Advanced diagnostic tools

To be truly predictive, modeling of fuel cell operation, for the PEMFC type, calls for exact knowledge of the elementary mechanisms involved in transfer of matter within cell cores, and thus of water management processes. CEA has developed two diagnostic tools: one for the characterization of water generation and flow inside the cell; the other one for the measurement of current densities, linked as these are, among other parameters, to the presence of water in the gas distributors.

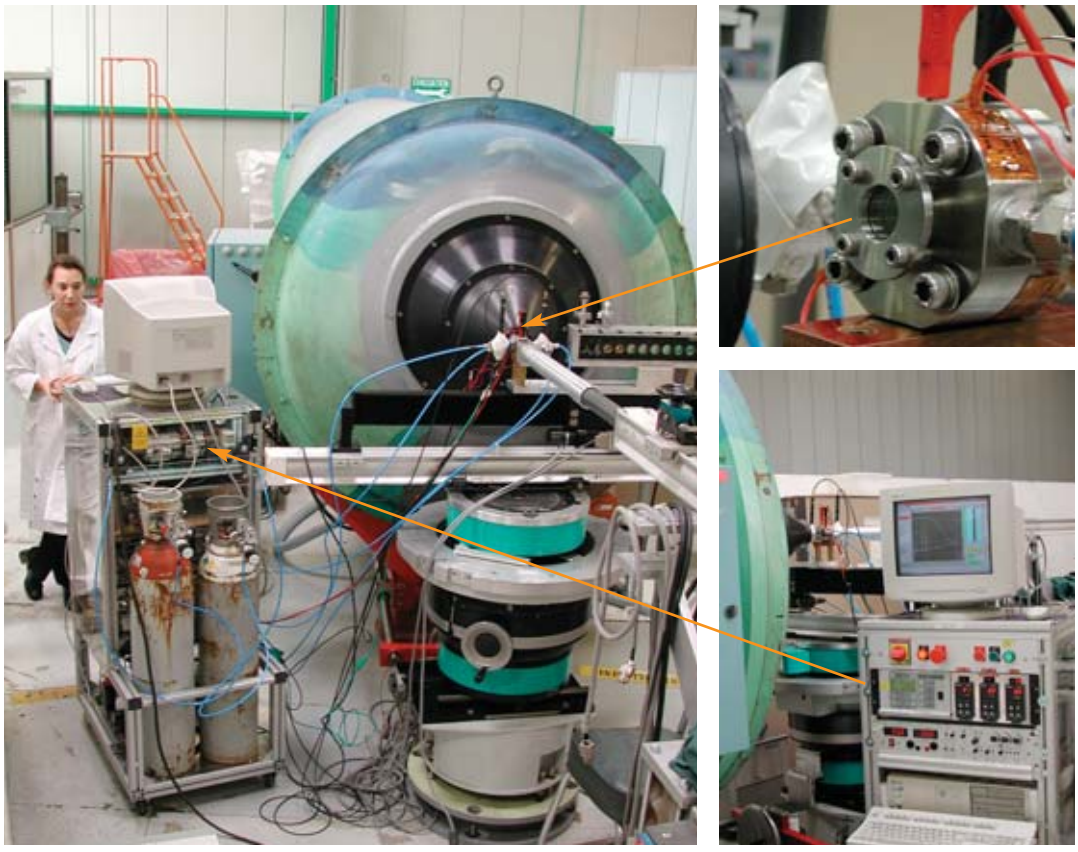
PEM fuel cell operation is strongly impacted by the presence of water. While a minimum level of water content in the **proton**-conducting membranes is required, to ensure good **ion conduction**, excess liquid water at the **electrodes** may impede access of gases to the reaction sites. The extent of swelling in the **polymer** membrane is the outcome of complex, as yet poorly controlled processes, such as electro-osmosis, back diffusion, **sorption** kinetics, and precarious equilibrium between water generated by the fuel cell and water introduced or extracted by the gases. Electro-osmosis refers to the transport of water by the current of protons, from the **anode** to the **cathode**, resulting in a concentration profile within the thickness of the membrane. This concentration gradient induces diffusion of water in the opposite direction (back diffusion), tending to even out the profile. Likewise, the gas-swept surface does not operate homogeneously between the gas inlet and outlet areas and depending on the gas distribution geometry. Optimization of fuel cell operation thus requires a good understanding of water management, and development of diagnostic tools to determine water-concentration profiles both across the membrane cross-section, and across the active surface.

On a more macroscopic scale, **current density** distribution reflects local energy-conversion performance, this being linked, among other factors, to electrochemical conditions in the vicinity of reaction zones, and thermalhydraulic processes in the gas distributors. Hence, two original tools have been developed and validated at CEA. The first one uses small-angle neutron scattering, (1) while the second one uses current density measurements.

Small-angle neutron scattering experiments

Neutrons are scattered, essentially, by **hydrogen** atoms, and thus are highly sensitive to water content, this water carrying the only atoms of hydrogen present inside a fuel cell (aside from the gas). A basic cell was constructed, exhibiting the highest possible transparency

(1) Small-angle neutron scattering (also known as central scattering): a technique for the investigation of matter, based on neutron (or X-ray) scattering at angles that may be as low as 0.005°. This allows investigation of zones of heterogeneity, of sizes ranging from a few **angstroms** to several thousand angstroms. With X-rays, these zones of heterogeneity are domains exhibiting different electron density from that of the remainder of the sample.



Fuel cell in position on the Paxe small-angle neutron scattering spectrometer in the Léon-Brillouin Laboratory (Saclay Center), for an investigation of membrane water content under varying operating conditions.

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to neutrons, with the ability to operate at varying temperatures and pressures, together with a transportable test bench. The latter is adequately protected, to enable operation close to a nuclear reactor, and is fitted with devices to record all the important parameters in the experiment, such as gas temperatures, pressures, and relative humidity levels, as well as electrochemical data. The intensity and position of the characteristic peak observed in small-angle scattering spectra with Nafion ® membranes vary greatly with water content. An analysis involving reference spectra recorded at equilibrium for different water contents, makes it possible to extract from each spectrum a concentration profile across the membrane's thickness (see Figure 1). Acquisition time for the spectra, allowing for an adequate statistic, is about 10 minutes, thus providing a means of monitoring the kinetics of water content variation in membranes according to operating conditions. Further, this technique provides the ability to differentiate between water contained inside the membrane, and water condensing in the gas distributors.

The feasibility of such experiments was demonstrated over two series of tests, carried out at the Léon-Brillouin Laboratory (CEA–CNRS, Saclay Center), investigating swelling of nearly dry membranes from water generated by the fuel cell. The influence of such parameters as gas distributor porosity, gas flow, current density, type of electrodes and membrane thickness was thus investigated. Among major findings, it was shown that good performance may be achieved with little membrane swelling, including at high current densities.

This technique should enable validation of **models** describing transfers of matter within cell cores, and thus water management in cells during operation, by comparison of calculated concentration profiles with those obtained experimentally.

> **Gérard Gebel**, **Olivier Diat**
Physical Sciences Division
Renaut Mosdale and **Sylvie Escribano**
Technological Research Division
CEA Grenoble Center

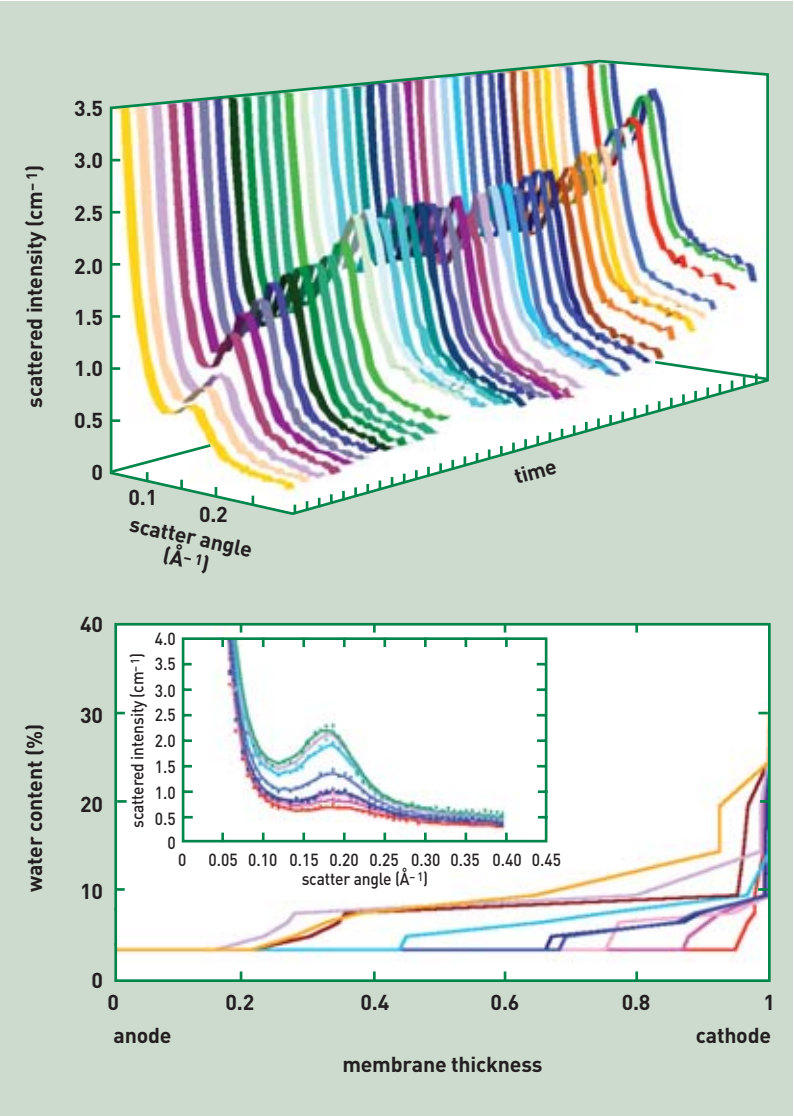


Figure 1.
Top, small-angle neutron scattering spectra as a function of time for a fuel cell during operation. A spectrum is recorded every 10 minutes, under varying operating conditions. Scattered intensity increases with membrane swelling. Bottom, water concentration profiles across the membrane, derived from the spectra shown (inset). A dry membrane would yield a horizontal line at 5% (residual water), whereas a fully swelled membrane would yield a horizontal line at about 35%. These profiles show that the membrane exhibits some swelling at the cathode, owing to water generation, but fairly little swelling overall, being even nearly dry at the anode.

Measurement of current densities

Distribution of current in the bipolar collector plates of a PEM fuel cell may be determined directly, by setting up instrumented subcells, electrically isolated from each other, or indirectly, by measurement of the induced magnetic field. The latter principle was selected, as its implementation occasions only limited perturbation, or even no perturbation, to current distribution. Thus, the technique used consists in measuring two components of the induced magnetic field, gradients for which are linked to the perpendicular component of current density via one of the Maxwell equations. In the stack case, current is perpendicular to the basic cells, and the two magnetic field components to be determined are contained in the plane of the bipolar plates (see Figure 2). Measurements are carried out by the displacement of probes carrying magnetoresistive sensors and thermocouples (to effect a correction for tempera-

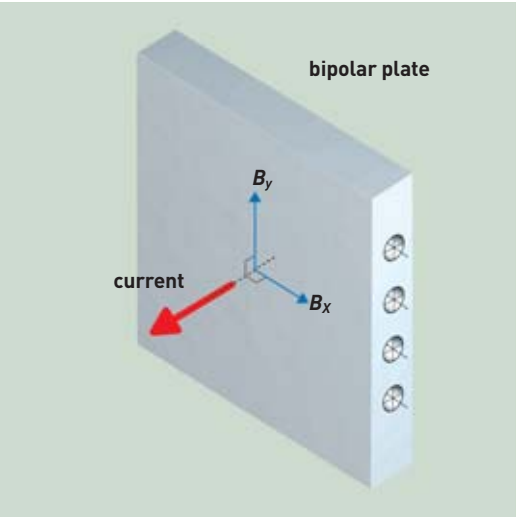
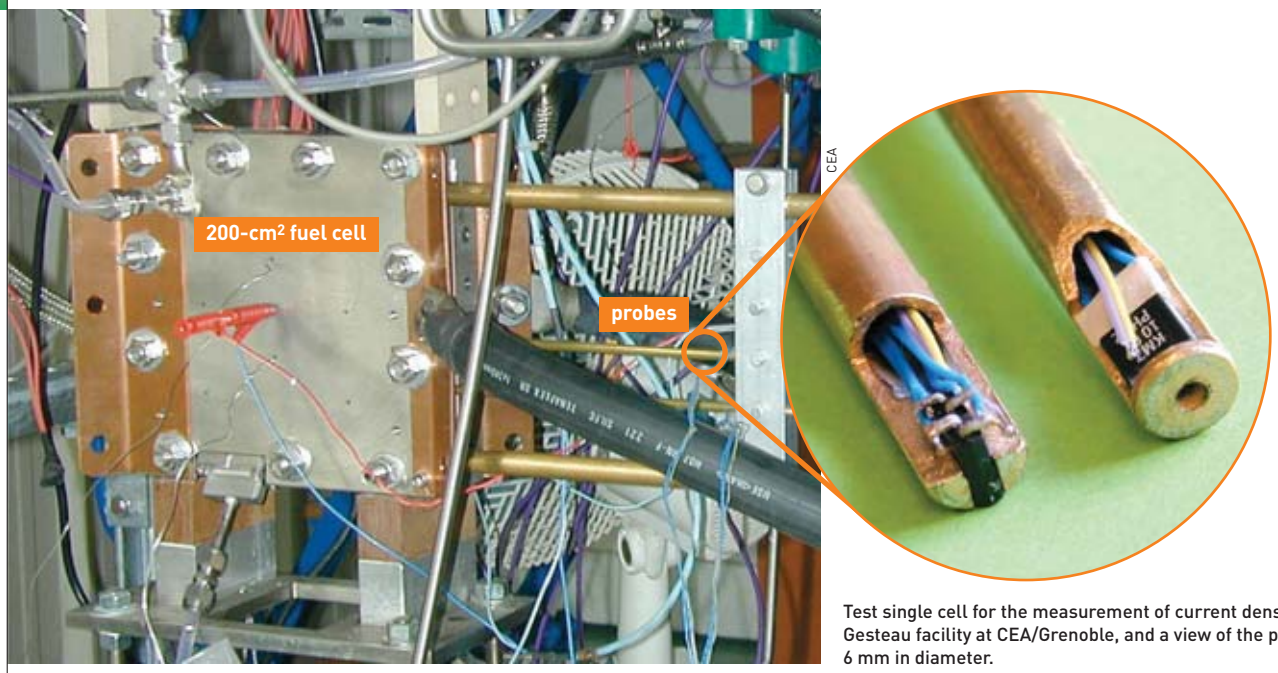


Figure 2.
Theoretical schematic of current density measurement.



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Test single cell for the measurement of current density, on the Gesteau facility at CEA/Grenoble, and a view of the probes used, 6 mm in diameter.

ture), within cavities bored into modified bipolar plates, or into intercalary parts.
Functioning of this instrument was validated on a 200-cm² single cell, making it possible, in particular, to evidence, for that cell, redistribution of current in gas distributor flooding conditions (see Figure 3). Further, initial trials on an actual stack have shown the instrument's ability to yield quantitative mappings of current densities in the direction perpendicular to the bipolar plates.
Developments under consideration are aimed at improving the system's operational capacity, through piloting of the sensors, allowing a simplification of the experimental procedure, and obviating the need for temperature corrections.

> **Roland Riva**, **Bruno Bador**, **Alain Memponteil**
Nuclear Energy Division
and **Pascal Schott**
Technological Research Division
CEA Grenoble Center

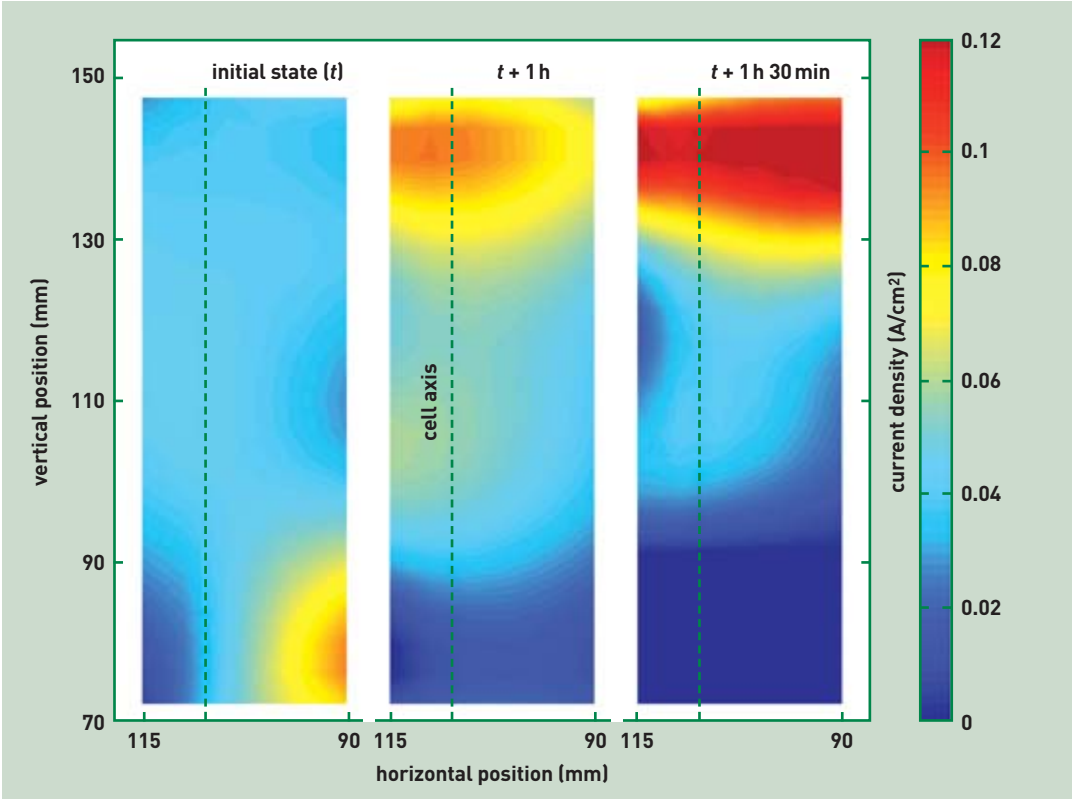

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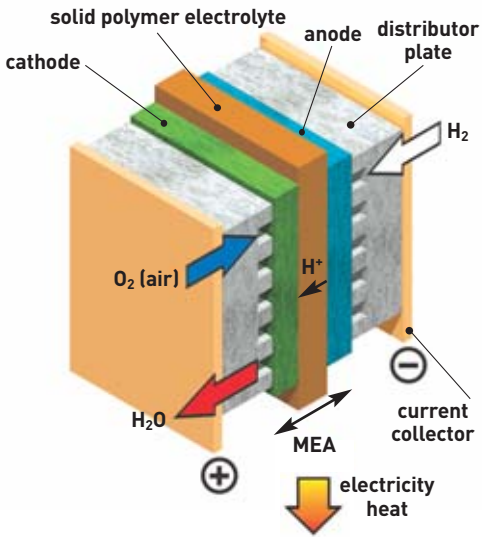
Figure 3.
Current density measurements carried out during flooding of the cathode compartment of a 200-cm² single cell. Current redistribution is visualized at top.

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.