

Chapter 3 - PEMFC : Details, Issues & Improvements

In this chapter we describe the PEMFC stack and the relevant research issues, as the platinum loading on the electrode or the different stack approaches and related manufacturing techniques, *e.g.* machined bipolar plates vs. woven metal collector.

3.1 - Operating Principles

The basic element of a fuel cell is the membrane-electrode assembly (MEA), it consists of an electrolyte phase in contact with a porous anode and cathode on either side. In a polymer electrolyte MEA the fuel - pure hydrogen or CO-free hydrogen-rich gas derived from another gaseous hydrocarbon - and the oxidant - oxygen or air - enter the anode and cathode respectively and generate electricity by the electrochemical oxidation of hydrogen and electrochemical reduction of oxygen.¹ A fuel cell stack consists of many individual cells connected in electrical series by bipolar separator plates. The different fuel cells reactions and MEA thicknesses are shown below ² :

FC	Anode Reaction	Cathode Reaction	Current Density A/cm ²	Thickness mm
PEMFC	$H_2 \rightarrow 2H^+ + 2e^-$	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1 (4 on O ₂)	0.5
AFC	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	1 (O ₂ only)	5
PAFC	$H_2 \rightarrow 2H^+ + 2e^-$	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	0.7	2
MCFC	$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$ $CO + CO_3^{2-} \rightarrow 2CO_2 + 2e^-$	$O_2 + 2CO_2 + 4e^- \rightarrow 2CO_3^{2-}$	0.15	2
SOFC	$H_2 + O^{2-} \rightarrow H_2O + 2e^-$ $CO + O^{2-} \rightarrow CO_2 + 2e^-$ $CH_4 + 4O^{2-} \rightarrow 2H_2O + CO_2 + 8e^-$	$O_2 + 4e^- \rightarrow 2O^{2-}$	1	0.7

Table 3.1 - FC Reactions and Current Densities

3.2 - PEMFC Module

The membrane-electrode assembly (MEA) is the heart of a FC. In every type of FC the MEA is « sandwiched » between two bipolar plates to « stack » together many individual modules, ensuring electrical contact between the electrodes. The FC stack is an electric series of modules. It is interesting to reach a full understanding of the elementary unit by decomposing its functions : we will try to describe the PEMFC in a simple, accessible way, by the description, with the help of illustrations, of the basic components of a fuel cell stack, *i.e.* Membrane, Catalyst, Electrode, Bipolar and End Plates.

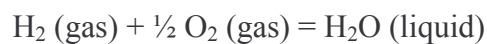
¹ This reaction is also called « electrochemical combustion ».

² For completeness I recall that Alkaline FC are still regarded by someone as a very promising technology - with high power density (up to 2 W/cm²) - although little industrial interest has raised in recent years. For a good defence of AFC, and precious informations see K. Kordesch : « FC & their applications », VCH 1996.

A commonly used technique to prepare the membrane electrode assembly (MEA) is by hot pressing of catalyst-coated electrodes on the membrane.³ An alternative procedure consists in spraying the catalysed electrode, on the membrane, with an electrolyte solution, such as liquid Nafion. During the manufacturing of MEA's, it is critical to ensure a good contact between the electrode, the catalyst and the electrolyte to create a three-phase boundary between gas, electrode and electrolyte, with fine gas diffusion, water removal at the cathode and heat transfer.

As experts clearly explain : « The secret of using PEM-film electrolytes lies in the method of bonding of electrodes to the surface, to give the most effective, three-phase electrolyte, electrocatalyst, gas-phase boundary, thereby making the best use of the electrocatalyst »⁴.

The energy of electrochemical engines is derived from the free Gibbs energy (ΔG) of the electrochemical reactions taking place. To allow convenient comparison with heat engines the efficiency is expressed in terms of the heat of combustion of the fuel. For a hydrogen/oxygen FC we have :



The free energy change in normal conditions (25°C, 1 atm.) is :

$$\Delta G = 237.25 \text{ kJ/mol ,}$$

the higher heating value (HHV) of hydrogen is :

$$\Delta H = 285.91 \text{ kJ/mol ,}$$

the theoretical maximum efficiency of the FC is :

$$\Delta G/\Delta H = 237.25/285.91 = 83 \% \text{ (98.1\% taking LHV).}$$

3.2.1 - The Membrane.

Electrolyte membranes used in FC and electrolyzers have the distinctive feature to block molecular species to let pass ions. The early PEMFC, conceived by Grubb⁵ were using hydrocarbon-type polymer membranes such as cross-linked polystyrene-divinylbenzene-sulfonic acid and sulfonated phenolformaldehyde. The Gemini Space Program 1 kW PEMFC - 30 kg weight and operating at 1.5/2 bars on pure hydrogen and oxygen - also employed polystyrene-divinylbenzene-sulfonic acid, but crosslinked with an inert fluorocarbon film. It was observed that hydrocarbon-based polymers suffered an oxidative degradation, due to the cleavage of the C : H bonds, affecting in particular the α -H where the functional sulfonic group is attached, thus limiting the cell life. In the eighties a much more stable perfluorinated membrane was developed by DuPont de Nemour - NafionTM - which is still the reference in Electrochemical PEM research. In 1992 a further development was achieved with a DOW membrane - XUS - which has allowed Ballard's stacks to almost double the current density

³ U.S. Patent No. 3,134,697

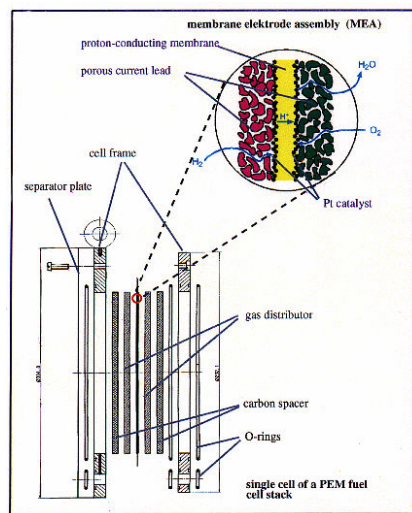
⁴ Professor Giuseppe Faïta *et al.* DeNora Parmelec, U.S. Patent N°5,482,792.

⁵ W.T. Grubb : « Proceedings of the 11th Annual Battery Research and Development Conference », PSC Publications Committee, Red Bank, NJ (1957) ; U.S. Patent No. 2,913,511 (1959).

from the earlier ones⁶. The membrane appears like a thin sheet of plastic, it has good mechanical strength and ideally has to ensure good ionic conduction while blocking electric current. The PEM has a very hydrophobic component - the (co) polymer - chemically bound to hydrophilic sulfonic groups (SO₃). Today the most used membranes are produced by Asahi and DuPont.⁷ Their cost varies from 500 to 900 US\$/m².

3.2.2 - Electrode

The current densities available from smooth electrodes are usually in the range of a few mA/cm² because of rate limiting processes such as the available area of reaction sites. The availability of porous electrodes has changed the specific conditions of current collection within the fuel cell and current densities up to 4A/cm² are today possible in laboratory experiments driven at optimal conditions, *i.e.* oxygen feed. The porous electrode has a high specific surface area enabling « dense » electron flow and the physical structure allows good mass-transport of reactants and products to and from the electrolyte interface. Porous electrodes, used in low temperature FC, *i.e.* alkaline and PEM, consist of a high surface area carbon black and a polytetrafluorethylene (PTFE) binder which acts as wet-proofing agent, with dispersed catalyst to increase the reaction rate.⁸ The composite structure of PTFE and carbon establishes an extensive adsorption surface within the porous electrode. The membrane-electrode assembly with gas-insulator plates is called FC module.



Graph 3.1 - FC stack and M&A (source KFA, Jülich).

3.3 - Module Key Parameters

Some specific measurements of electrochemistry are taken in the PEMFC research. Besides the electric current, voltage, temperature and ohmic losses, we find more specific T and p, membrane hydration and water transport.

⁶ K. Prater : « The Renaissance of the Solid Polymer Fuel Cell », Journal of Power Sources No. 29, 1990.

⁷ A variety of articles is offered in : J. of Electrochemistry, Electrochimica Acta and PSI General Energy volume and Dais web-page. One of the main goals of this latest years research has been the development of a membrane with same stability as DuPont's Nafions (112, 115, 117) at lower costs and with less or without the toxic fluorine *e.g.* hydrocarbon cross linkers in Dais (styrène-butylène) and PSI (styrene-grafted) membranes. Other are produced by 3M and Gore.

⁸ Specific PEM electrode are produced, for exemple, by Johnson Matthey (UK) and E-Tek (USA).

3.3.1 - Current density

The CD depends on gas-diffusion, membrane transportation capacity and catalyst efficiency. It gives, at the laboratory scale, in A/cm², a good indication of individual cell performance. Current densities of low-temperature FC are higher than other FC technologies : 1-2 A/cm², (air operation),⁹ whilst MCFC perform 0.15 A/cm² and SOFC reach 1 A/cm², these values may assume a working voltage of each cell of 0.65 volts.

3.3.2 - Overvoltage

The theoretical maximum voltage, called open circuit voltage (OCV), of a hydrogen/oxygen reversible cell, operating at 1atm and water product (HHV) will be numerically equal to the hydrogen Gibbs energy of reaction :

$$\Delta G = 237.25 \text{ kJ/mol,}$$

since 1 mol = 6.023 x 10²³ molecules (Avogadro's number), for each molecule of product this reaction has an electric charge equal to that on two hydrogen ions transferred from the anode to the cathode. The charge of a hydrogen ion is 1.602x10⁻¹⁹ coulombs, hence 2 x 6.23x10²³x 1.602 x10⁻¹⁹ units of electrical charge per mole cross the potential gradient created by the cell voltage (E). The product of the charge on the hydrogen ion and Avogadro's number is the Faraday (F = 96489 Coulomb/Volt) or, because the highest possible work of this reaction is ΔG , the OCV of a perfectly reversible FC is :

$$E_{\text{rev}} = - \Delta G/2F = 237.25 \times 10^3/2 \times 96489 = 1.23 \text{ volts.}$$

This theoretical voltage cannot be reached because irreversible losses occur when gases are not in the standard state and net current flows. Irreversible losses occur as well due to slowness of reaction, concentration changes due to diffusion, and finally for internal resistance. In low temperature FC - like PEM - the largest losses occur due to the cathodic (oxygen reduction) kinetics ; these can be heavily affected if too much water is flooding the cathode at high current densities.¹⁰

The overvoltage is the difference between the Open Circuit Voltage, V₀ (idle state) and the Terminal Voltage under operating conditions. The overvoltage is an indicator of the losses in a galvanic element under the conditions of delivering current. The ohmic resistance R is derived from current i ; R is determined by the kinetics of electrode reactions, by the physical structure (geometry) of the cell and the materials used. The relation is described by the equation :

$$V = V_0 - iR$$

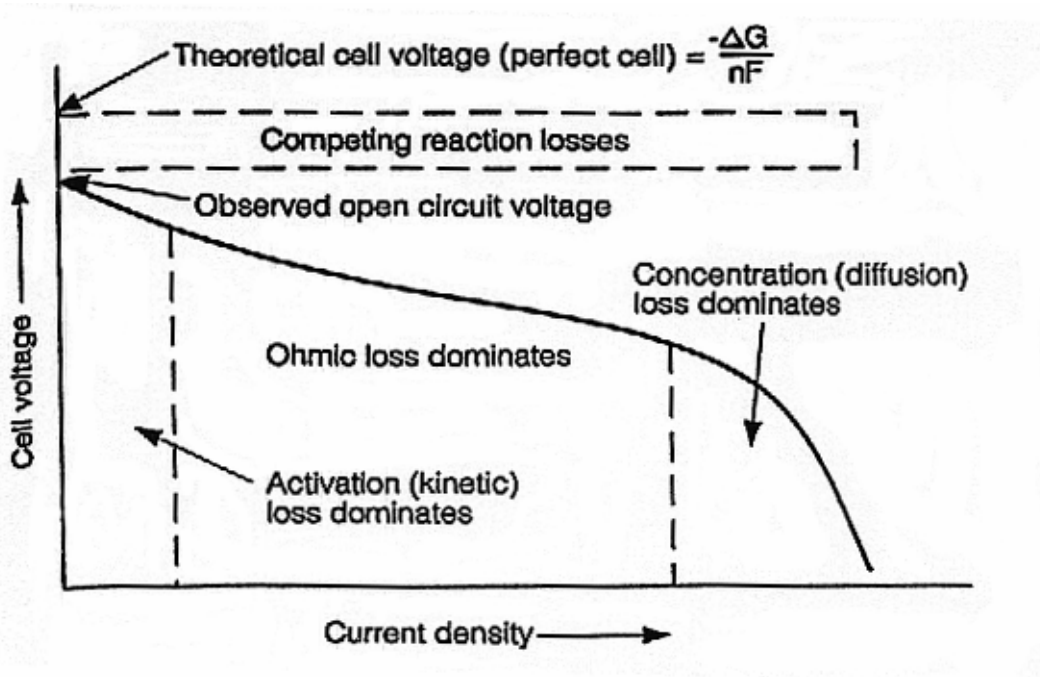
The internal resistance R arises from :

- **Activation polarisation** present at low current is due to the limited surface area and activity of the catalyst,

⁹ European Commission : « A 10 Year Fuel Cell Research, Development and Demonstration Strategy for Europe ».

¹⁰ See Ch.3.4.3.3 Water Removal.

- **Ohmic resistance** arising from the resistance of the electron and ion flow through the electrode and electrolyte
- **Concentration polarisation** begins at high currents and results from depletion of reagents at the three-phase boundary.



Graph 3.2 - Volts vs. A/cm^2

3.3.3 - Platinum loading

The amount of precious metal catalyst is a key parameter in FC economics since platinum, the ideal catalyst, costs approximately US\$ 20/gm. In PEMFC the content of Pt is measured in milligrams. cm^{-2} deposited on the electrode on a carbon black support. Crucial issue has been the development of manufacturing techniques for obtaining finer distribution of active metal particles to increase catalyst dispersion, thus minimising the noble metal content. From a reference value of 4 mg/cm^2 of the General Electric/Hamilton Standard-United Technology stack, the Gemini space flight model¹¹, the platinum loading is now between 1 and 0.5 on the anode and 0.5 at the cathode.

3.4 - PEMFC Stacks

A FC stack includes MEA sandwiched between bipolar plates, an humidification section (if the stack is internally humidified), cooling plates, end plates, water removal system, tie rods and possibly sealing.

3.4.1 - The Principle : Useful Voltage Output

¹¹ U.S. Patent No.3,134,697

A FC stack consists of many modules in electrical series. In such a configuration the electric current delivered will be that produced by each element, but the total voltage will be the sum of the voltages of each module.

3.4.2 - Bipolar Plates

Bipolar Plates (BP) are the interconnection element between MEA's ; they realize a more compact stack because the anode of one cell is in electrical contact with the cathode of the following one, while maintaining separation of reactants. In the field of stack engineering, for many years the main problem has been ensuring a series of FC modules in a compact frame by means of cheaply-produced BP.

The BP ensure electrical connectivity, gas distribution and separation, heat removal and management of the liquid water produced.

The stacks of the different FC companies can be distinguished by the design of the bipolar plates :

- Ballard started with graphite-machined bipolar plates but produces now metallic-grooved units. The design of grooves along the surface of the bipolar plate is of major importance for cell efficiency and durability : while at the anode a fine gas distribution, current collection, membrane humidification and heat transfer have to be preserved, at the cathode water removal and air delivery add complexity. It has been proven that a cross flow geometry in gas distribution improves reaction speed, but to ease water removal vertical grooves are more suited.
- De Nora has chosen to follow a metallic approach which is claimed to be best suited for mass production. Their design is characterised by a gasket matrix where electrode and collector are fitted. The collector, derived from electrolysis technology, is metallic - preferably aluminium - sheet and it can be produced with inexpensive techniques. The BP of De Nora FC is a flat metal frame, which accomplishes the functions of transmission of the electric current through the cell elements, the release of heat to the external environment, and gas separation.¹²
- Siemens' design involves corrugated metal sheets with an internal cooling fluid. The manufacturing is done by stamping techniques.¹³

3.4.3 - Stack Key Parameters

3.4.3.1 - Specific Weight (Power Density in kW/kg)

Ballard accomplished major progresses by replacing the DuPont membrane with a new, high conductive membrane from Dow Chemicals (XUS), but costs pushed the company to develop its own partially-fluorinated polymer. Power density (W/kg) improved of a factor 25

¹² U.S. Patent N°5,482,792.

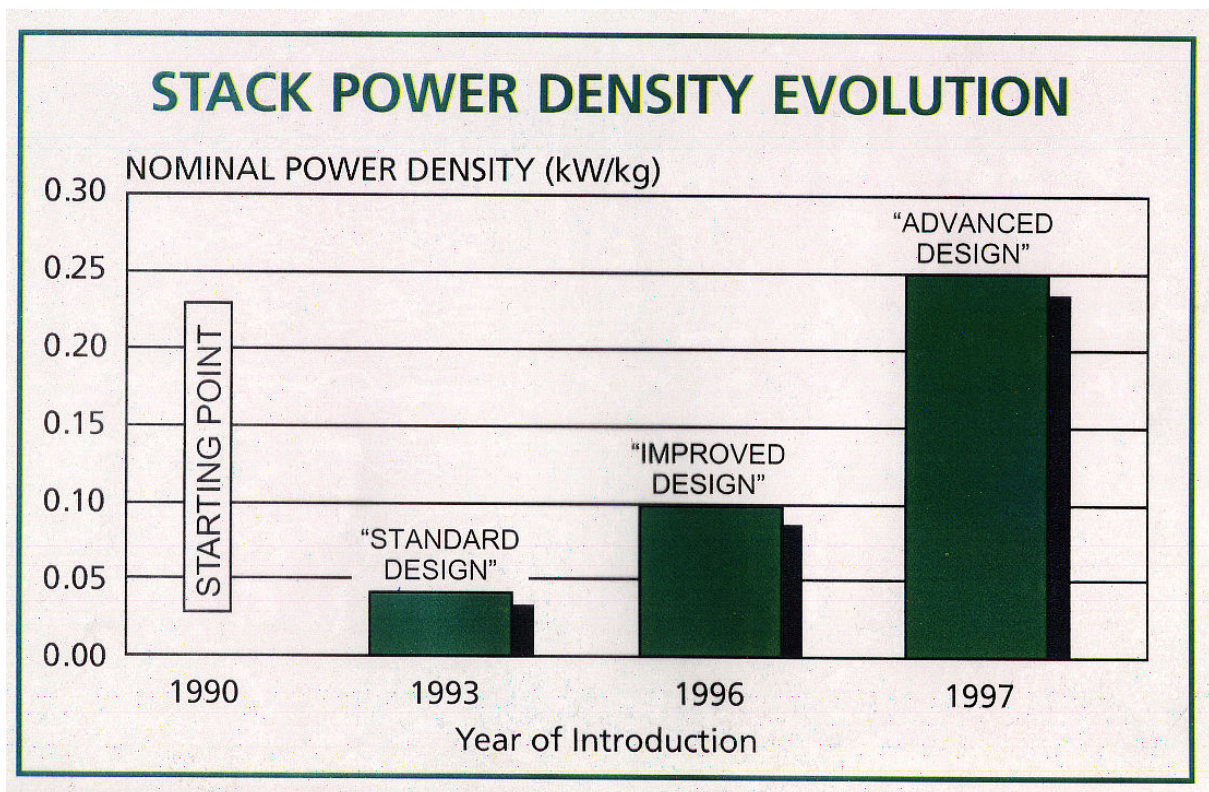
¹³ E. Grecksch & T. Moser : « PEM Fuel Cells : Development and Commercialisation », Intertech Conference, Chicago, september 1996.

(>1kW/lt), *i.e.* the same « box » which used to produce 1 kW now is rated to 25/30 kW.¹⁴ Moreover, the perspectives of cost reduction on all the FC components - *i.e.* catalyst diffusion,¹⁵ membrane, bipolar plates - make the Proton Exchange Membrane Fuel Cell the only alternative to ICE for transportation. Fresh assessments of this statement are found in hybrid car projects or battery substitution for full FC power.¹⁶ De Nora stacks have gone from 0.1 to 0.27 kW/kg ; air-cooled and air-breathing stacks are expected to increase these values.

3.4.3.2 - Specific volume (kW/lt)

Improvements in this domain reflect those registered above : Ballard's stacks have passed from 0.3 to 1 kW/lt (peak power). DeNora's have attained the threshold of 0.13 kW/lt requested by the European Community program to finance mobile applications. In the course of 1997 DeNora will present its new design stack, with 0.43 kW/lt to be employed in the HYDRO-GEN vehicle project.

In the Graph 3.3 below we can see the improvements in power density of De Nora stacks. The FC in 1993 delivered 0.05kW/kg doubled in 1996, while in 1997 this value has risen to 0.25kW/kg (0.32 peak). This 5-fold improvement was realized with thinner electrodes, but especially by advances in bipolar plate technology.



Graph 3.3 - Stack improvements - De Nora.

¹⁴ See : K. Prater : « SPFC for Transport and Stationary applications », Journal of Power Sources 61 (1996).

¹⁵ See Ch. 3.3.3 - Platinum loading.

¹⁶ Ballard developed the first generation bus with unoptimized stack at this purpose. See K. Prater, Journal of Power Sources, 1992,1994, 1996. See also A. Brunia, C.E. Kluiters, D. Schmal: « Battery selection and testing for a fuel cell/battery hybrid electric cars » TNO - Environmental Sciences, in 27th ISATA, 1994 Aachen, Gemany.

3.4.3.3 - Water Removal

One peculiarity of PEFC is that water is produced in the liquid state and not as steam, hence the need of good hydration of the membrane to provide ionic conductivity is balanced by the risk of electrode flooding. Normally the water is removed from the back diffusion at the cathode by an excess of air flow, typically twice what is required for oxidation in the stack. An original method of water management was introduced by Ballard,¹⁷ - « Anode Water Removal » - where excess air and a concentration gradient bring back the water to the anode to humidify the membrane and keep dry the cathode. In this way fuel and oxidant do not need to be water-saturated to humidify the membrane, whilst allowing low air pressure, high and stable peak current and water removal by the fuel stream.

3.4.3.4 - Heat removal

The stack needs to be cooled to 80°C. The management of heat can be performed by air or gas circulation within holes in the bipolar plates. In the case of liquid coolant, required for large systems, the water exhaust can be cooled down and re-cycled by mean of a water circulating system. This function can be optimised by an appropriate heat exchanger, to release heat at the fuel gas processing stage or for space heating.

3.4.3.5 - Anode and Cathode Pressure

The FC power increases with the operating pressure but systems become complicated ; it is therefore normal to operate the cell at near-atmospheric pressure. The most recent stacks developed by Ballard, Siemens and De Nora work between 1 and 3 bars. It is believed that vehicular FC systems will operate at a slightly higher (4 bars) pressure to obtain a higher current. Even if operation at high current has consequences on the voltage efficiency, the dynamic behaviour and the possibility of recovery from the gas exhausts are believed to be more suited for mobile applications.¹⁸

3.5 - Conclusions

We can see a feature of FC technology : it consists in the inherent interdependency of every element involved in the system. So, for exemple, research for an hydrogen/air FC to improve on the Alkaline technology (Hydrogen/Oxygen only) by a stable solid electrolyte - the membrane - converged with efforts to lower the platinum content in the catalyst by means of better dispersion of Pt particles on electrically conductive Carbon Black.

The improvements in the engineering of the stack and module have been impressive, considering the small amount of funds and the time frame to pass from lab scale innovations to pre-commercial testing of a bus having has a goal to be commercially operated on the roads of Chicago and Vancouver : Ballard's « Coldstream » or the NEBUS by DB and car-makers involvement confirms it.

It is reasonable to think that the unique peculiarities of the PEMFC technology, after having frozen budgets for AFC and PAFC mobile projects, will be increasingly supported from

¹⁷ K.B.Prater : « PEFC : a review of recent development », Journal of Power Sources, 51 (1994), pag.138.

¹⁸ Fuel processor for FCV might include a scroll expander recovering 10.2 kW on a 50 kW_{el} system at 70% efficiency (A.D.Little, Multi Fuel Reformers for FC in Transportation, May 1994) in Ch. 5.

national programs and private industry funds, for both transportation and power generation. The PEMFC has high energy efficiencies as well as environmental advantages and research is now devoted to achieve large cost reductions for fuel processor and system integration : compact and cheap alcohol and hydrocarbon reformers. Advanced Fuel Cell systems studies are providing the balance of plant (BOP) components for PEFC operation on commercially available fuels.

Direct Methanol Fuel Cells¹⁹ are being developed because no fuel processing system is required and methanol is a renewable fuel. However, DMFC suffer low current density ($0.3\text{A}/\text{cm}^2$) and reformer emissions can include formic acid and formaldehyde, which are hazardous to health.

¹⁹ M.P. Hogarth *et al.* Johnson Matthey : « Direct Methanol FC Technological Advances and further Requirements », in EFC News, March 1997, copyright « Platinum Metals Review ».