THE RENAISSANCE OF THE SOLID POLYMER FUEL CELL

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Historical background

The solid polymer fuel cell (SPFC) or SPE (a trademark owned by Hamilton Standard) fuel cell was first developed by General Electric (GE) for NASA in the 1960s [1]. It consists of two porous electrodes, which are lightly catalyzed on one surface, bonded on either side of a thin sheet of a hydrogen ion-conducting polymer, the solid polymer electrolyte. The backs of the porous electrodes are contacted by plates which contain channels through which a fuel gas is supplied to the back of the anode and an oxidant gas is supplied to the back of the cathode. Electrical contact to the electrodes may be made through these fluid flow field plates.

The perceived advantages of the SPFC for space applications were its high energy density compared to batteries, the absence of corrosive, liquid electrolytes, the relative simplicity of the stack design, and the ruggedness of the system.

The technology initially suffered from a limited operating lifetime, due to degradation of the membrane electrolyte. By 1964, GE had developed membranes based upon the cross-linking of styrene-divinylbenzene into an inert fluorocarbon matrix. SPFCs based upon these membranes exhibited lifetimes of about 500 h and were satisfactory for their use in seven Gemini missions.

In the mid-1960s, GE, working with DuPont, adapted DuPont's Nafion for use in the SPFC. This fully fluorinated material exhibited a substantially improved operating lifetime — in excess of 57 000 hours [2]. GE used Nafion in 1968 for the Biosatellite mission. At this point, long operating lifetime and low maintenance requirements could be added to the advantages of the SPFC.

By then, NASA had selected the alkaline fuel cell for use in the Apollo program. There had been a perception within NASA that the polymer electrolyte was intrinsically resistive and that the requirement for a higher power density fuel cell system for Apollo could be better met by the alkaline fuel cell. This, for all practical purposes, put the SPFC on the shelf for space applications for the next 20 years.

GE chose not to pursue commercial applications of the SPFC, probably because of the perceptions that, as compared with the phosphoric acid fuel

cell, the SPFC was more expensive (expensive membrane and high platinum loading) and more sensitive to CO poisoning. The latter concern was seen as precluding the use of common carbon-containing fuels with the SPFC and thus severely limiting its market potential. With the exception of limited work under the sponsorship of Los Alamos National Laboratory, solid polymer fuel cell technology lay dormant until about 1984.

The beginning of the renaissance

In 1983, the Canadian Department of National Defence (DND), in association with the National Research Council, determined that solid polymer fuel cell technology might satisfy some of the growing military power needs and have commercial applications as well, if it could be re-engineered for terrestrial applications and at a lower cost. In early 1984, Ballard began a two-year contract with DND to acquire SPFC technology and to evaluate its potential.
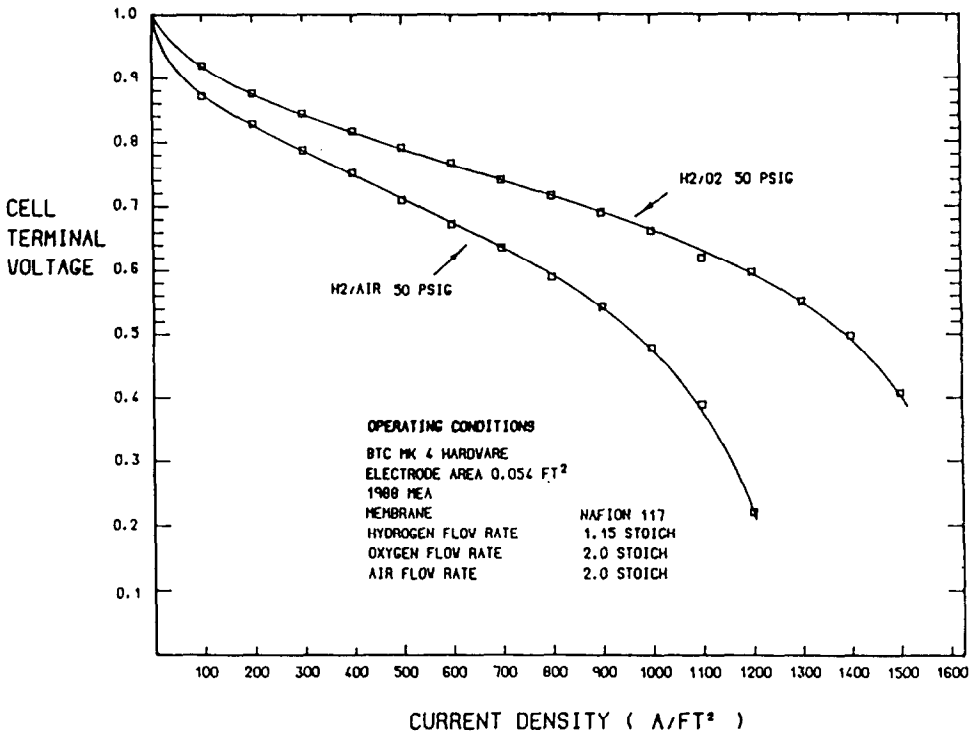

Fig. 1. Comparison of single cell performance on H_2/O_2 to performance on H_2/air.

Air as the oxidant

The initial focus of the Ballard/DND program was the development of stack hardware which would operate effectively on air, as well as on pure oxygen. This required improvements in the distribution of air to the back of the porous cathode, the removal of product water, and the manifolding of cells in a multi-cell stack.

Figure 1 shows the present performance of single cells operating on hydrogen/oxygen and on hydrogen/air at the same pressure. This cell had an active electrode area of 0.054 ft² (46.5 cm²) and used Nafion as the membrane electrolyte. Note that, at a given terminal voltage, the current (or power) produced using air is about 70% that obtained using pure oxygen at the same pressure. In this experiment, the air flow rate was five times that of the oxygen flow rate, so that the total oxygen passing through the cell was the same in each case.

Performance obtained in single cells is often difficult to maintain in multi-cell stacks. Figure 2, however, demonstrates comparable performance in a 54-cell stack. Again, performance on air is about 70% that obtained on pure oxygen.
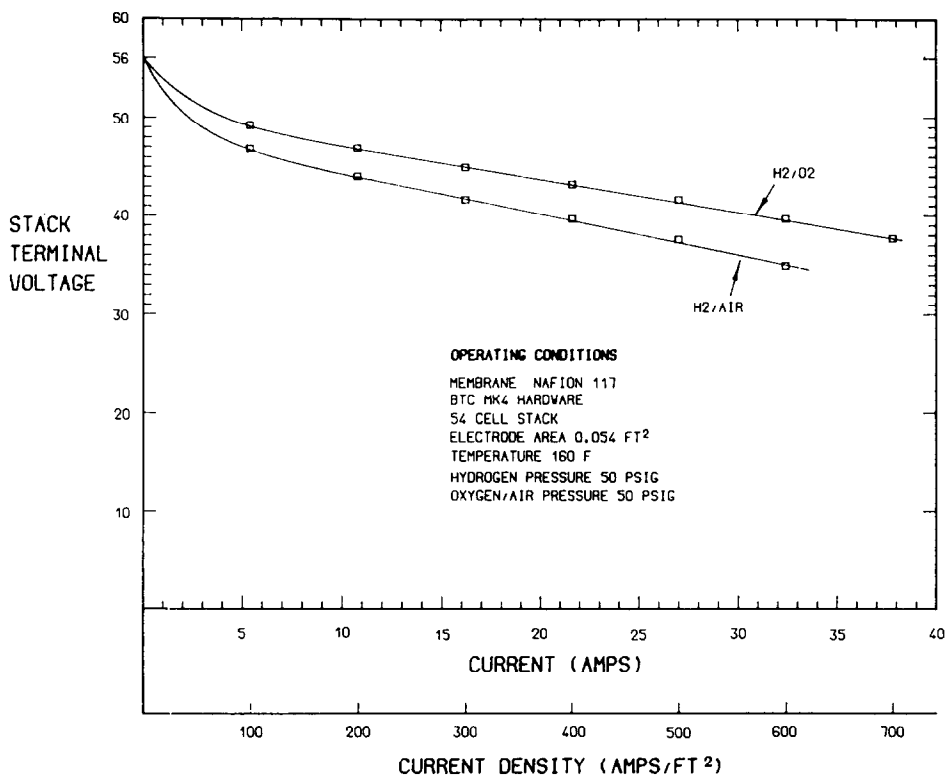

Fig. 2. Comparison of 54-cell stack performance on H_2/O_2 to performance on H_2/air.

Carbon-containing fuels

The second aspect of the Ballard/DND program was the demonstration of acceptable performance on reformed hydrocarbon fuels. These gas mixtures typically contain 70 - 80% hydrogen, 20 - 30% carbon dioxide and 0.1 - 1.0% carbon monoxide. The SPFC is essentially insensitive to the CO_2 in the gas stream, but very sensitive to the CO. Ballard developed [3] a selective oxidation process which is used to pre-treat the reformed fuel gas stream before it enters the fuel cell. Table 1 shows the performance of a 0.05 ft^2 electrode area cell when operated on pure hydrogen, hydrogen/CO_2, hydrogen/CO_2/CO, and hydrogen/CO_2/CO treated to selectively oxidize the CO. The anode contained a CO-tolerant catalyst, as well as platinum. The data shown reflect performance after 24 h of operation.

Note that, while the addition of 25% CO_2 to the fuel gas had a relatively minor effect on performance, the further addition of 0.3% CO dramatically reduced performance, even with the CO-tolerant catalyst. In fact, it was not possible to pass the reference 400 A/ft^2 at any meaningful voltage with CO present in the fuel gas. When fuel gas containing CO was passed through the selective oxidation process before entering the fuel cell, fuel cell performance was essentially identical to that observed with only CO_2 present.

Table 2 shows that this performance was retained in a 12-cell stack on the same fuel combinations. These data show performance after 24 h. Even after 500 h, performance on treated reformate was around 90% of that for pure hydrogen.

TABLE 1

Synthetic reformate/air performance MK 4 single cell/30 psig/185 F/Nafion 117

Fuel gas	Voltage (V)	Current density (A/ft^2)	Power (% H_2/air)
H_2	0.71	400	100
H_2/25% CO_2	0.68	400	96
H_2/25% CO_2/0.3% CO	0.71	200	50
Treated fuel	0.67	400	95

TABLE 2

Synthetic reformate/air performance MK 4 12 cell stack/30 psig/Nafion 117/400 A/ft^2

Fuel gas	Voltage (V)	Power (% H_2/air)
H_2	8.22	100
H_2/25% CO_2	8.05	98
Treated fuel	7.94	97

Cost reduction

Materials replacement/reduction

Cost reduction was addressed from two points of view — reduction in materials cost and improvement in performance. The Ballard cell uses low cost graphite for the fluid flow field plates, instead of the niobium used in the NASA cell plates. Ballard also determined that baseline performance could be obtained with significantly lower platinum loading on the electrodes than the 8 mg/cm^2 per cell which has been the standard. Los Alamos has recently reported good performance down to about 0.4 mg/cm^2 per cell [4].

Performance improvement/the membrane electrolyte

The most significant reduction in cost has resulted from improvements in performance. In 1987, Ballard received a new ion-conducting polymer membrane from Dow Chemical. The Dow membrane is a sulfonated fluorocarbon polymer [5], like Nafion. As shown in Fig. 3, when placed in the Ballard cell hardware, the Dow membrane produced four times the current (and power) at the same operating voltage as that obtained when using a Nafion membrane electrolyte [6]. The polarization data in Fig. 3 were obtained after 120 h of continuous, stable performance at 4000 A/ft^2 (4.3 A/cm^2).

As shown in Fig. 4, this performance was retained in a six-cell stack. The polarization data in Fig. 4 were obtained after 20 h of operation at
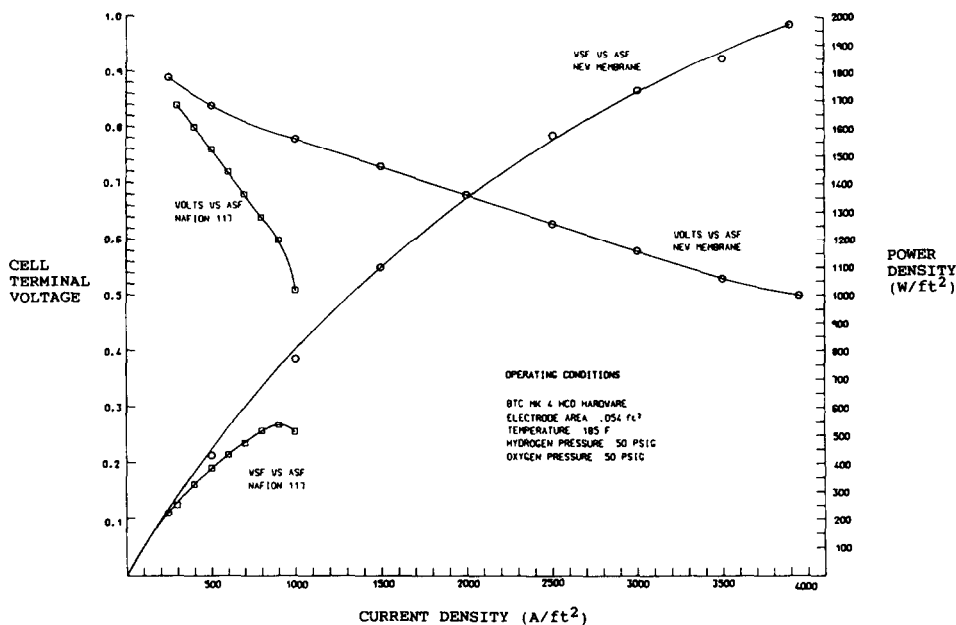

Fig. 3. Comparison of single cell performance of Dow membrane to Nafion.
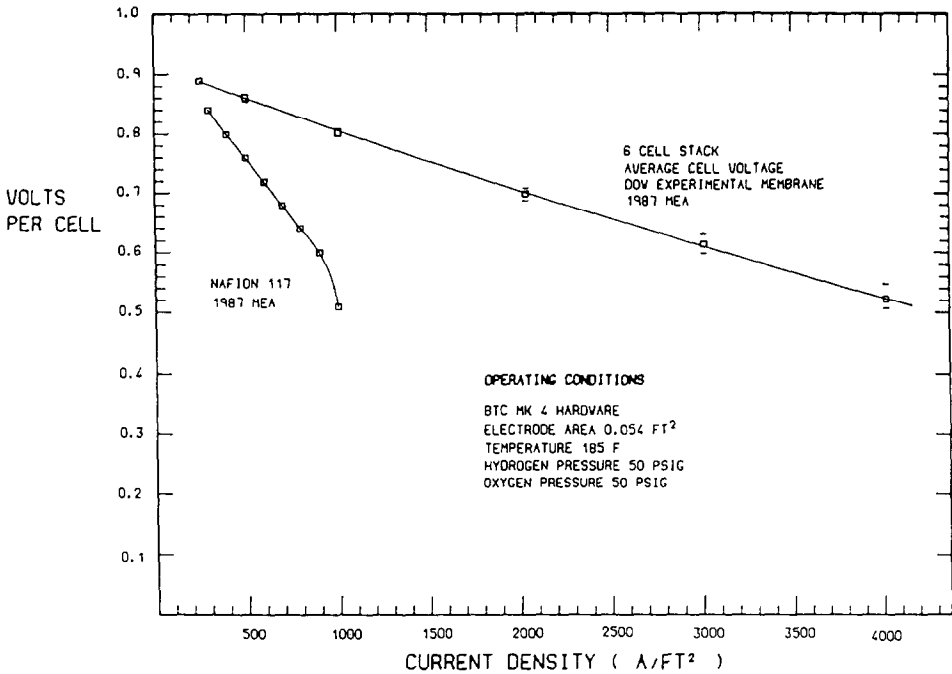
Fig. 4. Multi-cell stack performance on Dow membrane.

4000 A/ft². These data indicate that both the cell-to-cell gas manifolding and the thermal management design of the cell are sufficient for continuous operation at these current and power densities.

By increasing the operating pressure to 100 psig (7.8 atm) and the temperature to 215 °F (102 °C), current densities in excess of 6000 A/ft² have been obtained as shown in Fig. 5.

Performance improvements have also been achieved with Nafion 117. Figure 6 demonstrates a roughly 50% improvement in limiting current density in a single cell using the same Nafion 117 as the electrolyte. This improvement results from changes in the fabrication procedure for the membrane/electrode assembly.

Dow has provided several versions of its membrane for evaluation. These samples have varied in thickness, in equivalent weight, and, presumably, in other fabrication variables [6]. Figure 7 shows the variation in performance which has been obtained with the various samples as compared with the recent Nafion performance. The thicknesses of these membranes are tabulated in Table 3.

Based upon the data available to Ballard, it is not possible to determine which variables are most important to performance. It is clear, however, that there is substantial flexibility in the fabrication process which should allow for performance optimization for a variety of applications. It is also clear that the Dow material is, in all samples tested, superior to Nafion for this
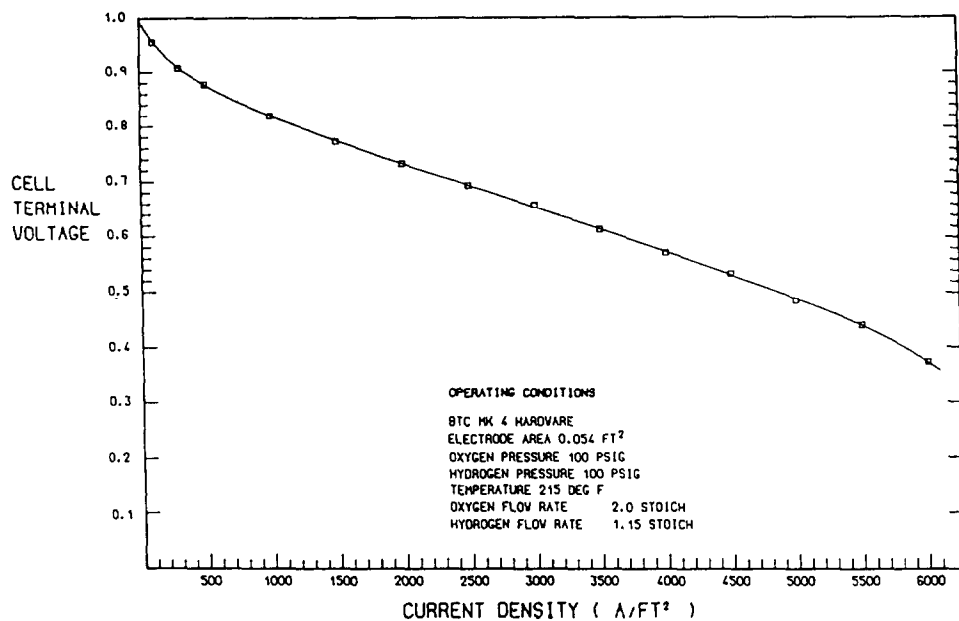
Fig. 5. High temperature, high pressure performance on Dow membrane.
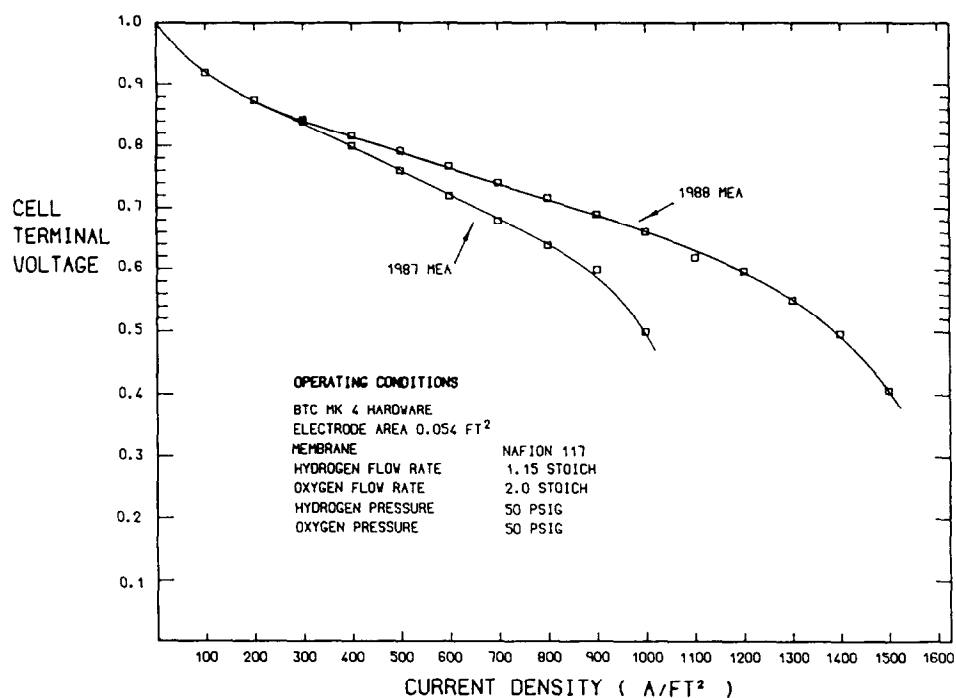

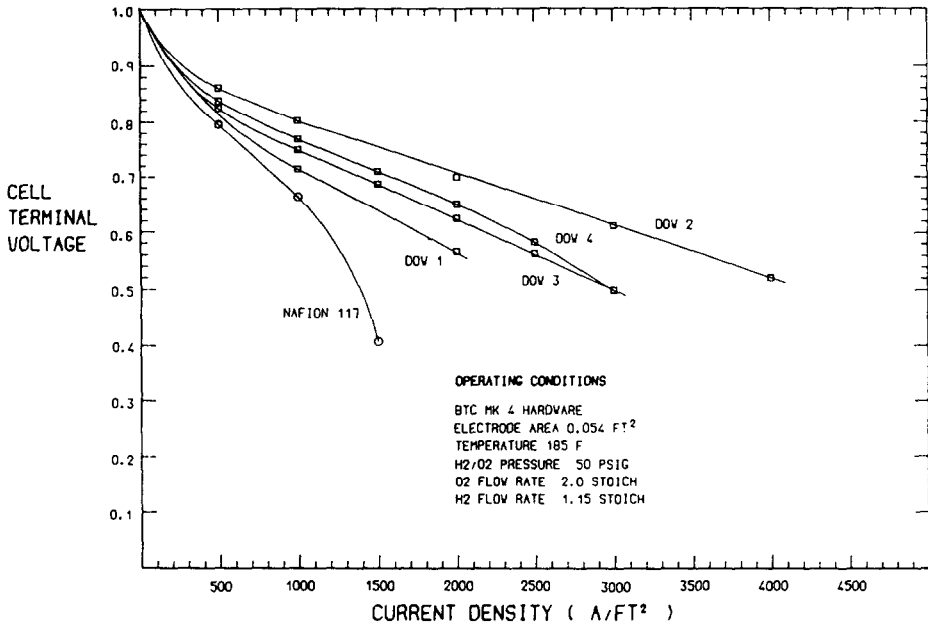Fig. 6. Comparison of 1987 and 1988 performance on Nafion membrane.

Fig. 7. Comparison of the performance of various Dow membranes with that of Nafion 117.

TABLE 3

Membrane thickness

Membrane	Thickness (in)
Dow 1	0.0067 - 0.0071
Dow 2	0.0035 - 0.0039
Dow 3	0.0052 - 0.0055
Dow 4	0.0063 - 0.0066
Nafion 117	0.0083 - 0.0087

application. The improvement in performance derived from the Dow membrane represents a substantial reduction in the size, weight and cost for an SPFC delivering a given amount of power.

Performance improvement/stack scale-up

Further size, weight and cost reductions were obtained by increasing the electrode size and, in the process, reducing the amount of peripheral material required in the stack. The original MK 4 hardware had an active electrode area of 0.054 ft^2 (7.8 in^2, 50.2 cm^2) but required graphite plates
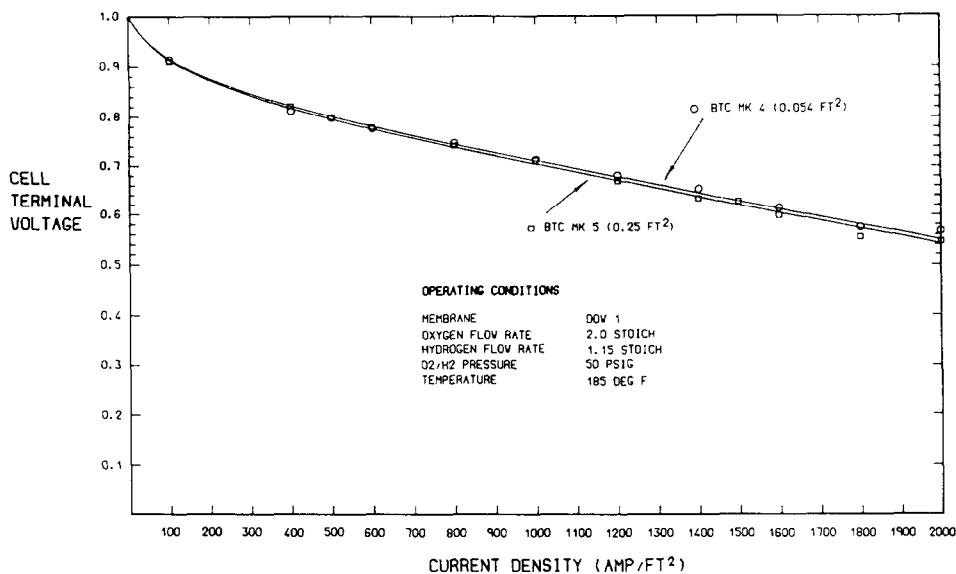
Fig. 8. Comparison of MK 4 and MK 5 hardware performance on H_2/O_2 with the Dow membrane.

and membrane electrode assemblies which were 5 in $\times$ 5 in (12.7 cm $\times$ 12.7 cm). The MK 5 hardware has an electrode area of 0.25 ft^2 with graphite plates and membrane electrode assemblies only 8 in $\times$ 8 in (20.3 cm $\times$ 20.3 cm). The hardware scale-up has increased stack power by a factor of 4.63, while increasing stack cross-sectional area and stack volume by only a factor of 2.56. As seen in Fig. 8, the scale-up was completely linear for hydrogen/oxygen using the Dow membrane. Perhaps more impressive, the scale-up was also linear for hydrogen/air performance as shown in Fig. 9.

Commercialization

In addition to advancing the state of the technology, Ballard is committed to commercializing solid polymer fuel cells. To that end, in 1987 Ballard delivered a 2 kW hydrogen/oxygen fuel cell consisting of two-54 cell MK 4 stacks containing Nafion electrolytes to Perry Energy Systems in Florida. The unit was housed in a container 1 ft in diameter and 2 ft long and was intended to power an unmanned submersible. Shortly thereafter, Ballard delivered an identical unit to the U.K. Royal Navy for evaluation.

The Perry unit has since been retrofitted with a single MK 5 Nafion-based stack in place of the two MK 4 stacks. The upgraded unit can provide up to 4.5 kW in the same volume as the original unit. This MK 5 unit provides the entire power requirements for a two-man submersible, which is now undergoing sea trials.
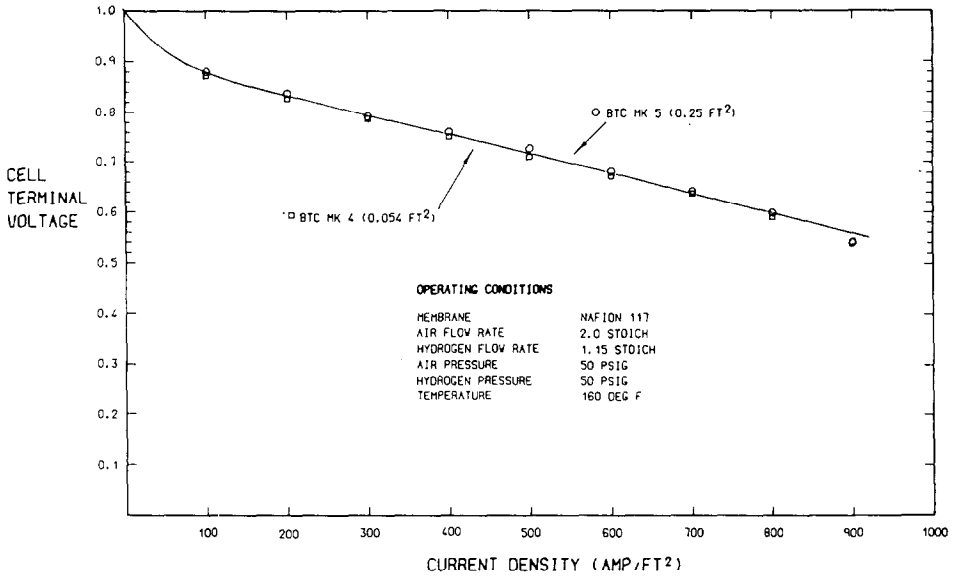
Fig. 9. Comparison of MK 4 and MK 5 hardware performance on H_2/air with Nafion 117 membrane.
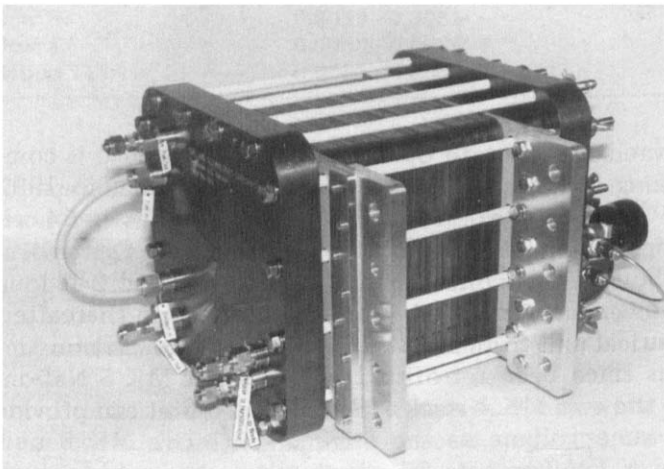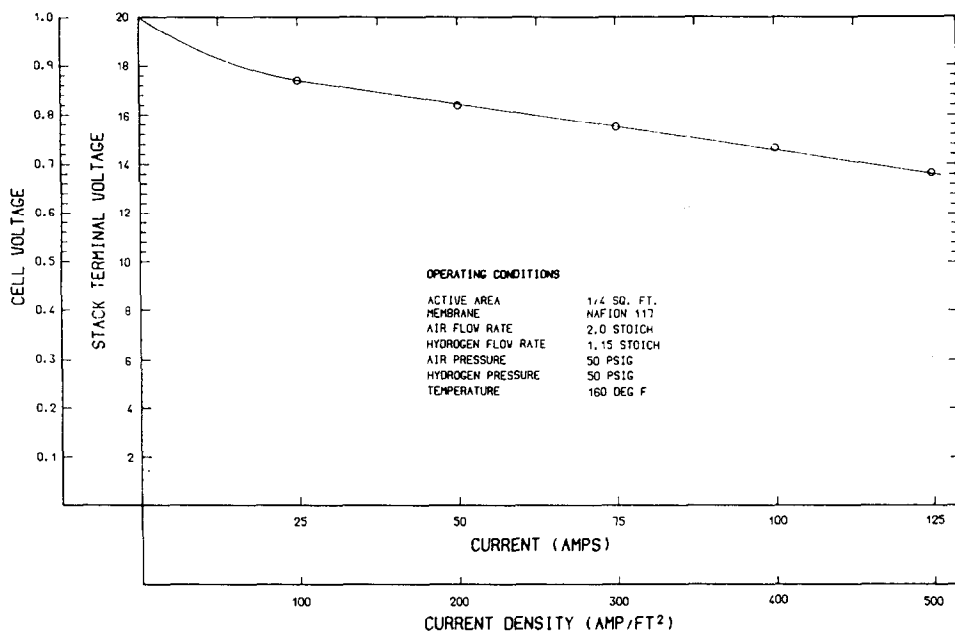

Fig. 10. MK 5 20-cell stack.

Fig. 11. Performance of 20-cell Nafion-based MK 5 stack on H_2/air.

Daimler-Benz is currently evaluating a 20-cell MK 5 hydrogen/air stack, which produces 2 kW using Nafion electrolytes. That stack, which is approximately 1 ft × 1 ft × 1 ft (30.5 cm × 30.5 cm × 30.5 cm), is shown in Fig. 10. The performance of that stack on hydrogen/air is shown in Fig. 11.

A 10 kW hydrogen/air MK 5 system using the Dow membrane will be delivered in September, 1989 for installation in the Dow chlor-alkali plant in Sarnia, Canada. This represent the first of a number of 10 to 50 kW installations planned for Europe, Japan, the U.S. and Canada over the next 18 months.

Conclusions

The substantial improvement in SPFC performance which has been demonstrated over the past two years has resulted in a reappraisal of the possible applications of this technology and the potential markets which are now open to it. Major companies, such as General Motors and Siemens, have significant programs in this area. It now appears that, after 20 years on the shelf, the solid polymer fuel cell is ready for commercialization and may open substantial markets for fuel cells which are not possible with any other fuel cell technology.

References

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