion RE112 membrane. 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. There is a linear decrease in the total reaction enthalpy as function of the cell potential for these lower cell potentials. This trend is observed independently of current density and membrane thickness. We propose that the main cause of power loss at high current densities is due to hydrogen peroxide formation. The total heat production was decomposed into reversible and irreversible effects (ohmic and non-ohmic). We show that it is possible to determine the overpotential of an electrode from its thermal signature.

Objectives

Monitor heat production of a PEMFC in order to
* elucidate energy losses
* investigate reaction routes and product states

Measurements & Apparatus

The fuel cell heat

•The fuel cell heat production is calculated from measuring various heat sources in a calorimeter. Equation 1.

•The calorimeter contains two heating elements regulated by PID controllers. We measure this heat and use it to obtain the other heat contributions.

•The heat contribution from the feed gases, Q_{gas}, is measured at nil current. The ohmic heating of the house is calculated from the measured potential drops, E_1 and E_2, and the total cell current, I. Equation 2.

•Thus we obtained all the heat from the fuel cell reaction and the electric power to finally obtain the reaction enthalpy and the thermoneutral potential. Equation 3.

•By separating the heat sources in the fuel cell one can obtain thermal signature of the overpotential, and use it to obtain Tafel constants, Equation 4 and 5. We report the Tafel behaviour obtained both by the classical potential approach and the thermal signature.

Figure 1 The cross section of the calorimeter used for the calorimetric measurements.

$$Q_{FC} = Q_{heaters, j=0} - Q_{heaters, j} - Q_{gas} - Q_{house\ ohmic} \quad (1)$$

$$Q_{house\ ohmic} = (E_1 + E_2)\ I \quad (2)$$

$$P_{FC} + Q_{FC} = -\frac{\Delta H}{F} j = E_{TN} \cdot j \quad (3)$$

$$Q_{FC} = -\frac{T\Delta S}{F} j + \eta j + R_{FC} j^2 \quad (4)$$

$$\eta = \frac{Q_{FC}}{j} + \frac{T\Delta S}{F} - R_{FC} j \quad (5)$$

Thermodynamics

The fuel cell reaction

•The work and heat from and electrochemical reaction adds up to the reaction enthalpy, ΔH, a.k.a. the thermoneutral potential, nFE_{TN}. Eq. 6 and 7.

•For any chemical process giving several products the total enthalpy equals the sum of the fractional reaction enthalpies. Eq. 8 and 9.

•Possible reactions for the PEMFC is given in Table 1 along with some thermodynamic data.

$$\Delta H = \Delta U - p\Delta V = q_{rev} - E_{rev} F \quad (6)$$

$$E_{rev} \cdot F = -\Delta G = T\Delta S - \Delta H \quad (7)$$

$$\Delta H_{tot} = \sum_{i=1}^{n} x_i \Delta H_i \quad (8)$$

$$\Delta H_{tot} = x_{H_2O_2} \Delta H_{H_2O_2, l} + x_{H_2O, l} \Delta H_{H_2O, l} \quad (9)$$
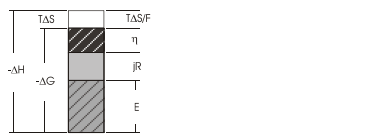

Figure 2. The thermodynamics energies (left side) and electrochemical potentials (right side) of an electrochemical reaction.

Table 1.   Standard state thermodynamic data for one mole product at 298 K. [1]

		$\Delta G°$ / kJ mol^{-1}	$E°_{cell}$ / V	$\Delta H°$ / kJ mol^{-1}	$E°_{TN}$ / V
$H_{2,(g)} + \frac{1}{2} O_{2,(g)} \rightleftharpoons H_2O_{(l)}$	a	-237	1.23	-286	1.48
$H_{2,(g)} + \frac{1}{2} O_{2,(g)} \rightleftharpoons H_2O_{(g)}$	b	-229	1.19	-242	1.25
$H_{2,(g)} + O_{2,(g)} \rightleftharpoons H_2O_{2,(l)}$	c	-120	0.62	-188	0.97

Results

Reaction Enthalpy of a the PEMFC

For a PEMFC run with 1 bar oxygen / hydrogen at 50 °C and different membrane differences;

•The thermoneutral potential of the fuel cell, E_{TN}, is found to be proportional to the cell potential, E_{TN}, when the cell potential is less than 0.55 V. Figure 3.

•For cell potentials below 0.55 V liquid water is not the only product.

•The calorimeter is run such that all water leaving the cell is liquid and thus reactions *a* and *c* in table 1 are the only likely reaction possibilities. This is observed elsewhere too. [2]

•The peak in the power/current curve takes place at the simultaneously as the drop in the reaction enthalpy. Figures 3 and 4.

•The inflection point in the cell potential curve also occurs simultaneously to the enthalpy drop. Figures 5 and 6.

•The loss in cell performance at low cell potentials is clearly related to hydrogen peroxide formation.

•The lowered thermoneutral potential is not directly related to membrane thickness or cell current. Table 2.

Table 2. Corresponding cell potentials, current densities and thermoneutral potentials recorded at 50 °C.

	E_{cell} / V	j / A cm^{-2}	$E_{thermoneutral}$ / V
Nafion 112	0.30	1.19 ± 0.10	1.37 ± 0.01
Nafion 115	0.31	0.950 ± 0.001	1.38 ± 0.01
Nafion 117	0.31	0.602	1.40 ± 0.02

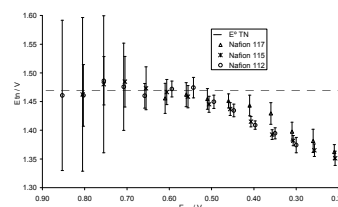Figure 3. Measured Thermoneutral Potential (ΔH j / n F) for the fuel cell as a function of cell potential. The values are measured at 50 °C, 1 bar oxygen / hydrogen and with Nafion112, 115 and 117 membranes.
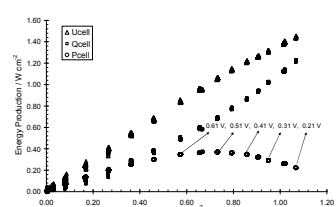

Figure 4. Measured energy conversions as a function of current density in a fuel cell. The values are measured at 50 °C, 1 bar oxygen / hydrogen and with Nafion 115 membrane.

Thermal signature of the Tafel slope

•We have thermal signature from the over-potential and plotted it as a function of the natural logarithm of the current density. We have demonstrated that the Tafel behaviour could be obtained from the thermal signature. Equations 10 and 11. Due to the change in the chemical reaction, as stated above, we believe that only cell potentials above 0.55 V should be used for obtaining the Tafel potential behaviour.

$$\eta_{thermal}\ (j / A\ cm^{-2}) / V = (0.488 \pm 0.008) + (0.070 \pm 0.006) \ln j, \quad j_o = (9.80 \pm 0.04) \cdot 10^{-4}, \quad \alpha = 0.40 \pm 0.06 \quad (10)$$

$$\eta_{electric}\ (j / A\ cm^{-2}) / V = (0.510 \pm 0.004) + (0.064 \pm 0.003) \ln j, \quad j_o = (3.46 \pm 0.01) \cdot 10^{-4}, \quad \alpha = 0.44 \pm 0.02 \quad (11)$$
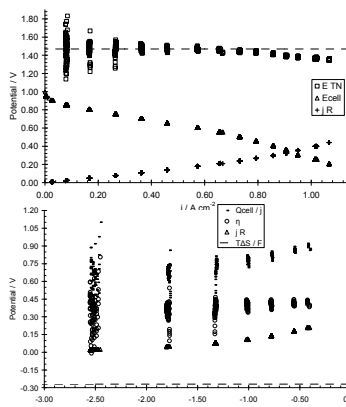

Figure 5. Measured potential in a fuel cell operated at 50 °C, 1 bar hydrogen / oxygen and with Nafion 115 membrane. The upper graph gives potentials as functions of current density while the lower graph gives the potentials as functions of the logarithm of current density.
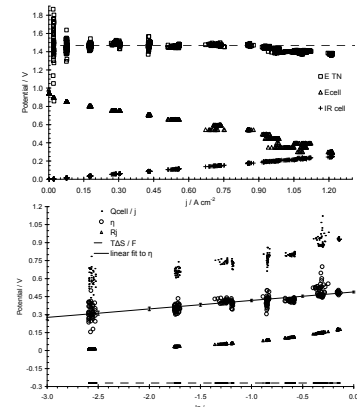

Figure 6. Measured potential in a fuel cell operated at 50 °C, 1 bar hydrogen / oxygen and with Nafion 112 membrane. The upper graph gives potentials as functions of current density while the lower graph gives the potentials as functions of the logarithm of current density.

References

1. G. Aylward and T. Findlay, *SI Chemical Data*, 5th edition, Wiley, New York, 2002

2. Ichiro Yamanaka, Direct synthesis of H$_2$O$_2$ by a H$_2$/O$_2$ Fuel cell, *J. Catal Surv Asia* (2008) 12:78-87.

3. Burheim et al., Electrochimica Acta, 2009. (resubmitted 2009.09.14)

Conclusions

•The PEMFC produce both water and hydrogen peroxide for cell potentials below 0.55 V

•It is very likely that the inflection point in the potential curve and the peak in the power curve is effected by the production of hydrogen peroxide.

•A calorimeter is a highly important diagnostic tool for the fuel cell research.