Fuel cells with direct hydrocarbon feeding

Introduction, in the medium term, of SOFCs onto the market
will depend on the ability of these fuel cells to operate under direct
hydrocarbon or biomass product feed conditions. For that purpose,
optimization must be achieved with respect to anode materials,
and appropriate operating conditions must be defined
for such materials.

The Solo test rig, set up at the Grenoble Center, allows investigation of SOFCs with a variety of fuels, and serves as an aid to modeling for processes occurring at the anode.

SOFC fuel cells presently offer a promising pathway for decentralized and environmentally friendly electricity generation. Owing to their high operating temperature (typically 750-950 °C for planar technology), they exhibit a high fuel flexibility. They can indeed be fed either by **fossil** fuels (**natural gas**, **LPG**, kerosene, diesel fuel…), refined to varying degrees, or alcohols (**methanol**, **ethanol**…) of moderate purity, obtained, for instance, from processing of **biomass**. The principle relies on direct conversion of the **hydrocarbon** into **hydrogen** inside the cell's **anode**, the hydrogen generated then being used conventionally to produce electricity by way of its electrochemical oxidation. The distribution infrastructure for such fuels, already available as it is, by contrast with the hydrogen infrastructure, would moreover facilitate fuel cell commercialization, allowing targeting of such markets as small **stationary** units for **cogeneration**, or **auxiliary power units** for heavy transport vehicles.

The high operating temperature of SOFCs does entail, however, a number of technological barriers, restricting durability and reliability for such systems. One research avenue currently being prioritized consists in getting that temperature down as low as possible. However, when a fuel cell is directly fed with hydrocarbons, the amount of hydrogen generated, available for electricity generation, is temperature-dependent. The same is also true of carbon-deposition reactions, which may result in anode fouling. There is a need, consequently, for each kind of fuel, to determine the optimum operating-temperature domain, from a technological standpoint, but equally in thermodynamic terms.

Direct hydrocarbon reforming

Chemical conversion of hydrocarbons into hydrogen is obtained either through **reforming** (I) or through partial oxidation (II). These two reactions should thus be promoted. Conversely, carbon deposition reactions may cause perturbations in the system, as e.g. the Boudouard reaction, and the hydrocarbon cracking reaction (III). These should be impeded as far as possible.
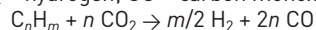
D. Michon-Artechnique/CEA

steam (H_2O) or carbon-dioxide (CO_2) reforming reaction (I)

hydrocarbons:

$$C_nH_m + n\,H_2O \rightarrow n\,CO + (n + m/2)\,H_2,$$
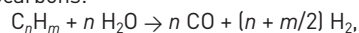
then $CO + H_2O \rightarrow CO_2 + H_2$ (water–gas shift reaction)

H_2 = hydrogen; CO = carbon monoxide

$$C_nH_m + n\,CO_2 \rightarrow m/2\,H_2 + 2n\,CO$$

alcohols:

$$C_nH_mO + (2n - 1)\,H_2O \rightarrow n\,CO_2 + (2n - 1 + m/2)\,H_2$$
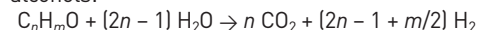
partial oxidation reaction (II)

hydrocarbons:

$$C_nH_m + n/2\,O_2 \rightarrow m/2\,H_2 + n\,CO$$

alcohols:

$$C_nH_mO + (n - 1)/2\,O_2 \rightarrow m/2\,H_2 + n\,CO$$
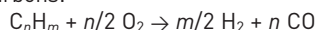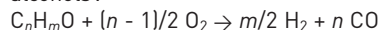
carbon (C) formation reaction (III)

$$2\,CO \longleftrightarrow C + CO_2 \text{ (Boudouard)}$$
$$C_nH_m \longleftrightarrow n\,C + m/2\,H_2 \text{ (cracking)}$$
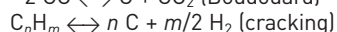
The domains in which each of these reactions predominate vary, depending on initial temperature and pressure conditions, and determine complex equilibriums between fuel gases (H_2, CO, **CH_4**…) and oxidation products (H_2O and CO_2). Partial equilibrium pressures for combustible gases, or the carbon fractions undergoing precipitation may be determined by means of thermodynamic codes. These allow determination of "safe" operating domains, for which the amount of hydrogen generated at the anode yields an **electromotive force** in the cell close to 1 volt, while restricting carbon deposition to a minimum.

Figure 1 shows such domains for three fuels, **methane**, being representative of natural gas, **propane**, representative of LPG, and ethanol, being the main product from biomass. The lower the target operating temperature, the higher the amount of oxidizer- steam or oxygen - that should be added to the fuel to preclude carbon deposition. Optimization of operating conditions for the system as a whole must be defined with regard to the potential for gas recirculation and heat recovery, to heat gases at the cell inlet.

Optimization of cell operating conditions

Once temperature and gas partial pressure conditions have been chosen, juxtaposition of the steam reforming (**endothermic**) and water-gas shift (**exothermic**) reactions results in a temperature gradient inside the cell, this being more or less pronounced according to the kinetics for each of these reactions. This point is illustrated in Figure 2, in which the calculated speed of each reaction is shown across the anode, under realistic operating conditions (target operating temperature 800 °C, **composite** nickel-yttria-stabilized zirconia anode, and **current density** of around 100 mA/cm². Depending on the anode material selected, and on the presence or otherwise of **catalyst** elements such as nickel or copper, reaction speeds may vary by a factor 1,000. Such variations have a direct repercussion on the temperature profile inside the basic cell, which may then reach several degrees C per millimeter.
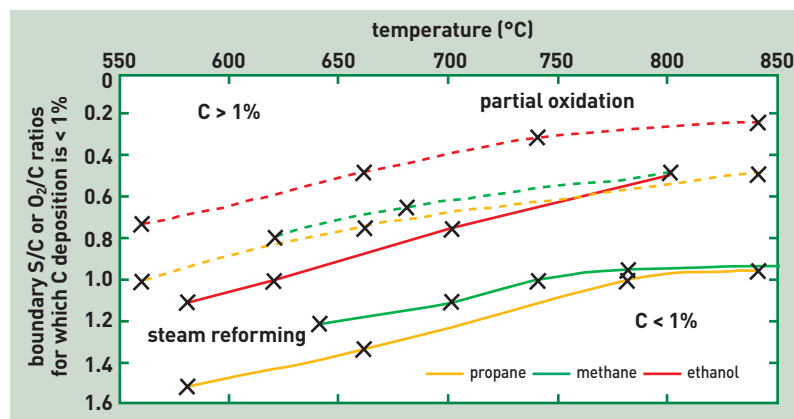

Figure 1.

Map of operating domains generating more, or less, than 1% carbon deposition, as a function of temperature and steam/carbon (S/C) or oxygen/carbon (O_2/C) ratio, for an overall pressure inside the cell of 1 **atmosphere**. Two conversion reactions are subjected to investigation, for three fuels.
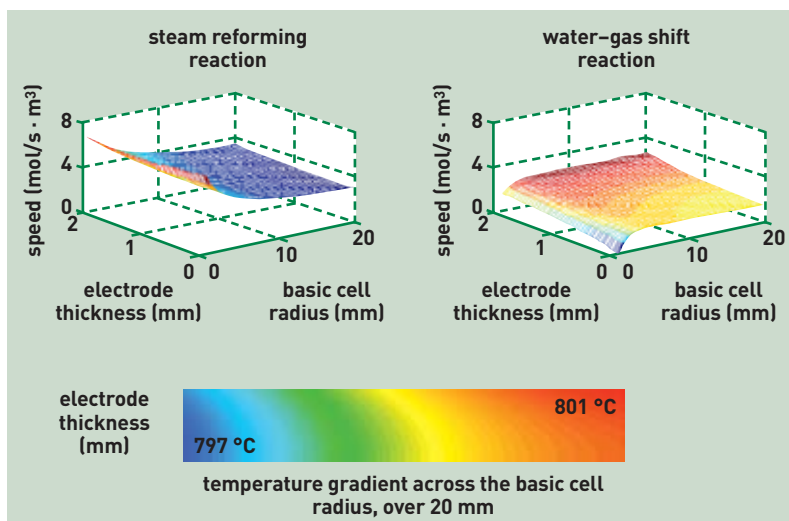

Figure 2.

Distribution of reaction speeds for the steam reforming and water–gas shift reactions inside the composite nickel–yttria-stabilized zirconia anode, together with corresponding temperature profile. Reaction enthalpies at 800 °C are of 242 kJ/**mol** and – 38.6 kJ/mol respectively. Depending on operating conditions and reaction kinetics, the resulting temperature gradient may range from 1–20 °C over 20 mm.

The whole challenge of operation with direct fuel conversion at the anode lies in controlling the initial gaseous mixture and the reaction speeds, to achieve so-called "autothermal" operating conditions, i.e. conditions allowing thermal equilibrium of the basic cell with its environment. This point is currently targeted by many approaches, combining experiment and **modeling**.

Such an approach, based on an understanding of local processes, represents the indispensable intermediate stage, intervening between the choice of basic components, in particular the materials and fuels, and the sizing of the entire system, taking on board its gas supplies, together with thermal and electrical management.

> Julien Vulliet, **Jérôme Laurencin**,
Bertrand Morel and **Florence Lefebvre-Joud**
Technological Research Division
CEA Grenoble Center