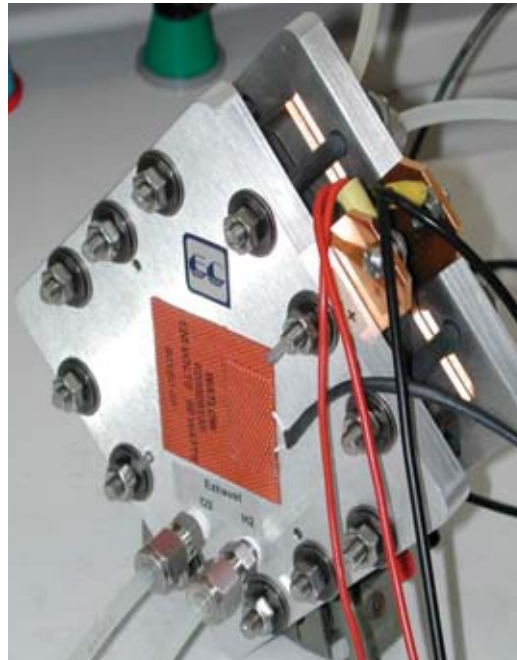




Development of new catalysts: enzymatic catalysis

Whereas corrosion of metallic materials by bacteria is a process dreaded by metallurgists, the mechanisms of such corrosion, involving specific enzymes as they do, are of great interest as regards fuel cells of the PEMFC type. Indeed, adding enzymes having the ability to reproduce biocorrosion phenomena enables enhanced rates to be achieved for the reactions occurring at the anode and cathode.



PEM fuel cell pilot used to carry out trials for the development of new catalysts.

Two papers, published in scientific journals at the end of 2002, ⁽¹⁾ suggest using marine sediments to generate electricity. The authors built a fuel cell of which one **electrode**, the **anode**, was buried in sediment (**anaerobic** environment), while the other, the **cathode**, was positioned close to the surface (water more or less saturated with dissolved oxygen). Their findings showed that it is colonization of the anode surface by specific **bacteria** that enhances, to a remarkable degree, the efficiency of **electron** transfer.

At the same time, and independently from these investigations, two French teams, one from CNRS (Chemical Engineering Laboratory, Toulouse), the other from CEA (Laboratory for Investigation of Aqueous Corrosion, Saclay Center), filed two joint patent applications, under the headings "Pile à combustible utilisant des enzymes en tant que catalyseurs des réactions cathodique et/ou anodique" ("Fuel cell using enzymes as cathode and/or anode reaction catalysts"), ⁽²⁾ and "Pile à combustible utilisant des biofilms en tant que catalyseurs des réactions cathodique et/ou anodique" ("Fuel cell using biofilms as cathode and/or anode reaction catalysts"). ⁽³⁾ Both indeed refer to the selfsame

phenomenon: bacteria can be used to generate electricity.

Making use of a dread phenomenon

The investigations carried out at CEA and CNRS on the bacterial **catalysis** (or biocatalysis) of anode and/or cathode reactions further highlighted the crucial role played by **enzymes**. Anecdotally, these investigations were being conducted, initially, under the aegis of European research programs and networks concerned with seawater corrosion of stainless steels, with the assistance of an Italian team from the National Research Council (CNR: Consiglio Nazionale delle Ricerche, Institute of Marine Corrosion of Metals, Genoa). In well-defined conditions, steel coupons immersed in the sea undergo surface colonization by microorganisms having the ability to increase considerably the rate of dissolved oxygen **reduction**. These microorganisms attach to the material's surface by secreting **polymers** forming an adhesive film, known as a **biofilm**. The phenomenon of the biocatalysis of oxygen reduction, induced by marine biofilms, has been known for some ten years, this being a dreaded process, as it causes severe corrosion of stainless steels. Hence, it is as a rule strenuously resisted. On the other hand, if physicists choose to promote the process, by selecting appro-

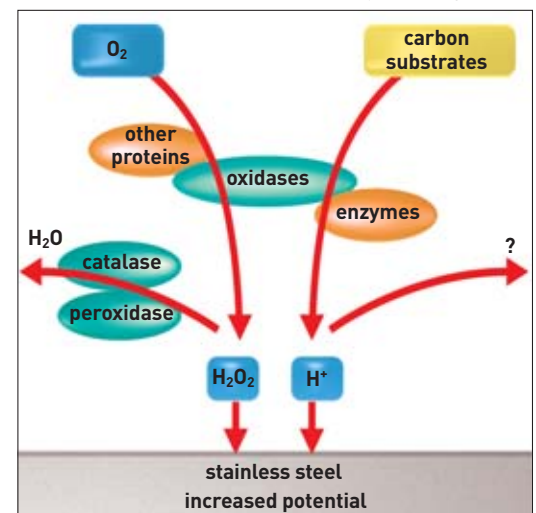


Figure 1. "Enzymatic model" for stainless steel biocorrosion in natural water. In this model, oxidases, in the presence of sugar (carbonaceous substrates) and oxygen [O₂], catalyze formation of hydrogen peroxide [H₂O₂] and acid radicals [H⁺]. Presence of hydrogen peroxide and acid at the material-biofilm interface induces an increase in the free corrosion potential of stainless steel. However, presence of other enzymes, such as catalases or peroxidases, results in catalysis of hydrogen peroxide degradation (into water H₂O), while diffusion or dilution may equally limit biofilm acidity at the interface.

(1) D. R. Bond *et al.*, *Science* 295 (2002), pp. 483–485; and L. M. Tender *et al.*, *Nature Biotechnology* 20 (2002), pp. 821–825.

(2) Application for patent 02 01488 of 7 February 2002.

(3) Application for patent 02 10009 of 6 August 2002.

priate operating conditions, the growth of these marine microorganisms renders stainless steel materials as effective as platinum, with respect to oxygen reduction. The benefits of bacterial catalysis, in the context of fuel cells, then become apparent. The outcome of investigations of biocatalysis mechanisms was the highlighting of the major part played by enzymes in increasing the rate of cathode corrosion reactions; physicists thus refer to the enzymatic model of stainless-steel biocorrosion in natural waters (see Figure 1).

Selecting the appropriate enzyme

As far as biocatalysis in fuel cells is concerned, initial trials went for the cathode reaction, this being as a rule the limiting step in PEM fuel cells. In this type of cell, the catalyst for the anode and cathode reactions is platinum. The first stage consisted in looking for an enzyme reproducing the observed biocorrosion processes, while being nontoxic, easily handled, and not overly expensive. A number of oxidase types showed ability to reproduce the electrochemical behavior of stainless steels in natural waters (see Figure 2). Of these, glucose oxidase was selected for trials in a PEM cell, this enzyme being at the same time nontoxic, inexpensive (it is currently one of the cheapest oxidases available), and relatively easy to use.

Enhanced reaction rate

An initial campaign of tests, carried out on a PEM fuel cell in an aqueous medium, found major enhancements in cathode reaction kinetics (by a factor 10–100 or greater, according to output power) at ambient temperature. Experiments were also carried out with a laboratory H_2-O_2 fuel cell, with graphite electrodes and 1 mg/cm^2 platinum loading. When glucose oxidase, together with its glucose substrate, was added into the cathode compartment prior to operation, increased output power from the fuel cell was observed (see Figure 3). Research work is ongoing, both of a fundamental nature (electrochemical characterization of this catalysis process, relationship between substrate and enzymes...) and of a technological character (optimization of enzyme and substrate introduction, scale effects, influence of the substrate...).

Broader perspectives

Demonstration of such biocatalysis processes on conductor materials hints at new prospects, with the highlighting of an electrochemical connection between materials and microorganisms. Biofilms, owing to the bacteria and/or enzymes they contain, may be electrochemically active, thus conferring on conducting materials unexpected behavior characteristics. It is in the context of such perspectives, broader than the application to fuel cells, that the European EA-Biofilm (Electro-Active Biofilm) Program was launched, in September 2004.

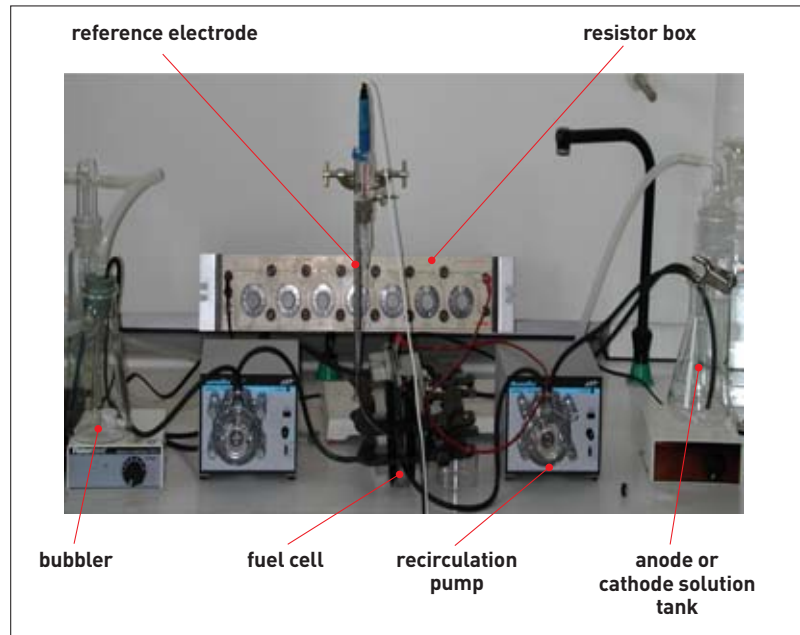
> Damien Féron* and Alain Bergel**

*Nuclear Energy Division

CEA Saclay Center

**Laboratory of Chemical Engineering

CNRS Toulouse



Experimental bench used to carry out tests on an aqueous-medium H_2-O_2 fuel cell, to investigate the influence of introduction of enzymes into the cathode compartment on power output.

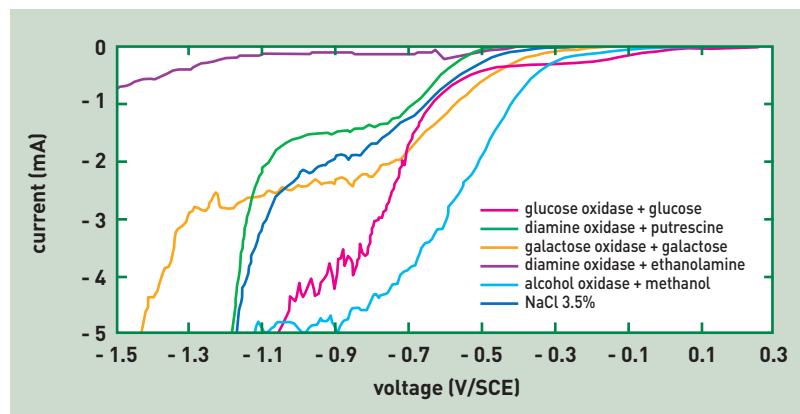


Figure 2. Comparison of the currents, expressed in milliamperes (mA), of cathode reactions, for five oxidases, as a function of voltage, expressed in volts versus a reference electrode - the so-called "saturated calomel electrode" (V/SCE). The curves show that cathode intensities reach a maximum with alcohol oxidase and glucose oxidase. The two diamine oxidases correspond to two distinct amines.

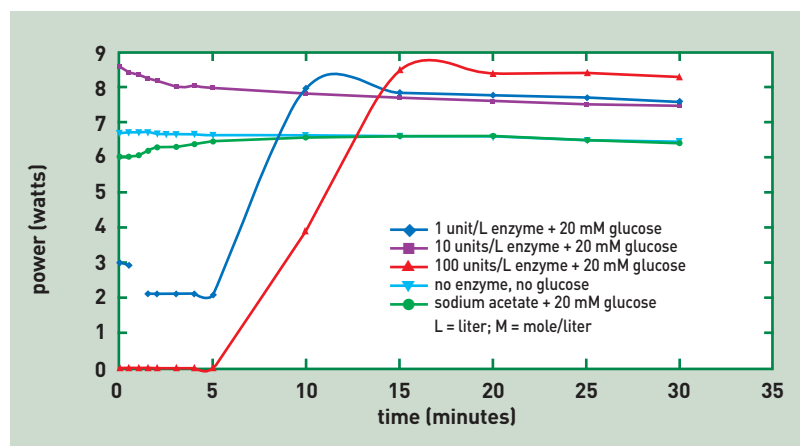
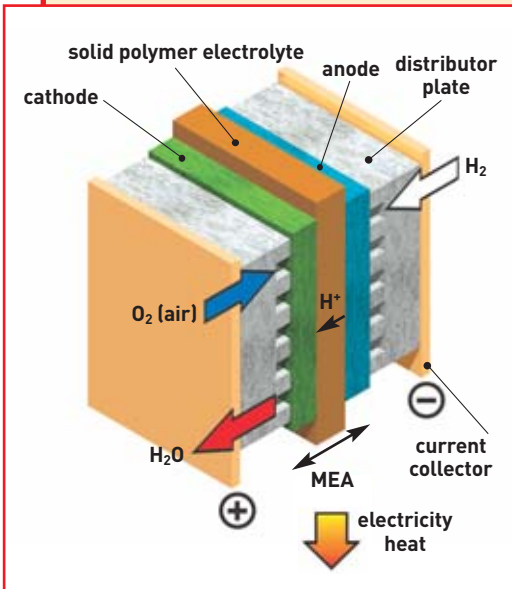


Figure 3. Output power as a function of time, from an H_2-O_2 fuel cell in which enzymes, together with their substrates, have been introduced, at various concentrations, into the cathode compartment. The two curves with "no enzymes" refer to tests carried out before and after use of enzymes. Adding glucose oxidase results in a 15–25% increase in output power.

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/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.