

PEMFC systems: the need for high temperature polymers as a consequence of PEMFC water and heat management

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Abstract

The proton exchange membrane fuel cell (PEMFC) is usually operated at elevated pressure, requiring the use of a compressor. Also the operating temperature is low, generally below 80 °C. For many applications, a somewhat higher operating temperature would be preferable. This paper describes the reasons for pressurised operation at, or close to, 80 °C in terms of water and heat management issues. It is concluded that a new type of proton conducting material is highly desirable, having many of the good Nafion properties, but based on a proton conduction mechanism that does not require the presence of large amounts of water in the electrolyte.

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1. Introduction

It is quite common to operate proton exchange membrane fuel cell (PEMFC) systems at pressures of 2–3 bar (a) and at or below 80 °C. Pressurised operation requires that the system includes a compressor, possibly an intercooler and an expander to reclaim part of the energy that was required for compression. A typical air management system is given in Fig. 1. The relevant components are

- a compressor or blower;
- the humidifier, which may be integrated with the cooling circuit;
- the stack (cathode);
- a water separator;
- a pressure release device (backpressure controller or expander);
- a cooling circuit: pump, buffer and heat exchanger.

In case of pressurisation above about 1.6 bar an air cooler is required. Cooling of the inlet air can also be done by injection of water into the compressor, this option is however not considered here.

For many systems, the use of a compressor is not a viable option. In particular this is the case for small systems. These systems require low airflows, for which efficient compressors are not available. Also noise and wear may not be acceptable. Such systems are operated close to atmospheric pressure. In this case, the operating temperature will be limited to 60–65 °C. This may or may not be acceptable,

depending on the application. Some applications however, would benefit from a higher operating temperature in order to make use of the waste heat or to reduce heat rejection problems. This paper addresses why PEMFC systems have difficulty in being operated at both a low pressure and high (>70 °C) temperature.

2. Theory

Application of Faraday's law yields the relation between the current I and the dry air feed (g/s) [1].

$$q_{\text{air}} = \frac{M_{\text{air}} I \lambda_{\text{air}}}{n N e x} \quad (1)$$

where I is the current produced (A), n the number of electrons involved in the reaction (in this case, $n = 2$), e is elementary charge ($1.6022\text{E}-19$ Coulomb), N the Avogadro's constant ($6.022045\text{E} \pm 23 \text{ mol}^{-1}$), λ_{air} is the air stoichiometry (the inverse of the oxygen utilisation), x the fraction of oxygen in air (0.20946), M_{air} the molar mass of air (28.964 g/mol)

For the remainder, all calculations are based on the general gas law.

$$\frac{PV}{T} = R$$

and the associated equations

$$p_i = \frac{m_i}{V} \frac{R}{M_i} T$$

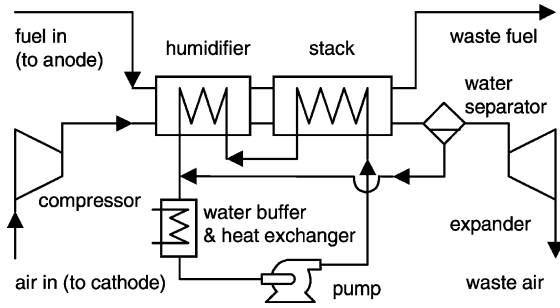


Fig. 1. Simplified lay-out (intercooler not shown).

to calculate the partial pressure for each component in a gas mixture and

$$p = \rho \frac{R}{M} T$$

for calculations on gas mixtures, in which the weighted harmonic mean \bar{M} of the individual molecular weights M_i of the gases present in masses m_i in the gas mixture is calculated using

$$\bar{M} = \frac{m_1 + m_2 + \dots}{m_1/M_1 + m_2/M_2 + \dots}$$

The calculation of $p_{\max, \text{H}_2\text{O}}(T)$, the maximal water vapour pressure as function of temperature, was done using a polynomial approximation of water vapour pressure data taken from [1].

3. Experimental

To assess the effect of pressure and temperature on cell performance, a 7 cm² cell was operated at 1, 1.5 and 2.5 bar (a), and at temperatures of 65 and 80 °C. An air stoichiometry of 2 was maintained by continuously adjusting the cathode flow rate as function of current density. The MEA was made using E-Tek electrodes and a membrane prepared by filling a 50 μm 85% porous substrate (Solupor) with Nafion ionomer [2]. Both anode and cathode gases were fully humidified. Polarisation curves obtained with this cell under various P, T conditions are given in Fig. 2.

Although the PEMFC can be operated over a wide range of the displayed curves, it should be noted that cell efficiency is proportional to cell potential, and is in first approximation given by $\eta_{\text{cell}} = 0.8V_{\text{cell}}$ (V_{cell} in volts, η_{cell} is with respect to LHV, at 100% H₂ utilisation). For that reason, operation at a potential lower than 0.6–0.7 V hardly is attractive. Power density curves are given in Fig. 3. Opting for the highest power density is tempting in order to reduce the power specific size, weight and cost of the stack.

However, compression of air takes energy, and these losses should be accounted for. The polarisation curves given in Fig. 2 can be corrected to account for the losses for compression. A straightforward way to do this is to

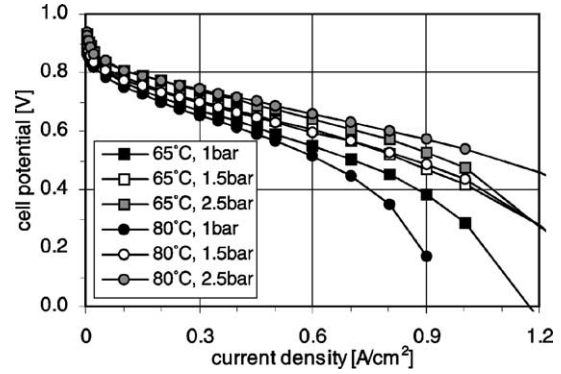


Fig. 2. PEMFC polarisation curves.

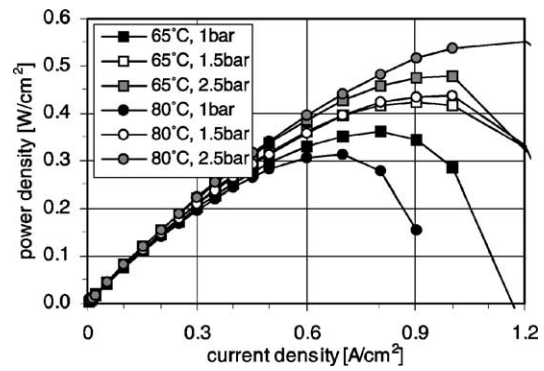


Fig. 3. Power density curves.

reduce the cell potential at given current I with a voltage ΔV , such that $I\Delta V$ equals the power required for compression of the air required at that current. The amount of air depends on the operating conditions. At an individual cell potential of 0.675 V and an air stoichiometry of 2, the air consumption of a 50 kW system is 150 Nm³/h. The calculated compressor power as function of pressure ratio is given in Fig. 4 ([3], based on 20 °C inlet temperature and 70% compressor efficiency).

Using the calculated energy consumption for air compression, the curves of Fig. 2 were corrected, see Fig. 5. For the 50 kW (gross power) system referred to in this paper the compressor uses 8.6 kW, equivalent to 17% of the power

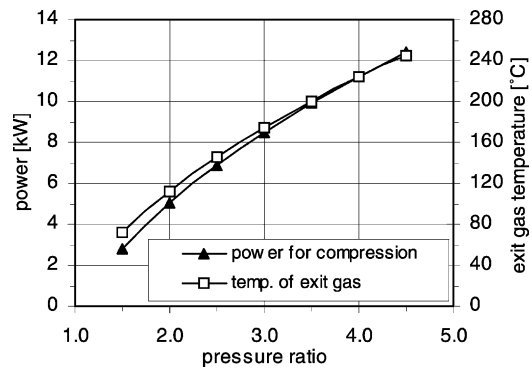


Fig. 4. Calculated shaft power and gas exit temperature for compression of 150 Nm³/h air.

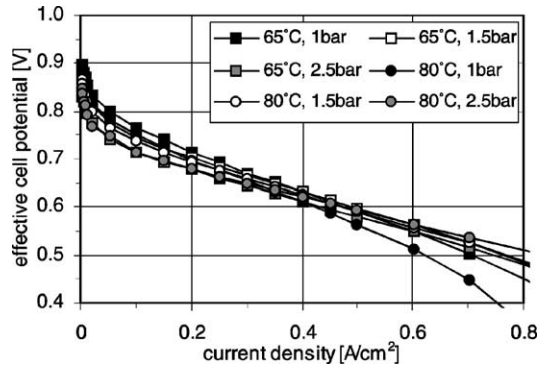


Fig. 5. $V_{\text{effective}}$, based on Fig. 2, corrected for energy consumption for compression.

produced by the fuel cell. The actual power losses will be slightly higher due to losses in the drive motor and power electronics. On the other hand, for large systems for which a compressor expander can be used the losses can be reduced. For very small systems (less than several kW), more severe losses must be accounted for, since small air compressors are not likely to attain 70% efficiency.

Ultimately, the two parameters that are of relevance for the system developer and user are the net power density and the system efficiency. For the system dealt with here, the efficiency is mainly determined by cell efficiency and losses for compression. Using the approximate relation between cell potential and cell efficiency, $\eta_{\text{cell}} = 0.8V_{\text{cell}}$, the system efficiency is given by $\eta_{\text{system}} = 0.8V_{\text{effective}}$. The effective cell potential can also be used to calculate the net power density. The resulting relation between net cell power density and system efficiency is given in Fig. 6. From this, it is concluded that the net effect of pressurisation is negligible at preferred operating conditions, that is, at current densities of less than about 0.6 A/cm². So, if for reasons of efficiency, high cell potential/low cell current density operation is preferred, and if no net system power gain is achieved under such conditions, then why would one prefer pressurised operation? The reason is that at pressurised conditions, the water vapour pressure has less effect on water balance, gas flow rates and gas composition. In the following, this will be shown for the air system only.

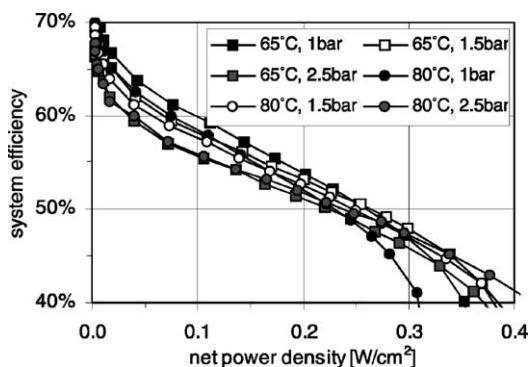


Fig. 6. Relation between system efficiency and net power density.

4. Consequences of high relative humidity

The performance of the PEMFC strongly depends on the conductivity of the polymer [4], which is strongly related to the relative humidity of the gas the cell is in contact with. The requirement of working at saturated gas conditions may perhaps not make it impossible to operate the PEMFC at low P and relatively high T , but such conditions require an adapted design of stack and system. High water vapour pressures lead to strong dilution of reactants by water vapour and large heat exchange surfaces.

In terms of water management, the following occurs in the cathode line.

4.1. Humidifier

The air is humidified and heats up to stack temperature. Using saturation vapour pressure data found in literature [1], the consequences of working at 100% RH are analysed. First of all, the addition of water vapour increases the volume of gas flowing through the system (when pressure is kept constant). Especially at high temperature and low pressure, the increase in gas volume is substantial (Fig. 7). The hydraulic implications of the increase in gas volume have to be taken into consideration in the design of the fuel cell stack and the system. The pressure drop in a tube is given by the equation

$$\frac{dp}{dl} = -\frac{\lambda^l}{d} \frac{1}{2} \rho v^2 \quad (2)$$

where dp is the pressure drop over length dl , λ^l the dimensionless friction factor, d the inside pipe diameter, ρ the average gas density over length dl , and v the average gas velocity. The pressure drop is proportional to the product of the gas density and the square of the gas velocity, although λ^l is dependent on the Reynolds number, and therefore gas velocity as well. The effect of humidification is that due to the addition of water vapour, the gas density decreases whereas the gas volume increases. The lower gas density results in a lower pressure drop in pipes and bends. The

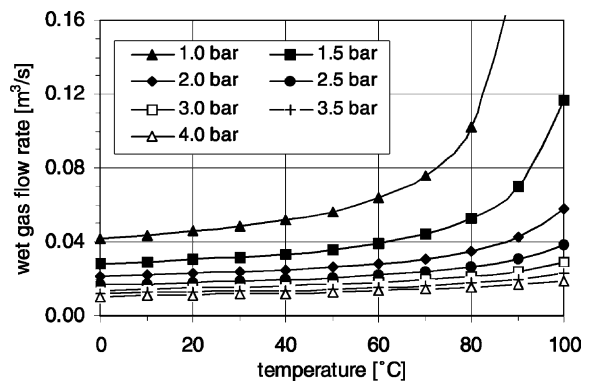


Fig. 7. The calculated wet gas volume at various temperatures and pressures. The original dry gas flow rate used in this calculation is 150 Nm³/h, or 0.042 Nm³/s.

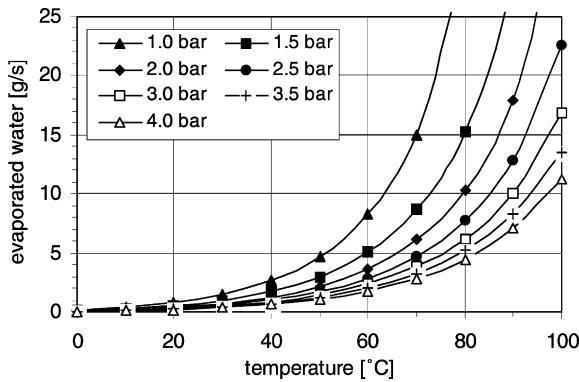


Fig. 8. The amount of water required to humidify 150 Nm³/h of initially dry air, as function of temperature and pressure.

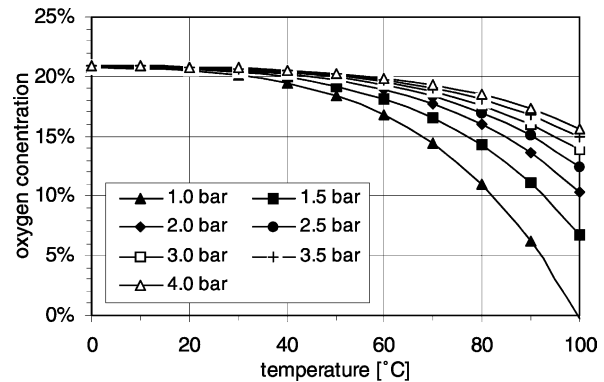


Fig. 10. Calculated oxygen concentration in fully humidified air, in dependence of pressure and temperature.

increased volume however will have a much stronger effect, resulting in an increased pressure drop. This can be compensated for by increasing the diameters of flow channels in the fuel cell stack and system piping. This will however, result in increased system volume and weight.

A trivial consequence of humidification is that water is consumed (Fig. 8). This will particularly becomes relevant if the water that is produced in the stack is not sufficient to compensate for the water used in the evaporator. The evaporation of water takes energy (Fig. 9). This energy can be taken from the cooling circuit, in which case no extra energy is required. The waste heat of a 50 kW fuel cell stack operating at 0.675 V individual cell potential (the basis for these calculations) under condensing conditions is 61 kW. Comparing this number with the values given in Fig. 9, it can be concluded that there should generally be no problem to fulfil this heat demand.

4.2. Cathode

The addition of water vapour results in a dilution of the oxygen present in air (Fig. 10). The concentration shown here is that at the cathode inlet. It can be concluded that working at low *P*, high *T* conditions leads to high oxygen dilution, which decreases cell performance. Since oxygen is

used in the fuel cell reaction, the downstream part of each cell is exposed to substantially lower concentrations.

Under the conditions assumed here (50% oxygen utilisation), half of the oxygen is used by the electrochemical reaction taking place in the fuel cell. Since this reduces the volume of gas, some of the water originally present in the vapour phase will condense out to form liquid water. This produces heat, which has to be removed by the stack coolant circuit. Also, some water is produced, in addition of the water produced by the electrochemical reaction. So, in the cathode, a two-phase flow is established.

4.3. Water separator

The liquid water is separated from the cathode exit gas by a water separator. The amount of water that is collected should match the amount needed for humidification. Fig. 11 shows the water surplus of a system as function of *P* and *T*. Negative numbers indicate a net water loss from the system. One way to prevent a system from turning into a net water consumer is to cool the water separator, such that it now becomes a condenser. This may seem unattractive since it apparently increases the amount of heat that has to be discarded to the surroundings, which is very undesirable for automotive applications. Theoretically, this is not the

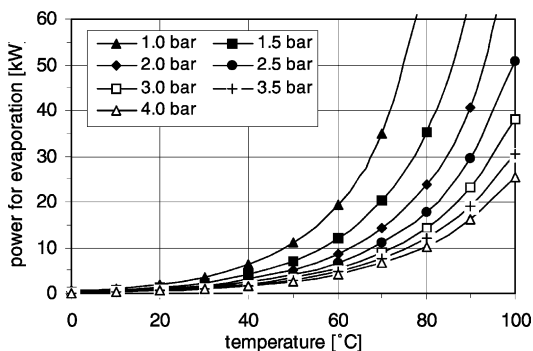


Fig. 9. The power required to fully humidify 150 Nm³/h of initially dry air, as function of temperature and pressure.

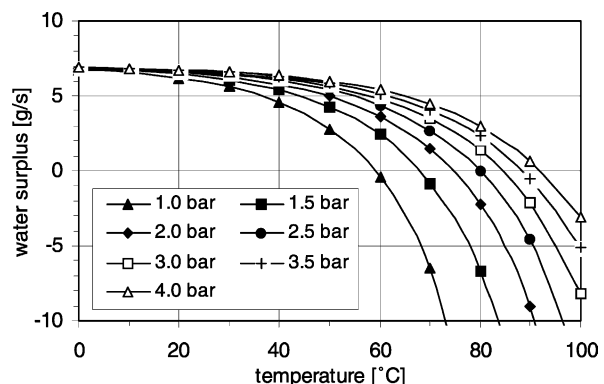


Fig. 11. Water surplus for the system shown in Fig. 1.

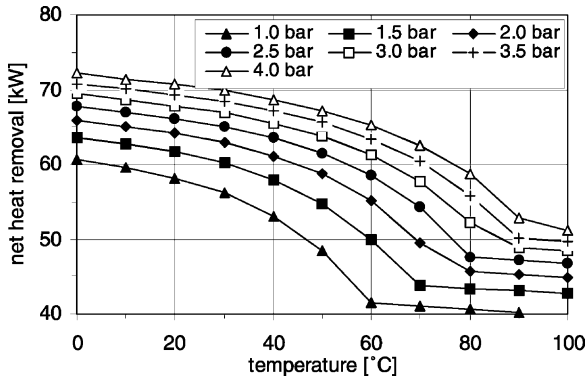


Fig. 12. The calculated amount of sensible heat that has to be discarded to the surroundings.

case however since under these conditions a large amount of heat is taken from the stack coolant flow, to provide the heat required for evaporation of the large amount of water for humidification. So, there is merely a shift of the heat removal problem.

4.4. Overall heat management

One can try to match heat sources and sinks, to avoid the need for external heating and to reduce the amount of heat that has to be discarded by a radiator. Even if such matching could be done perfectly, a net cooling duty is still necessary. This is shown in Fig. 12. At low temperatures, the water content of the cathode exit gas is low. Little heat is removed in the form of latent heat, but as sensible heat instead. As temperature increases, cathode exit gas humidity increases, and the net sensible heat removal from the system is reduced. At even higher temperatures the water separator has to be cooled in order to become a condenser, e.g. at 60 °C for the 1 bar situation. For high operating pressures, the heat removal by latent heat is relatively low, since most water is in the liquid form. In addition, a significant cooling duty is required for the inter cooler.

5. Discussion

From Fig. 12 it seems logical to conclude that working at low P and high T is most attractive. A compressor is not required, and heat rejection to the surroundings is minimised. However, to make such a system work, huge amounts of water have to be evaporated in the humidifier, requiring large amounts of heat. The water condenser has to make up for the water used in the humidifier and therefore has to withdraw large quantities of heat from the humid cathode exit flow. In the calculations used to produce Fig. 12, the heat sources and sinks are coupled. This is however, not realistic at high T , low P combinations, as can be deduced from Fig. 13. Here, the sum of the duties of the air cooler after the compressor, the humidifier, the condenser and the external

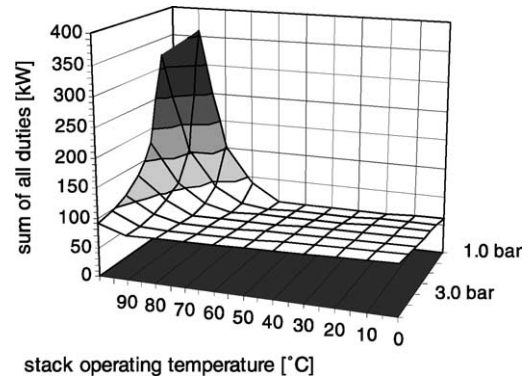


Fig. 13. Sum of duties of air cooler, humidifier, condenser and external heat exchanger as function of stack operating temperature and pressure.

heat exchanger (e.g. car radiator) is presented. From Fig. 13, it can be concluded that working at high T and low P will lead to huge heat duties (hence sizes) for the heat exchanging components. In combination with the large wet gas volumes (Fig. 7), there will be a large effect on system size.

To resume the essentials of all the above, an analysis is made of six system cases, each in the range of 40–50 kW (gross) power (Table 1). The systems are operating at 65, 80 °C and 1, 1.5 and 2.5 bar based on single cell performances given in Table 1. It is assumed that the systems all operate at a current density of 0.6 A/cm². This assumption implies that the systems use the same amount of reactants (H₂: 30 Nm³/h, air: 145 Nm³/h). In the table, a new term is introduced, the “relative pressure drop factor” derived from Eq. (2): $\rho_{T,p}(V_{T,p})^2 / \{\rho_{80^\circ\text{C},2.5\text{bar}}(V_{80^\circ\text{C},2.5\text{bar}})^2\}$. Here, $\rho_{x^\circ\text{C},y\text{bar}}$ is the humid gas density at $x^\circ\text{C}/y\text{bar}$, whereas $V_{x^\circ\text{C},y\text{bar}}$ is the wet gas volume at $x^\circ\text{C}/y\text{bar}$. The reference is the 80 °C/2.5 bar case. Assuming equal stack design and system piping in all 6 sample cases, and neglecting the effect of the Reynolds number, the “relative pressure drop factor” is presented as an indicator for the effects of operating conditions on pressure drops in the system.

From Table 1, it can be concluded that the most pronounced differences in the sample systems are in the amounts of heat that have to be rearranged in the systems, and in the relative pressure drop factors. It is also concluded that working at atmospheric pressure and temperatures of 65 °C and higher is rather complicated. The 80 °C/1 bar case is the most extreme. The high wet gas flow has significant consequences for the pressure drop in the system. The heat required for humidification can be equal to the waste heat of the stack, making it difficult to humidify the gases with the stack coolant water. The oxygen concentration at the cell inlet drops to just 11%. Also, the sum of all heat exchanger duties is increasing significantly, leading to large system dimensions.

It seems that the use of a compressor is inevitable if heat rejection to the surroundings demands for operating temperatures of close to 80 °C. For many applications a different parameter setting would be much more attractive though.

Table 1
Overview of essential numbers for six sample systems

	65 °C			80 °C		
	1 bar	1.5 bar	2.5 bar	1 bar	1.5 bar	2.5 bar
Power at the rate of 600 mA/cm ² (kW)	39.6	43.5	46.3	37.0	43.0	47.4
Compression losses (kW)	0	2.8	6.7	0	2.8	6.7
Net power (kW)	39.6	40.7	39.6	37	40.2	40.7
Wet gas flow rate (m ³ /h)	241	145	80	358	184	93
Oxygen concentration ^a (%)	15.7	17.5	18.9	11.0	14.3	17.0
Duty of air cooler (kW)	Not required	0.3	4.3	Not required	Not required	3.5
Heat requirement humidifier (kW)	25.1	15.1	8.4	66.7	34.2	17.3
Heat production stack ^b (kW)	69.8	64.9	61.4	76.8	67.4	61.2
Duty condenser (kW)	6.7	Not required	Not required	44.2	15.1	Not required
Net system cooling duty (kW)	51.4	50.1	57.3	54.3	48.3	47.4
Sum of all duties ^c (kW)	101.6	80.3	74.1	187.7	116.7	82
Relative pressure drop factor ^d	16.4	3.8	0.7	41.9	6.9	1

^a At cathode inlet.

^b Includes heat released due to condensation of water as a result of gas volume reduction.

^c Sum of absolute value of duties, relevant for overall system dimensions.

^d $\rho_{T,p}(V_{T,p})^2 / \{\rho_{80^\circ\text{C},2.5\text{bar}}(V_{80^\circ\text{C},2.5\text{bar}})^2\}$, Relevant for the pressure drop in the system.

Preferably, the temperature should be even higher. That is, close to or above 100 °C. The pressure should be close to atmospheric to avoid compressors. For cars, the higher operating temperature helps to alleviate the problem of heat rejection to the surroundings¹. For stationary applications, the benefit of a higher operating temperature would be in the more versatile use of the waste heat for space heating and hot tap water.

This paper demonstrated the effect of maintaining 100% relative humidity conditions on operating conditions. The need for operation at such high relative humidity is linked to the characteristics of Nafion and similar proton conductors. It will be clear that as long as such polymers are used in the PEMFC, the problems of pressurised operation and heat and water management will not be solved. This will only be the case if a new type of proton conductor is found, allowing for

operation at higher temperatures and low relative humidity. Preferably, such a polymer should still have the good properties of Nafion type polymers: cold start capabilities, toughness and good proton conductivity.

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¹The problem of heat rejection is evident when examining current experimental fuel cell vehicles, such as the Daimler Chrysler Necar 4, which have radiators that are substantially larger than those found in the standard ICE powered cars.