

PEMFC low-temperature fuel cells

Low-temperature fuel cells of the PEMFC type are the subject of much research work, with a view to improving their performance, and achieving cost reductions. Solutions involve development of new polymer (electrolyte) membranes, improvements to cell cores (membrane-electrode assemblies), development of novel catalysts, new bipolar plate concepts, whether metallic or composite, an innovative gas distribution concept, as well as optimization of fuel-cell systems. Advanced diagnostic tools, associated to modeling resources, enable CEA to avail itself of a full range of options for the expert assessment, and, most importantly, for the design, and aid to the sizing, of fuel-cell systems.

Development of new proton-conducting membranes

In fuel cells of the PEMFC type, current ion-conductive membranes, though they exhibit highly attractive performance and high stability, however involve major disadvantages, restricting their suitability for widespread utilization. Research work is underway, aiming to improve these membranes, and develop novel membranes, and innovative concepts.



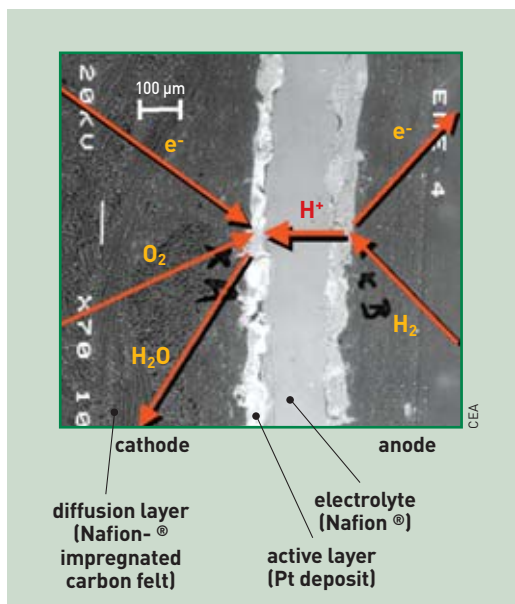
Mechanical analyzer, used to investigate the static and dynamic response of polymer membranes subjected to compression, shear or stretching stresses.

The core of low-temperature fuel cells comprises a very thin **ion-conductive** membrane, sandwiched between two **electrodes** (see Box C, *How does a fuel cell work?*). The membrane is a solid **polymer electrolyte** having as its main functions, on the one hand, to transport **protons** from the **anode** to the **cathode**, while remaining an excellent isolator for **electrons**,

and, on the other, to separate the gaseous **hydrogen** from the oxygen. Its thickness ranges from 10 to 100 **microns**. This is a tradeoff between gains in performance, entailing the lowest value possible, to keep down **ohmic loss**, and maintaining mechanical properties and impermeability to gases, which improve with greater thickness.



Photograph, taken under scanning electron microscopy, of the core of a low-temperature fuel cell. The core comprises a very thin ion-conductive membrane (solid polymer electrolyte of the Nafion® type) sandwiched between two electrodes.



Limitations of current membranes

The reference materials, in terms of performance and stability, are the perfluorosulfonic acid polymers, ⁽¹⁾ of the Nafion® (du Pont de Nemours and Co.) type. However, the excessive cost of such polymers (some €700/m²) is unacceptable, when providing motive power for a vehicle that requires some ten square meters of membrane to achieve adequate fuel-cell power. Moreover, their **ion conductivity** is strongly dependent on water content, precluding any operation at temperatures higher than 80 °C, and making for peculiarly complex water management in the system as a whole. Further, permeability of such membranes to **methanol** has put a brake on direct methanol fuel cell (DMFC) development for portable applications. Research in the membrane area is thus focusing on fabrication of alternative, less costly, stable membranes, with the ability to function at higher temperatures, and impermeable to methanol. To date, the ideal membrane does not exist, and teams

from the various expertise centers at CEA are working, in collaboration with CNRS, both on improving existing membranes and developing new structures, and innovative concepts.

Sulfonic acid polyimide-based membranes

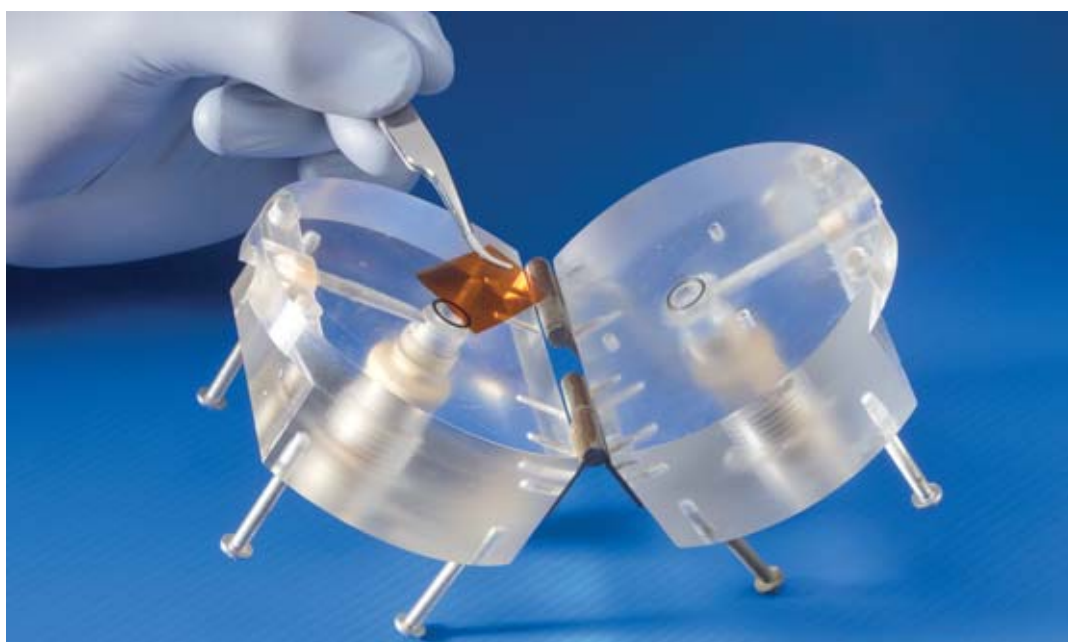
Thermostable, sulfonic acid heterocyclic aromatic polymers represent one of the more promising avenues of research. CEA and CNRS are conducting a joint effort to develop sulfonic acid polyimide-based membranes, ⁽²⁾ going for an original synthesis path using sulfonic acid **monomers**, affording the ability to control charged monomer distribution along the chains. An ambitious program, with support from the French Ministry in charge of research, via the **PACo Network**, bringing together various laboratories from public-sector research and industry, has enabled expertise to be grown in the areas of **composite** synthesis, forming and **formulation**, characterization, and structural investigation, through to cell trials, with an emphasis on investigation of stability. Membranes have thus been prepared on a semi-industrial scale.

Findings from this program have led not only to identification of the main degradation mechanism (**hydrolysis** of the imide functions), but also, most crucially, to development of *ex-situ* aging test protocols, enabling fast qualification of new structures. These membranes exhibit an original structure: the polymer chains are oriented in lamellar domains of about 10 **nanometers**, the domains in turn exhibiting orientation parallel to the film surface. This microstructure, showing no evolution with swelling, induces highly **anisotropic** swelling and transport properties. Finally,

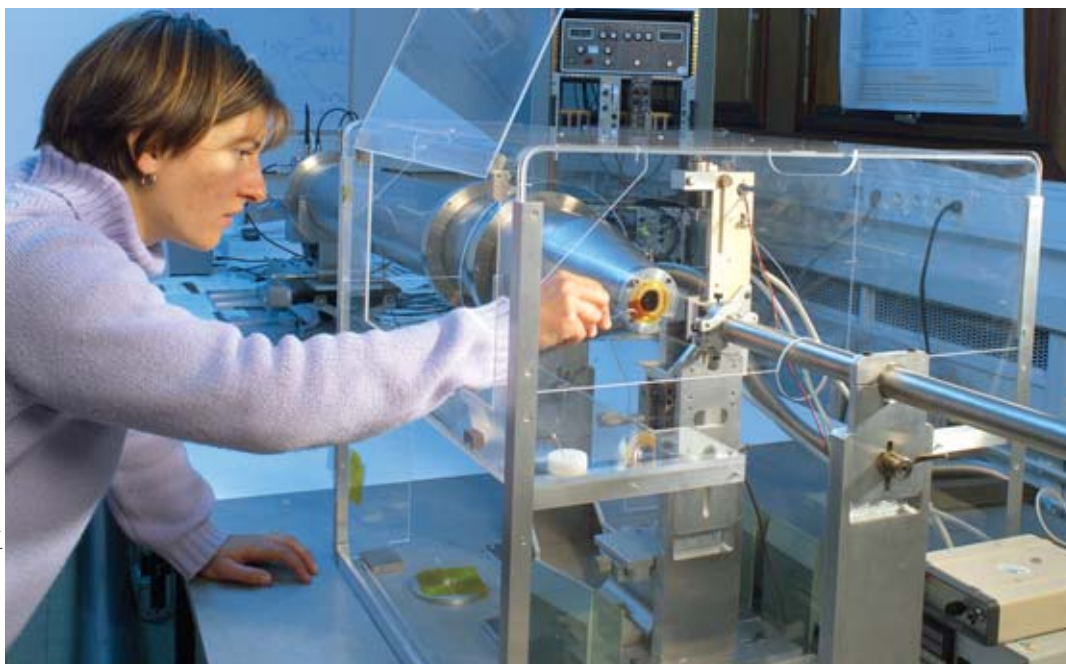
(1) Perfluorosulfonic acid polymers feature a main chain consisting in CF₂ units (all hydrogen atoms associated to carbon being substituted by fluorine atoms), and fluorine pendant chains, terminating in sulfonic acid groups (SO₃H), effecting proton exchange.

(2) Sulfonic acid polyimides: polymers bearing imide functions (O=C-N-C=O), and proton-exchanging sulfonic acid groups (SO₃H) directly bonded to the main chain.

Mercury-electrode cell, used to determine polymer membrane ion conductivity by impedance spectrometry.



D. Michon-Artequique/CEA



Small-angle X-ray scattering camera enabling investigation of membrane structure at nanometric scale.

multilayer membranes were prepared, for the purposes of optimization of these membranes, in terms of performance and durability, these varying inversely with sulfonic function content.

Improvement of properties through chemical modification

Research priority is given to improving the stability of sulfonated polyaromatic-based membranes, which remain the sole membranes available for consideration as alternatives to Nafion[®]. Work is ongoing on development and testing of new structures, of acknowledged stability, but presenting issues of solubility and difficult forming. Appropriate chemical modifications are used to introduce a degree of flexibility, and thus improve mechanical properties. Similarly, though at present most membranes do not exhibit in-cell longevity higher than about one thousand hours, chemical modifications may bring gains by a factor 5–10, adequate for a majority of utilizations. However, prior identification will be required, of the mechanisms responsible for degradation.

Concurrently, new avenues of research are being explored, in collaboration with CNRS, including membrane preparation through the plasma path (deposition and **polymerization** from a vapor phase), or synthesis of new fluorine membranes, matching Nafion[®] at lower cost, while providing the ability to adjust properties according to application or forming requirements, which is not conceivable with commercially available US or Japanese membranes.

Hybrid materials for high temperatures

High-temperature operation (> 120 °C) is one of the goals set by automotive manufacturers, to facilitate heat rejection (50% of output power), while obviating the need to resort to oversized radiators (*see Box on Fuel cells: an automobile manufacturer's take*). This calls for extremely stable materials, further exhibiting the ability to transport protons in the absence of free water. The solution lies in hybrid materials, based on inor-

ganic conductors dispersed in an organic matrix. However, such materials must have the ability to function at cell start-up, hence at low temperature. A number of programs are targeting development of this type of materials, through introduction of dispersed inorganic materials (clays, mesoporous silica...) into a thermostable polymer matrix.

Membrane-electrode assembly optimization

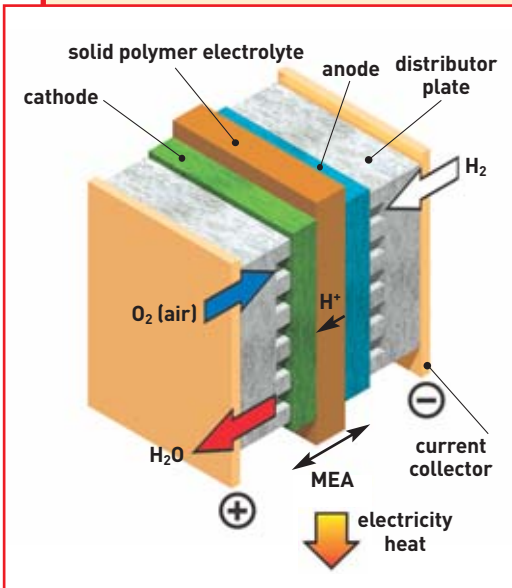
Whichever materials are selected for future fuel cells, the membrane-electrode assemblies will require optimization, in terms of both performance and durability. The thin impregnated layer on the electrodes, ensuring the bond between **catalyst**, current collector and membrane, is invariably made from Nafion[®]-based materials, which gives rise to electrode-membrane interfacing issues, shifting the issues relating to use of Nafion[®] from the membrane to the electrode. Complete sulfonic acid polyimide-based membrane-electrode assemblies were fabricated and tested, allowing first-time operation of a wholly Nafion[®]-free unit. However, performance is poorer than what obtains when using Nafion[®] around the catalyst, and polyimide in contact with the membrane. This finding highlights the difficulty of evaluating the actual value of a material when in-cell testing is carried out, and the need to develop reliable diagnostic tools.

> **G rard Gebel**

Physical Sciences Division
CEA Grenoble Center

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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/cm². 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.