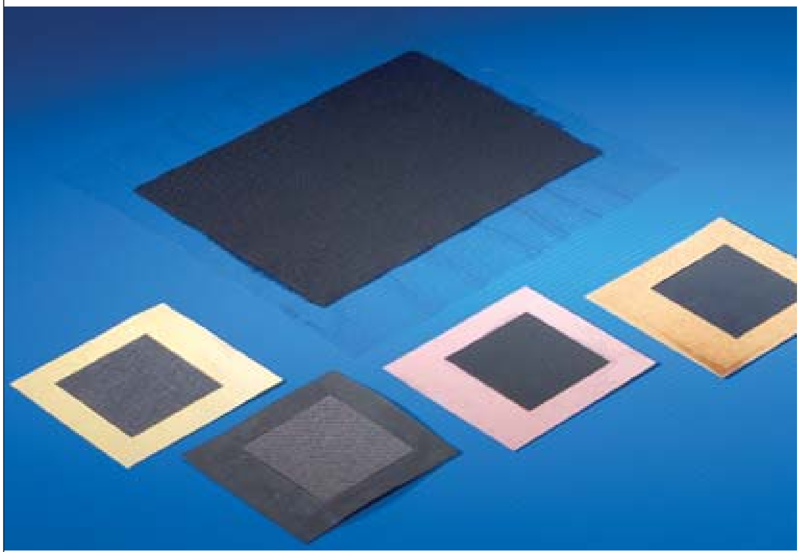
Fuel-cell core optimization

Bringing fuel cells of the PEMFC type to market will entail overcoming scientific and technological barriers, particularly with regard to membrane–electrode assemblies, which are the core of such fuel cells. Advances are being made, in terms of the development of new materials (membranes, catalysts) and fabrication processes, and improving the reliability of these assemblies.



D. Michon-Artechnique/CEA

Membrane–electrode assemblies made by société PaxiTech (see *PaxiTech: first CEA spin-off in the NET sector*). Such assemblies come in a variety of sizes, featuring diffusion layers and connectors of varying thicknesses and of different kinds.

Construction of the core of a fuel cell involves the assembly of two **electrodes** and a **proton**-exchange membrane. The electrodes comprise two layers: an *active layer*, consisting in **catalyst** and **electrolyte** material, in contact with the membrane, and a *diffusion layer*, obtained by depositing carbon and a hydrophobic **polymer** onto a carbon-fiber substrate.
Operational issues in a fuel cell are directly related to the membrane–electrode assemblies (MEAs) (see *Development of new proton-conducting membranes*) providing the **electric power**, with an **efficiency** that is dependent on operating conditions, these in turn being dictated by the application.
Consequently, current developments, whether in terms of materials or technologies, aim at improved adequation of cell cores to their utilization environment (the system). An ideal solution would be to simplify the system, by way of solutions for the issues that, rather than involve additional auxiliary components (gas humidifier, compressor, purifier), would entail modification of the cell core.

Investigating extreme conditions

The approach implemented, in collaboration with manufacturers or industrial users of fuel cells, consists in observing and interpreting cell core behavior in specific, demanding operating conditions, for the purposes, initially, of selecting those components showing the best ability to meet the application-dictated specifications; and, subsequently, designating avenues for the design of innovative components.
As one of the research efforts conducted in this manner, investigations of carbon monoxide (CO) poisoning of **anode** catalysts by the CO present in **reformate fuel** (**hydrogen** generated from **hydrocarbons**) have shown this problem could be greatly attenuated, or even resolved, by substituting pure platinum with appropriate tri-metallic catalysts, and raising cell temperature above 100 °C (see Figure 1). Such catalysts restrict CO **adsorption**, and favor low-potential CO **oxidation**, thus freeing up active sites for the hydrogen oxidation reaction.
Other work, carried out in under-humidified or dry gas operating conditions and at high temperatures (≥ 120 °C), highlight the extent to which electrode chemical composition (**formulation**) needs to be reconsidered, if acceptable performance is to be achieved in such drastic conditions (see Figure 2). Investigations are addressing, in particular, the adequation of the diffusion layers – these being the connecting components between the gas distributors (bipolar plates) and the active layers, where the reactions take place – to utilization conditions. The aim is to establish correlations between materials (woven or nonwoven carbon-fiber-based substrates, functionalized by microporous deposits), their properties (microstructure, **conductivities**, compression, diffusion…), and their performance.

Greater durability

Aside from spot cell-core performance in extreme operating conditions, interest at CEA is also directed at cell

D. Michon-Artechnique/CEA

D. Michon-Artechnique/CEA

Coating (top) and spraying (bottom) benches at CEA/Grenoble, where large-surface-area electrodes are fabricated. On the coating bench, a membrane is undergoing coating with ink consisting in platinum–carbon and electrolyte, to form the active layer. On the other bench, carbon powder and polymers solvated in ink are sprayed to form the diffusion layer. The aim is to develop functionalized electrodes to meet application requirements.

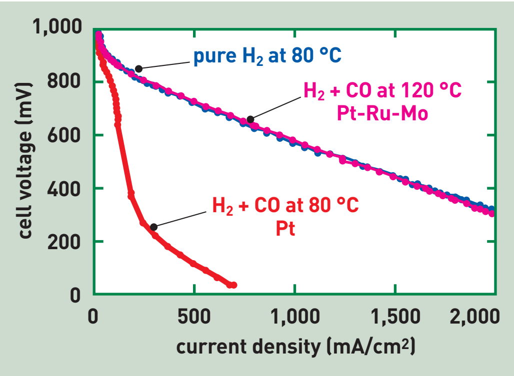


Figure 1.
Performance of a PEM fuel cell operating with CO-contaminated fuel, as shown by output voltage as a function of current density. To cure the anode catalyst poisoning problem, the solution consists in use of a tri-metallic catalyst (platinum [Pt]–ruthenium [Ru]–molybdenum [Mo]) and raising operating temperature to 120 °C.

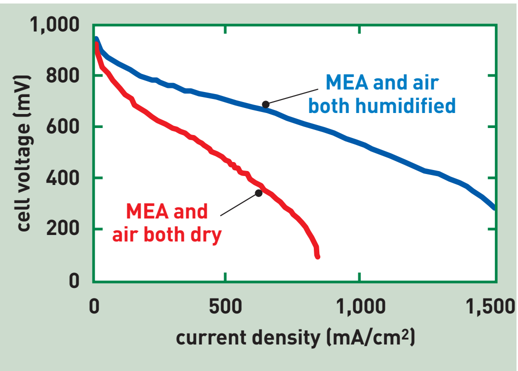


Figure 2.
Performance of a PEM fuel cell operating with under-humidified or dry gases, as shown by output voltage as a function of current density. To resolve the issue of operation in dry gas conditions, the aim is to define the chemical composition of cell cores able to function with no humidification.

core durability, presently limited by the gradual degradation of the various components (diffusion layers, active layers, and membranes), or of their interfaces. What is at stake here is the development of aging protocols that are representative of applications (whether static operation over extended periods, or cyclic operation), and diagnostics, both *in situ* (analyses of active surface areas, local measurements of voltage, temperatures…) and *ex situ* (analysis of the mechanical stresses induced by fabrication and fitting into the cell, *post-mortem* examination of electrodes and interfaces), to identify and interpret these degradations.

Mastering fabrication processes

Understanding cell cores further requires mastering their fabrication processes. Facilities have been set up, to enable going over from manual electrode fabrication to semi-automated fabrication. These are associated to characterization resources, both *in situ* – namely fuel cell test benches, adapted to specific trials (detailed electrochemical analyses and modeling, operation at temperatures from – 20 °C to 120 °C, use of gas mixtures…) – and *ex situ* – such as instruments for the measurement of electrical and mechanical properties (traction–compression machine, electric resistance measuring device), and scanning electron microscopes (conventional SEM, and low-energy–high-resolution FEG-SEM) and transmission electron microscopes (conventional TEM, and high-resolution HRTEM with chemical analysis) – to determine the influence of the various fabrication parameters on performance and durability.

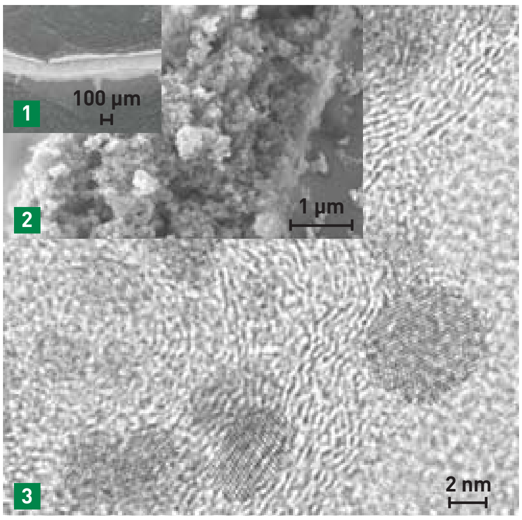
D. Michon-Artechnique/CEA

Pacmaille test bench at CEA/Grenoble, on which detailed electrochemical investigations are carried out, enabling cell core characterization, including, in particular, dynamic modeling of active layers.

Innovative concepts for catalysts

Upstream of such research work, as for membranes, innovative pathways are being explored, with respect to catalysts, with the fabrication of functionalized nanoparticles, hosting both the catalytic function and the proton-conduction function, development of new processes using chemical or physical deposition in a plasma environment, or investigation of enzymatic catalysis.

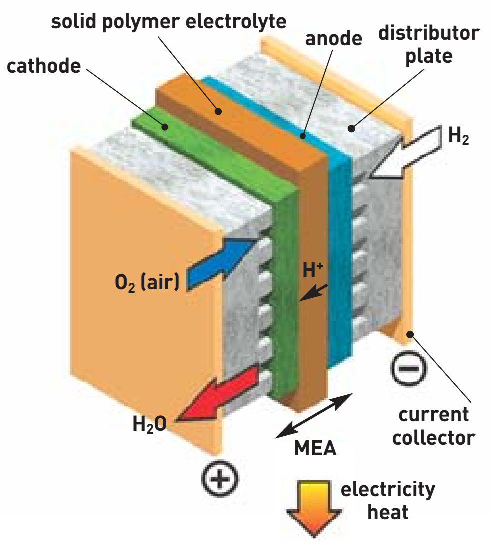
> **Sylvie Escribano**
Technological Research Division
CEA Grenoble Center



CEA

Analysis, by means of scanning (SEM) and transmission (TEM) electron microscopy, of a cell core and its components.
1 Membrane–electrode assembly, as observed under SEM.
2 Active layer of an electrode, examined under high-resolution FEG-SEM.
3 Catalyst, consisting in platinum-based nanoparticles on a carbon powder substrate, as seen by HRTEM.

C How does a fuel cell work?



Operating principle of the fuel cell: the example of the proton-exchange membrane fuel cell. MEA stands for membrane-electrode assembly.

The fuel cell is based on a principle discovered quite some time ago, since it was in 1839 that Sir William Grove constructed the first electrochemical cell working with hydrogen as its fuel, thus demonstrating the ability to generate electric current through direct conversion of the fuel's chemical energy. Since the fuel cell has the special characteristic of using two gases - hydrogen H_2 and oxygen O_2 - as its electrochemical couple, the oxidation-reduction reactions occurring inside the fuel cell are particularly simple.

The reaction takes place inside a structure (the basic electrochemical cell), consisting essentially in two electrodes (the anode and cathode), separated by an electrolyte, i.e. a material that lets ions through. The electrodes employ catalysts, to activate, on the one side, the hydrogen oxidation reaction, and, on the other, the oxygen reduction reaction.

In the case of an acid-electrolyte cell (or proton exchange membrane fuel cell), the hydrogen at the anode is dissociated into protons (or hydrogen ions H^+) and electrons, in accordance with the oxidation reaction: $H_2 \rightarrow 2\ H^+ + 2\ e^-$. At the cathode, the oxygen, the electrons and the protons recombine to yield water: $2\ H^+ + 1/2\ O_2 + 2\ e^- \rightarrow H_2O$. The principle of the fuel cell is thus the converse of that of water electrolysis. The thermodynamic potential for such an electrochemical cell, consequently, stands at around 1.23 volt (V). However, in practice, the cell exhibits a voltage of about 0.6 V for current densities of 0.6-0.8 A/cm^2. The efficiency of such a fuel cell is thus equal to about 50%, the energy dissipated naturally being so dissipated in the form of heat.