

## Solid polymer fuel cells for pulse power delivery

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Received 8 November 1996; accepted 27 November 1996

### Abstract

Solid polymer fuel cells have been identified as suitable sources for the delivery of short duration, high power pulses. A number of membrane/electrode assemblies, cell designs and component materials have been tested under continuous load conditions to enable an optimised fuel cell to be constructed and to allow comparisons with pulsed load conditions. Each cell was subjected to pulsed loads of one second duration to identify the best cell components and the power losses associated with this regime. Best performance was obtained with low equivalent weight, thin membranes with high catalyst utilisation and optimised flow designs.

*Keywords:* Fuel cells; Proton exchange membrane; Applications/military

### 1. Introduction

Electromagnetic (EML) and electrothermal chemical (ETC) launchers have received a great deal of interest in recent years as conventional powder-charge guns have practically reached their design limitations. These launchers require enormous energy of short duration (~10 MJ for EML and 5 MJ for ETC). The supply must be low voltage (100 V) but very high current and preferably capable of delivering repetitive pulses. Solid polymer fuel cells are likely candidates for powering such a system as a result of their high gravimetric and volumetric power densities along with their rapid response times.

Solid polymer fuel cells have been the subject of intensive research and development in recent years due to the high power densities they offer [1]. Additionally their low operating temperatures (<100°C), fast start-up, low emissions, quiet operation and system robustness has seen them targeted at a wide range of applications. Improvements in membrane/electrode assembly technology, catalyst utilisation, cell design and materials manufacturing issues has seen a steady increase in performance whilst reducing cost.

The aim of this investigation was to operate a single fuel cell on short duration, pulsed loads to achieve maximum power densities by minimising power loss from each component of the system. The performance of the cell under

continuous load was compared to pulsed mode operation to assess the gains achieved by this regime.

### 2. Theory

A fuel cell is an electrochemical device which converts the free energy of an electrochemical reaction directly into electrical energy. This conversion takes place without any intermediate thermal step and so, in a similar manner to a battery, Carnot cycle restrictions are avoided.

A proton exchange membrane fuel cell (PEMFC) consists of two electrodes separated by a polymer membrane electrolyte. Hydrogen (fuel) is supplied to one electrode and oxygen or air (oxidant) is supplied to the other. At the anode, electrons are released to the external circuit as hydrogen is oxidised to protons which migrate across the membrane surrounded by a cluster of water molecules. Oxygen is reduced at the cathode, combines with the migrating protons, and water is produced.

PEMFCs use ion-exchange polymers as electrolytes; these are electronic insulators but excellent proton conductors. The electrolytes most commonly used are perfluorinated sulfonic acid membranes, which consist of a fluorocarbon polymer backbone, similar to PTFE, to which sulfonic acid groups have been chemically bonded. The acid groups are immobile within the polymer but the acidic protons are free to migrate. Commonly used electrolytes include the Nafion™ series of membranes manufactured by DuPont.

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The electrolyte is used in the form of a thin membrane, typically 75–175  $\mu\text{m}$  thick. The electrodes are prepared by applying catalyst, normally platinum black or supported platinum, to one surface of a support material. The electrolyte is then sandwiched between the anode and cathode electrodes to form a membrane/electrode assembly (MEA). The electrodes are connected to the external circuit by current collectors into which gas and fluid flow-channels have been formed. These channels supply hydrogen gas to the anode and oxygen or air to the cathode whilst facilitating product water removal from the cell.

### 3. Operating principles

The temperature and pressure of operation for a PEMFC can have a significant effect upon its performance [2]. Operating temperatures are usually in the range of 50 to 100°C. If adequate humidification is available, cell performance increases with temperature due to increased proton mobility within the polymer electrolyte. This effect is limited by the glass transition temperature of the electrolyte, which for Nafion™ 1100 is  $\sim 125^\circ\text{C}$ . The potential of the cell increases with increasing gas pressure according to the equation:

$$E_p = E_1 + b \log P$$

where  $E_p$  is the cell potential at pressure  $P$ ,  $E_1$  is the cell potential at 1 bar and  $b$  is related to the Tafel slope for the reaction. In practice, diminishing performance gains mean that useful gain is lost at approximately 6 bar. Whereas the majority of PEMFC development presently concerns cells optimised to run on air only, fuel cells with oxygen are capable of achieving the highest power densities [3,4].

Generally the thinner the membrane used as the electrolyte the lower its contribution to the ohmic resistance of the cell. Thin membranes also reduce mass transport limitations as the transport of water across them is facilitated. Much of the development work has been carried out with Nafion™-117 (equivalent weight 1100, thickness 7 mil), a membrane developed in 1962 specifically for the chlor-alkali industry. Recently, membranes have emerged that have been developed specifically for fuel cell use, such as those manufactured by DuPont, Dow Chemical, Asahi Glass, and W.L. Gore and Associates Inc. These membranes tend to be thinner and of lower equivalent weight compared to Nafion™-117. Power densities up to 3  $\text{W cm}^{-2}$  have been reported for advanced membranes of this type [1], achieved by enhanced electrolyte conductivity and improved water retention capability.

Humidification of the membrane is essential to performance because the resistance of the electrolyte increases dramatically if it dries out. Humidification is effected by saturation of the reactant gas streams prior to entering the cell.

### 4. Experimental

Fuel cell performance was characterised by two distinct methods. Steady-state performance was assessed from polarisation plots obtained over a range of temperatures and pressures with dry and humidified anode gas. Performance of the cell under pulsed load conditions was monitored indirectly from the power output of the cell over the pulse length (1 s).

Two basic, single fuel cell designs were employed for this work; a commercial cell (Electrochem Inc.) with a 50  $\text{cm}^2$  active area, and a circular cell with an active area of 100  $\text{cm}^2$ , designed and built by Loughborough University. The fuel cell was connected to a load unit and in series with a power supply to provide the additional voltage required for control. A digital voltmeter (Solartron 7151) and shunt resistor were used to measure voltage and current, respectively. Experiments requiring loads less than 250 A were effected by use of a Hewlett Packard 6050A load and a TCR power supply. Pulses were delivered by placing a solid-state relay-array in the circuit and switching it via a timer. Pulse profile data were recorded on a logger fitted with a transient data capture module (Solartron 3535D and 3535F) set to record voltage and current at 500  $\text{s}^{-1}$ , and an oscilloscope (Gould DataSys 840 DSO).

After assembly of a new fuel cell it was operated potentiostatically (0.5 V) until it reached maximum operating temperature, then allowed to cool. This was repeated several times until consistent performance was obtained. After collecting data under a specific set of conditions the cell was allowed to cool to near ambient temperature before embarking upon another experiment to allow for identical warm-up procedures between each.

### 5. Results

#### 5.1. Steady-state performance

To assess the effect that each fuel cell component has on the overall efficiency, performance data were collected as each component (e.g. MEA, current collector, and gas-flow design) was sequentially replaced.

A number of membrane electrode assemblies have been tested in the 100  $\text{cm}^2$  cell (Tables 1 and 2). In each case they have been tested at cell temperatures of 30, 50, 70 and 80°C and at pressures of 2/3, 3/4 and 4/5 bar ( $\text{H}_2/\text{O}_2$ ).

Table 1  
Membrane electrode assemblies

Membrane	Electrocatalyst (mgPt $\text{cm}^{-2}$ )	Gas diffusion backing
Nafion™-117	1.0 or 4.0	graphite paper
Nafion™-115	1.0	graphite paper
Nafion™-112	1.0	graphite paper
Experimental (50 $\mu\text{m}$ )	1.0	graphite paper
GORE-SELECT™ (30, 40 $\mu\text{m}$ )	0.3	graphite paper

Table 2  
Peak power output from each membrane electrode assembly

Membrane	Peak power ( $\text{mW cm}^{-2}$ )
Nafion™-117	300 @ 0.51 V
Nafion™-115	525 @ 0.50 V
Nafion™-112	670 @ 0.49 V
Experimental (50 $\mu\text{m}$ )	600 @ 0.50 V
GORE-SELECT™ (40 $\mu\text{m}$ )	1035 @ 0.49 V
GORE-SELECT™ (30 $\mu\text{m}$ )	1600 @ 0.50 V

The performance derived from each membrane differs considerably (Fig. 1). The newer membranes produce a significant power increase over the traditional Nafion™-117.

The gas pathways formed in the current collector also have an effect on fuel cell performance (Fig. 2). The 50  $\text{cm}^2$  cell from Electrochem Inc. incorporates standard ‘radiator’

pathways whereas the 100  $\text{cm}^2$  cell incorporates an optimised, centre-fed gas system developed at Loughborough University. Differences are most pronounced at high current densities where gas access and good water management is essential.

Changing the current collector materials appeared to have a relatively minor effect (Fig. 3). The metal collector has a marginally poorer performance at higher current densities.

5.2. Pulse-power performance

Fuel cell performance under pulsed load conditions (Fig. 4) broadly follows the sequence observed for continuous loads. The data shown here comprise the best performance of membrane/electrode assembly regardless of the temperature and pressure required. In general it can be seen

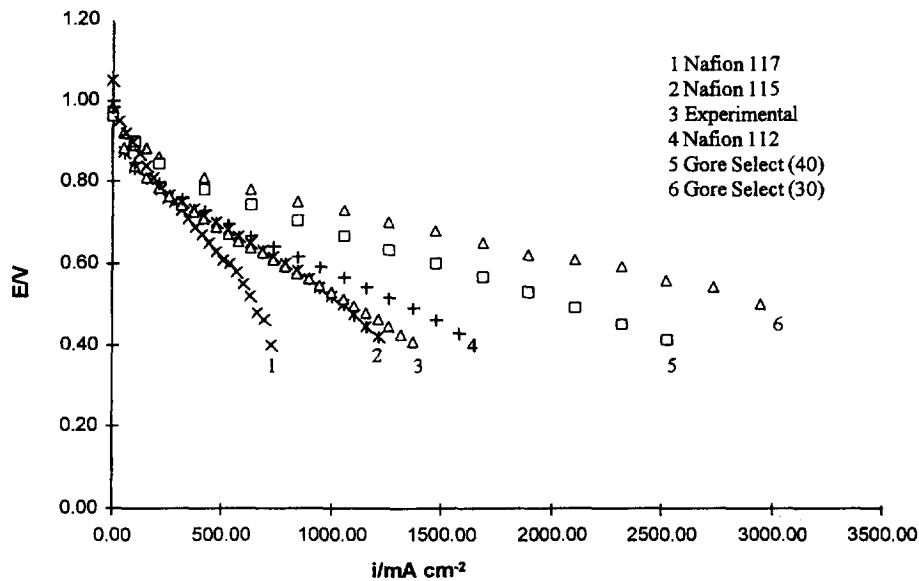


Fig. 1. Comparison of different membranes.

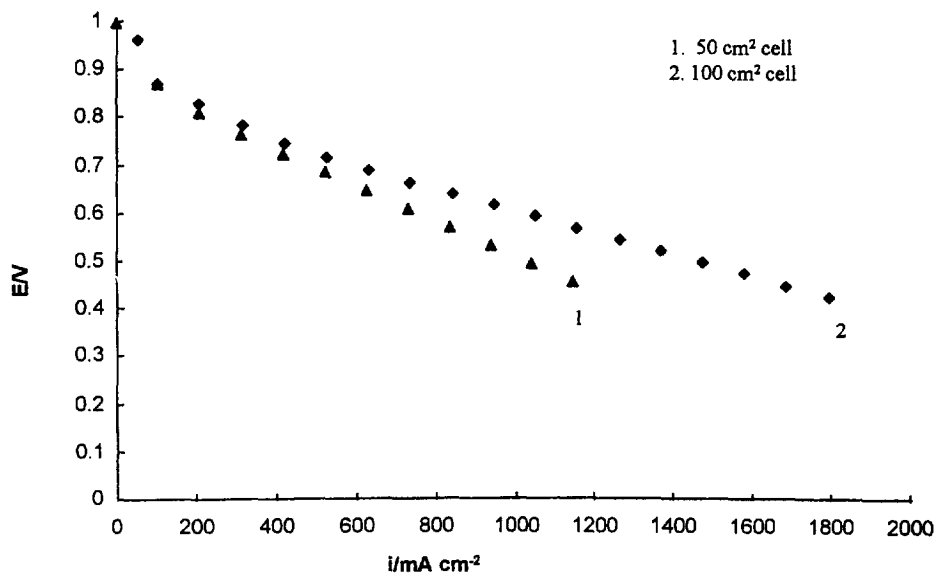


Fig. 2. Comparison of different cell types.

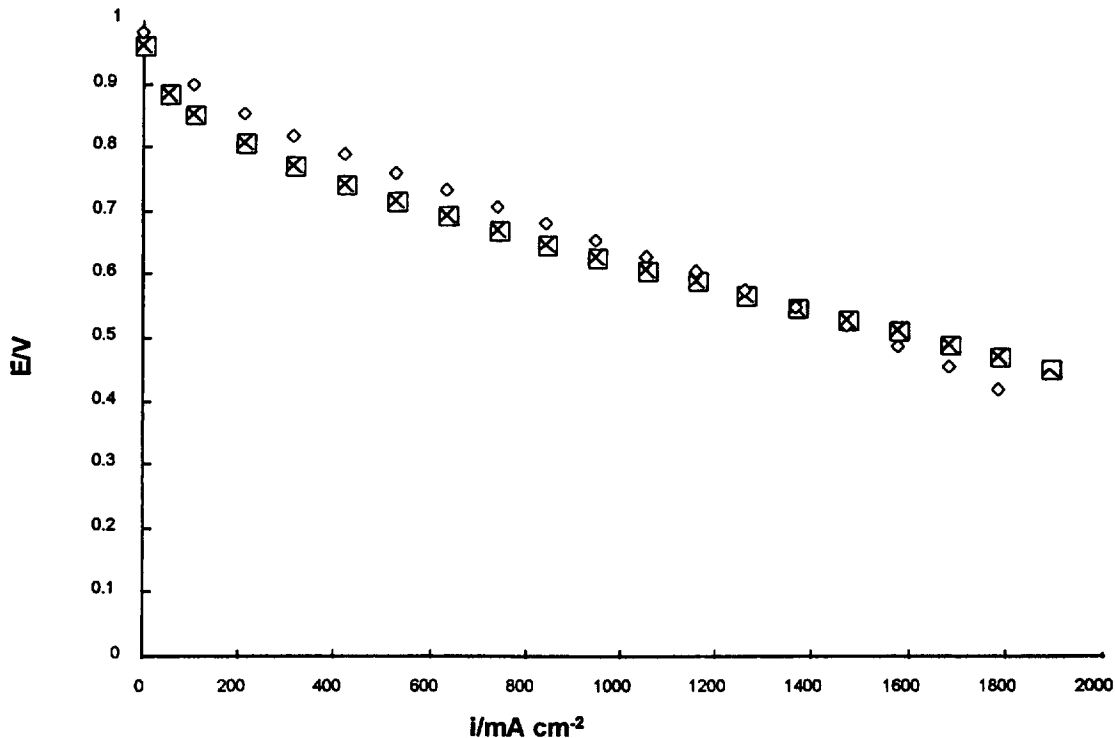


Fig. 3. Comparison of current collectors.

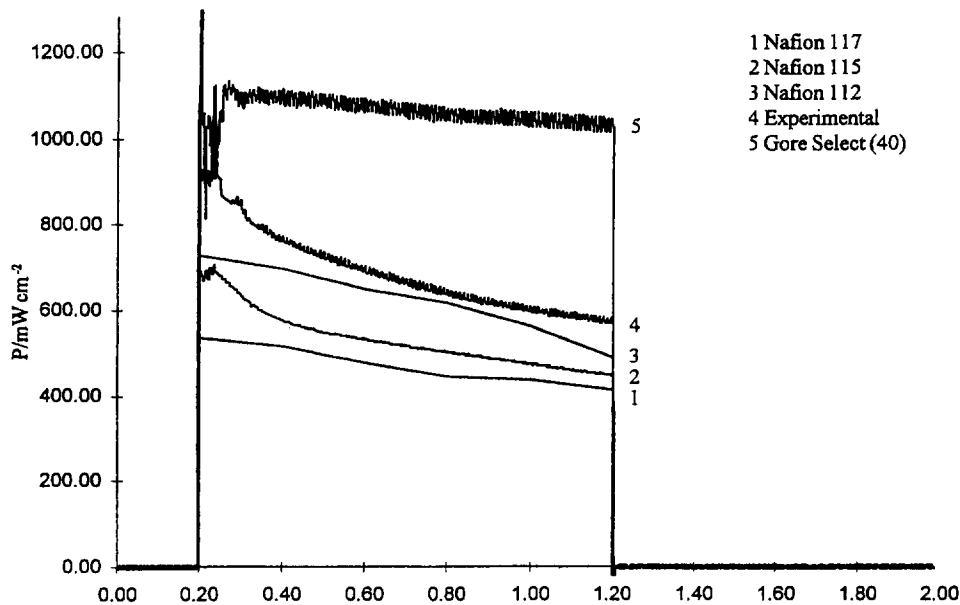


Fig. 4. Comparison of membrane/electrode assemblies under pulse conditions.

that an approximate doubling of performance is obtained in comparison with continuous operation over the course of a one second pulse, however, in the millisecond region of the pulse the power output is much greater.

Power from the GORE-SELECT™ membrane was not significantly higher under pulse load conditions, which was mainly due to load unit limitations preventing the use of a sufficiently high current. In the near future pulse data with high performance membrane electrode assemblies will be re-assessed using a high-power, custom-built load unit (1000 A, 2 kW) coupled to two parallel-connected lead-acid bat-

teries (Powersafe VH51, Chloride Industrial Batteries Ltd.) to provide additional voltage for control (series connected fuel cells would not require this additional supply).

The effect of temperature and pressure varies with each membrane/electrode assembly (Tables 3 and 4). Generally each membrane/electrode assembly performs better when pulsed at higher temperatures (70 or 80°C), in line with steady-state observations.

The effect of humidification upon the cell performance varies with each membrane/electrode assembly and again follows the trend set in the steady state: the Nafion™ mem-

Table 3  
Power delivered by the 100 cm<sup>2</sup> fuel cell during a 1 s pulse at  $P = 3/4$  bar H<sub>2</sub>/O<sub>2</sub>

Temperature (°C)	Power at 0.05/0.05 s/mW cm <sup>-2</sup>				
	50	70		80	
Membrane	Dry	Humid	Dry	Humid	Dry
Nafion™-117	460/350	530/450	510/350	540/405	510/350
Nafion™-115	430/205	690/600	620/430	690/560	N/A
Nafion™-112	620/540	830/600	710/520	915/690	710/460
Experimental (50 μm)	560/480	770/480	690/540	765/540	720/580
GORE-SELECT™ (40 μm)	820/780	1000/1020	950/880	1080/1030	1075/1020

Table 4  
Pulse power delivered by the 100 cm<sup>2</sup> fuel cell at  $T = 70^{\circ}\text{C}$ , without humidification

Pressure/bar (H <sub>2</sub> /O <sub>2</sub> ) Membrane	Power at 0.5 s/mW cm <sup>-2</sup>		
	2/3	3/4	4/5
Nafion™-117	320	350	355
Nafion™-115	430	430	320
Nafion™-112	510	520	510
Experimental (50 μm)	595	540	460
GORE-SELECT™ (40 μm)	865	880	870

branes dry out very easily if the anode gas is dry and the problem becomes worse for the thinner membranes so pulse performance is greatly enhanced with humidification. The Experimental membrane, which clearly demonstrated its steady-state preference for dry gas feeds, was unable to sus-

tain a voltage for the duration of the pulse if it was fed with humidified gas. The GORE-SELECT™ membrane (40 μm) showed a small preference for humidification at higher temperatures. It is anticipated that the thinner GORE-SELECT™ membranes will be more dependent upon humidification.

Changing the current collector material used in the cell from graphite to platinum coated aluminum makes a considerable difference to the pulse power performance obtained (Fig. 5). The metal collector is significantly worse under a pulsed regime as cell voltage is lost over the time period. This is probably as a result of the effects of corrosion of the metal collectors on the membrane. On dismantling the cell it was apparent that some of the platinum had flaked off and exposed the nickel interlayer, which had subsequently reacted in the cell.

The overall geometry of the gas flow channels incorporated into the current collectors also has a marked effect on pulse power performance. The optimised 100 cm<sup>2</sup> cell delivers

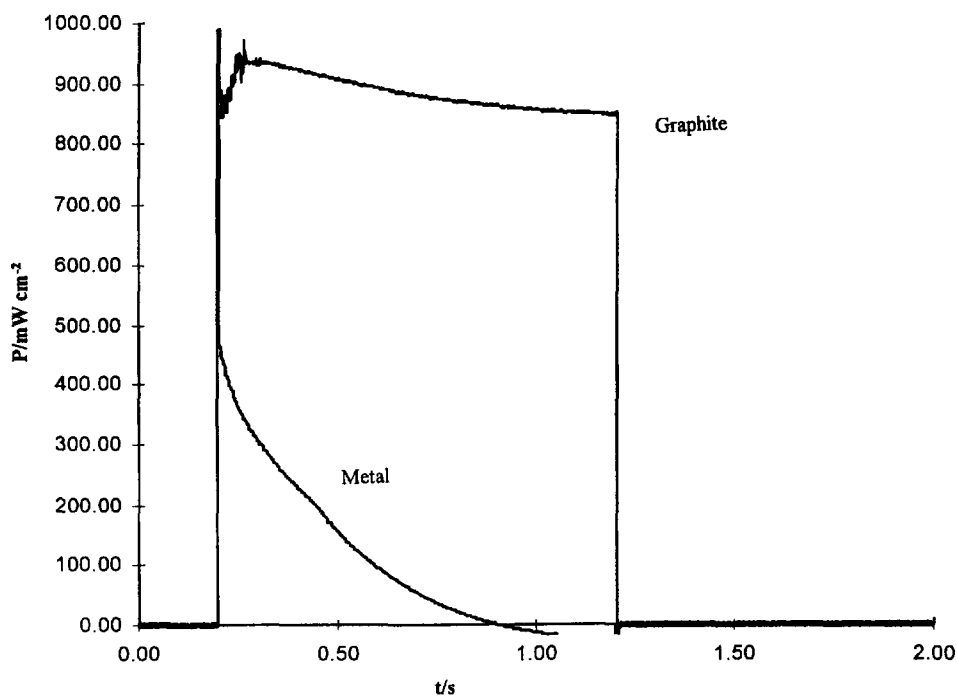


Fig. 5. Comparison of metal and graphite current collectors.

considerably more power and the voltage loss rates over the duration of the pulse are less than is observed for the 50 cm<sup>2</sup> cell.

## 6. Discussion

### 6.1. Steady-state performance

Steady-state performance of a typical fuel cell is affected by a number of factors which lead to the commonly observed polarisation graphs (Fig. 1). Initial loss of voltage when a load is applied (activation overpotential) is caused by the relatively poor performance of the cathode electrocatalyst. This loss may be minimised by increasing the number of active catalyst sites at the membrane surface (high surface areas) and by increasing the transport efficiency of the membrane. The GORE-SELECT™ membranes have a very high catalyst efficiency since they utilise less platinum per unit area than the other membrane/electrode assemblies and yet have the best performance. This, in conjunction with higher membrane conductance, produces better performance over the whole of the polarisation curve. It is likely that even thinner membranes (5–30 μm) will produce further performance increases, although at the expense of the open circuit voltage from increased gas crossover through the membrane.

At moderate currents the voltage loss from the cell is linear and is due to ohmic effects. The gradient of this slope is principally due to ionic and electronic resistive losses in the membrane/electrode assembly and the current collectors. In addition, the cell performance may be sustained only if the cell design offers sufficient gas access and product water removal, without which the electrodes become flooded. Thin membranes have lower ionic resistance and therefore less voltage loss with increasing current.

Electronic resistance between the membrane/electrode assembly and the current collector should be minimised by use of more electrically conductive materials (e.g. metal) rather than the poorly conducting graphite generally used. Continuous results with platinum coated aluminum collectors were not significantly better than results with graphite (Fig. 3). However, this is likely to be due to differences in water management since the graphite plate is partially porous and acts to 'wick' the water away from the membrane/electrode assembly whereas the metal collector cannot do this and thus does not sustain high currents. The difference in water management was very apparent when running the cells; the graphite cell can be run with the gas outlet on either side of the cell closed for some time but the metal cell required a large through-flow of gases to maintain a stable voltage. Some modifications to the flow channels in the collector will prevent this problem. Another reason for the lack of success with metal collectors may be due to the fact that the electrode backing between the electrocatalyst and the membrane is

teflonised carbon paper which will be a major contribution to resistive loss.

At the time of the continuous experiments, corrosion of the collector was not evident so it was not a contributing factor in the overall performance of the cell.

The effect of optimised gas channels on the performance is demonstrated by comparison of a conventional 'radiator' design (the 50 cm<sup>2</sup> cell) with an optimised flow field (the 100 cm<sup>2</sup> cell) configuration (Fig. 2). The optimised design can sustain higher current densities with less operator intervention.

At very high current densities, mass transport limits cause the cell potential to drop rapidly to zero. The high performance membranes do not appear to have reached this limitation, even at 0.4 V per cell. In fact, the cell design restricts further increase in performance because of its inability to remove water and waste heat efficiently at these high currents. It should be possible to extend this limit with cells designed for removal of large quantities of water and with the incorporation of cooling plates. Such cells are currently being constructed.

### 6.2. Pulse power performance

Pulse power performance is governed by different criteria when compared to the steady state. The instantaneous voltage drop is caused by ionic and electronic resistive losses within the membrane/electrode assembly and cell. GORE-SELECT™ membranes prove to have superior ionic conductance to other conventional membranes (Fig. 4). The other membranes follow the general trend observed during continuous load experiments.

The remainder of the voltage loss during the pulse is governed by diffusion of reactant gas through the electrode backing, charge transfer at the reaction sites and double-layer discharge. The rate at which the voltage drops during the pulse (Table 3), assuming the rest of the cell is constant, is determined by the ability of the membrane/electrode assembly to sustain high currents. If the pulse load chosen is too high then mass transport limits will quickly reduce the power to zero. It is apparent from the drop in power from 0.05 to 0.5 s that the GORE-SELECT™ membrane is superior; its voltage drop is slight over the duration of the pulse even though the load current was higher than that used for the other membranes.

The effect of temperature and humidification on the pulse performance broadly followed the trend observed during continuous load experiments. The membranes performed best at elevated temperature and, generally, with humidification. The only exception was the Experimental membrane which had shown its preference for dry gas streams in steady-state measurements, making it ideal for air-breathing systems. Under pulse loads, with humidification, the voltage dropped rapidly to zero. The Experimental membrane is superior in its water retention/affinity and thereby facilitates water

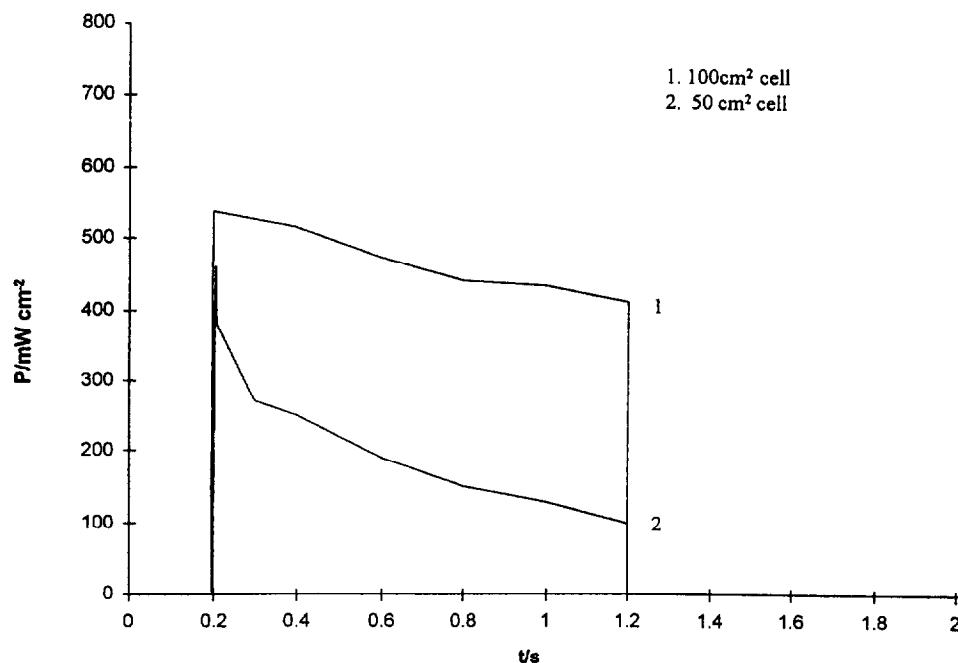


Fig. 6. Comparison of cell designs under pulse conditions.

transport through the membrane from the cathode to the anode.

The effect of pressure on pulse performance was generally negligible, which suggests that gas access to the membrane is sufficient, even at the lowest pressure investigated. In fact, the pulses carried out at low pressure were often marginally better. In the case of the Experimental membrane there was a significant loss of performance at higher pressures which is not easily explained since the pressure differential between cathode and anode was maintained at 1 bar in each experiment.

The contribution of the gas flow design to the pulse performance could be observed, assuming the differences in electrode manufacture are minimal, by comparison of the 50 and 100 cm<sup>2</sup> cell with Nafion<sup>TM</sup>-117 at similar temperatures and pressures (Fig. 6). It is apparent that the optimised 100 cm<sup>2</sup> cell is superior under pulse load conditions since instantaneous voltage drop is less. A good cell design for continuous load conditions is evidently also a good design for pulse loading.

A comparison of the pulse load profiles of metal and graphite current collectors (Fig. 5) with all other factors remaining constant should have provided evidence of ohmic losses from the membrane/electrode assembly to the collector. However, since the current collector showed evidence of corrosion after the pulse power experiments, the loss of power during the pulse must be primarily attributed to this problem. In the future, collectors fabricated from nitrided titanium (currently under construction) will be tested and these should have much superior resistance to corrosion.

## 7. Conclusions

In summary, the contribution of individual components to the overall performance of the fuel cell have been studied with the aim of achieving maximum power output under pulse load conditions. Generally, pulse mode operation of the cell yields a gain of 1.5 to 2.0 times the continuous power output. Thus it should be possible to achieve  $\sim 3 \text{ W cm}^{-2}$  with the existing GORE-SELECT<sup>TM</sup> membrane (30  $\mu\text{m}$ ) and even higher power densities with thinner membranes. The principal contributions to better performance include the use of thin membranes with high catalytic activity and optimised design of the gas flow channels within the current collectors. Future work will include the testing of even thinner membrane electrode assemblies supplied by W.L. Gore and Assoc. and DuPont and further studies of non-graphite current collectors and gas flow designs. Ultimately, a fuel cell stack will be developed utilising the best combination of components to deliver pulse power, with a target power density of  $6 \text{ W cm}^{-2}$ , equivalent to  $5 \text{ kW dm}^{-3}$ .

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