

Review

Fuel cells for chemicals and energy cogeneration

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Abstract

Fuel cells (FCs) are mainly applied for electricity generation. This paper presents a review of specific FCs with ability to produce useful chemicals at the same time. The chemical cogeneration processes have been classified according to the different types of fuel cells. Thus, it is shown that a flow alkaline FC (AFC) is able to produce hydrogen peroxide. In aqueous acid or neutral FCs, hydrogenations, dehydrogenations, halogenations and oxidations, together with pollution abatement solutions, are reported. Hydrogen peroxide and valuable organic chemicals can also be obtained from polymer electrolyte FCs (PEFCs). A phosphoric acid FC (PAFC) allows the selective oxidation of hydrocarbons and aromatic compounds, and the production of industrial compounds such as cresols. Molten salt FCs (similar to molten carbonate or MCFCs) can be applied to obtain acetaldehyde with high product selectivity from ethanol oxidation at the anode. Solid oxide FCs (SOFCs) are able of chemical cogeneration of valuable industrial inorganic compounds such as nitric oxide with high yields. Although the number of related papers in the literature is small, the potential economic interest of this emergent field, related to the recent commercial development of fuel cells, is demonstrated in some cases, and the corresponding results encourage the development of FCs with electrocogeneration of useful chemicals with high added value and electricity.

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Keywords: Fuel cells; Cogeneration; Electrocogeneration processes; Electrosynthesis; Electrocogeneration

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1. Introduction

Fuel cells (FCs) are devices that continuously produce electric energy and heat whereas a fuel and an oxidant are being fed to the electrodes. Chemical energy is directly converted into electricity and heat without involving combustion cycles. Thus, the thermal–mechanical–electric sequence with Carnot's theorem limitations used in the conventional indirect technology is

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Table 1
Types of fuel cells according to the electrolyte employed and their main characteristics

	AFC	PEFC	DMFC	PAFC	MCFC	SOFC
Temperature (°C)	60–90	80–110	80–110	160–200	600–800	800–1000
Electrode material	Metal or carbon	Pt-on-carbon	Pt-on-carbon	Pt-on-carbon	Ni + Cr	Ni/Y ₂ O ₃ –ZrO ₂
Electrolyte	NaOH/KOH	Polymer membrane	Polymer membrane	H ₃ PO ₄	LiCO ₃ –K ₂ CO ₃	ZrO ₂ with Y ₂ O ₃
Primary fuel	H ₂	H ₂ reformat	CH ₃ OH	H ₂ reformat	H ₂ /CO reformat	H ₂ /CO/CH ₄ reformat
Oxidant	O ₂ /air	O ₂ /air	O ₂	O ₂ /air	CO ₂ /O ₂ /air	O ₂ /air
Practical efficiency (%)	60	60	60	55 ^a	55–65 ^a	60–65 ^a

^a The production of additional electric energy by means of thermal energy cogeneration is not considered.

avoided [1]. The overall efficiency in FCs to produce profitable energy is about twice that obtained by means of conventional combustion engines. In addition, selective reactions with small environmental impact take place. As they do not have mobile parts, they do not produce noise [2]. As a result, FCs have many real applications.

Usually, fuel cells are classified according to their working temperature or to the electrolyte employed [1]. There are fuel cells of low and high temperature. In the first group we found aqueous FCs (such as alkaline or AFCs), direct methanol FCs (DMFCs), polymer electrolyte FCs (PEFCs) and phosphoric acid FCs (PAFCs). The molten carbonate FCs (MCFCs) and solid oxide FCs (SOFCs) operate at high temperatures (from 500 °C). The electrolytes can be aqueous, molten and solid. The aqueous electrolytes are used in the low temperature FCs (the temperature can be increased in pressurised systems). The molten electrolytes are usually employed at high temperatures and the solid electrolytes (such as oxide mixtures), at quite higher temperatures. Table 1 shows different types of fuel cells, classified according to the electrolyte employed, together with their main characteristics.

A fuel cell is essentially an energy converter, but it may be also considered as a chemical reactor depending on the operating mode: (i) electric power generation (properly working as a FC); (ii) generation of electric power plus useful chemicals; (iii) generation of only useful chemicals as electrolytic cell, resulting from the consumption of external electric power. The fuel cell technology can be successfully employed in electrolytic applications: for example, when the generation rate of the corresponding product is desired to be increased, just as the hydrogen production (towards a hydrogen-based economy). In this case, the electrolysis voltage (and therefore, the consumption of electricity) required for splitting water into hydrogen and oxygen by the fuel cell electrolyzer can be significantly lowered with available heat from e.g., burning cheap natural gas, thus reducing the cost. This is based on high temperature fuel cells [3]. In this review, however, we will only consider the second operation mode, which we will refer to chemical cogeneration or electrocogeneration [4,5]. In the cogeneration process, the main products are the chemical compound of interest and the current delivered.

As shown in the schema of Fig. 1, chemical cogeneration processes basically involve a conventional fuel cell (the fuel cell reactor), in which the fuel and the oxidant are separately introduced, an external load for using electrical energy or dissipate it, and a system for recovering the useful chemicals produced.

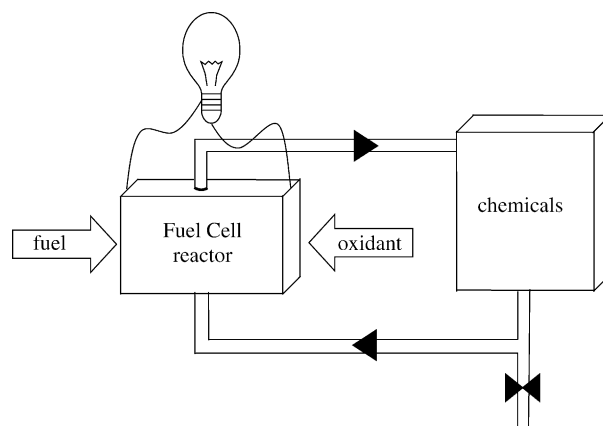


Fig. 1. Principles of operation of a fuel cell reactor generating chemicals and energy.

Many cogeneration processes for different types of FCs have been described. Most of the chemicals obtained have been thought to be commercially attractive because they appear to be interesting from the economic and/or the environmental point of view, and have been patented. This review describes and compares the main cogeneration processes reported in the literature. Reactions in FCs are quite selective and thus, their reactions are classified by the type of reactants and products obtained. In each section, the inorganic products are considered first. Afterwards, the generation of organic compounds through reactions such as hydrogenations, dehydrogenations and oxidations, involving hydrocarbons, benzene, alcohols, ketones, and their derivatives, with increasing complexity, is described. Depending on the system, the fuel cell performance to obtain the indicated products will be characterized by its current efficiency, its selectivity with respect to the product obtained, and/or its current and power densities.

2. Electrocogeneration processes

The cogeneration processes require favorable thermodynamic and kinetic conditions. On the other hand, the operation of the cogenerating devices for a suitable production of energy and chemicals need the use of aspects involved in the fuel cell technology. Thermodynamics is a useful tool to start trying devices for cogeneration, but practical kinetic aspects will finally determine the cell performance.

Electrocogeneration processes have been developed according to different needs:

- To simplify a complicated chemical industrial process in a one-step production.
- To develop alternative process when the demand of a final product decays.
- For environmental reasons.

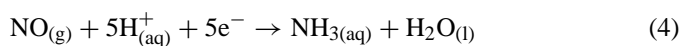
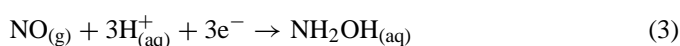
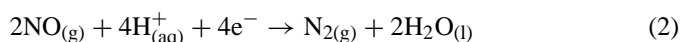
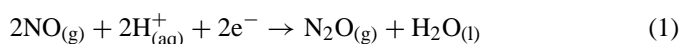
The processes cogenerating energy and chemical substances are very similar to those involved in conventional heterogeneous catalysis. In this sense, it appears that the catalysts used in heterogeneous chemical processes can serve as a guide to choose suitable electrocatalysts for cogeneration processes. The main advantages of the cogeneration methods over the conventional catalytic ones are the following:

- The reactants are fed separately and therefore, they do not compete for the same catalytic sites, the explosion danger is reduced and safety increases, the reactor can be reduced in size, and the products can be easily separated from the reactants.
- Cogeneration of electricity and chemical products is efficient.
- The use of the reactants is efficient and they can be recirculated.
- The electrochemical devices can operate at temperatures much smaller than many of the conventional catalytic processes.
- When necessary, the use of separators in the electrochemical cells avoids undesirable reactions.
- Corrosion of reactors and pipelines is smaller.
- Production in the electrochemical reactor is mainly controlled by the external load.
- The selectivity of the process can be controlled by changing the external load (which can vary the electrode potential) or the electrode catalyst.

Earlier systematic cogenerative studies started in the middle of the XXth century. They consisted of an exploratory evaluation of FCs as reactors for producing chemicals at low temperature. Main attention was focused in hydrocarbons and petroleum derived fuels [6], as well as in their oxidation mechanism, intermediates and products.

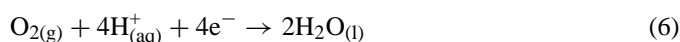
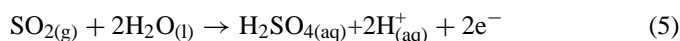
2.1. Chemical cogeneration in aqueous electrolyte FCs

Fuel cells with acid, alkaline, and neutral aqueous electrolytes have been proposed for different applications [7–20]. Hydroxylamine [7,8], acids [9,10], and hydrogen peroxide [11–13], have been obtained from inorganic reagents using different media. Complex organic compounds have also been produced from organic fuels [14–18]. The first FC reported in this field involved the electroreduction of NO in acid media [7,8] according to the following reactions:



The selectivity for each path depends on the catalyst and potential. In general, reaction (1) is favored above 0.5 V versus the reversible hydrogen electrode (RHE), whereas reactions (3) and (4) predominate at potentials below this potential. The production of hydroxylamine by reaction (3) has received particular attention, since it is an intermediate in the production of Nylon-6 and its chemical cogeneration may solve some manufacturing problems. In this case, an H₂–NO cell containing two porous Pt black electrodes and HClO_{4(aq)} as the electrolyte was utilized [7]. Anodic reaction was hydrogen oxidation to protons related to the overall reactions (R1)–(R3) listed in Table 2 with standard *emf* values of 1.59, 0.50, and 0.84 V, respectively. Hydroxylamine can also be electrogenerated in gas phase [8]. The FC reactor then consisted in a proton-conducting separator (a solution of H₂SO₄ held in a silica-wool disk) between a graphite-PTFE-Pt anode and a carbon whisker-PTFE-Fe phthalocyanine cathode. NO was carried with helium into the cathode compartment, while H₂ and water vapor were circulated through the anodic compartment. After 2 h of operation in short-circuit, room temperature, and atmospheric pressure, a mean current density of 8.9 mA cm⁻² circulated and N₂O (0.76 μmol cm⁻²), NH₃ (13.4 μmol cm⁻²), and NH₂OH (189 μmol cm⁻²) were generated. Selectivity to NH₂OH was 93%. It has also been claimed that NO present in power plant effluents and automobile emissions can be processed in such FC [8].

The cogeneration of sulfuric acid allows controlling pollution from mining operations or effluent streams from stationary power plants, both sources of SO₂ [9]. This requires the use of a divided flow cell with the electrode compartments separated by a cation exchange membrane and 3.0 M H₂SO_{4(aq)} as circulating electrolyte. Relatively high conversions, between 89 and 55% could be achieved using planar or GDEs catalyzed by platinum, at low sulfur dioxide concentrations. The corresponding anode and cathode reactions at the catalytic electrodes are:



leading to the overall reaction (R4) in Table 2 (the standard *emf* of the cell is $E^{\circ} = 1.06$ V). Currents close to 0.125 A cm⁻² were obtained at room temperature and about 0.2 A cm⁻² at 60 °C, in contrast with the temperature of 400 °C utilized in the conventional process. In addition, oxidation of dissolved sulfur dioxide in liquid phase was successfully carried out in a hybrid cell that combines a gas diffusion cathode and a packed bed anode catalyzed by platinum. Currents of 80 mA cm⁻² were generated working at room temperature with 0.5 M SO₂.

Hydrogen chloride has many applications as a chemical intermediate in the hydrochlorination of rubber, in the production of vinyl and alkyl chlorides, in the separation of cotton from wool, and for etching semiconductor crystals. HCl and electricity can be obtained by a H₂–Cl₂ acidic FC represented by the diagram Pt|H_{2(g)}|HCl_(aq)|Cl₂|Rh [10], in which the overall reaction is (R5) in Table 2. The cell operates at 50 °C with gas diffusion electrodes (GDEs), a separator, and 3.0 M HCl_(aq) as electrolyte.

Table 2
Selected chemical cogeneration processes involved in different types of FCs, classified according to the electrolyte

FC reactor	Reactions	Electrocatalysts	References
Aqueous FC			
HClO _{4(aq)}	2NO _(g) + H _{2(g)} + → N ₂ O _(g) + H ₂ O _(l) (R1)	Pt ^{a,b}	[7,8]
HClO _{4(aq)}	2NO _(g) + 3H _{2(g)} + 2H _(aq) ⁺ → 2NH ₂ OH · H _(aq) ⁺ (R2)	Pt ^{a,b}	[7–9]
HClO _{4(aq)}	NO _(g) + 3H _{2(g)} → NH _{4(aq)} ⁺ + H ₂ O _(l) (R3)	Pt ^{a,b}	[7,8]
H ₂ SO _{4(aq)}	2SO _{2(g)} + O _{2(g)} + 2H ₂ O _(l) → 2H ₂ SO _{4(aq)} (R4)	Pt ^{a,b}	[9]
HCl _(aq)	H _{2(g)} + Cl _{2(g)} → 2HCl _(l) (R5)	Pt ^a and Rh ^b	[10]
OH _(aq) ⁻	H _{2(g)} + O _{2(g)} + OH _(aq) ⁻ → HO _{2(aq)} ⁻ + H ₂ O _(l) (R6)	Pt ^a and C ^b	[11–13]
HClO _{4(aq)}	H _{2(g)} + RCH = CHR _(g) → RCH ₂ CH ₂ R' (R7)	Pt ^{a,b}	[14]
KCl _(aq)	C ₂ H _{4(g)} + Cl _{2(g)} → ClCH ₂ CH ₂ Cl _(l) (R8)	Pt ^{a,b}	[15]
KCl _(aq)	C ₂ H _{4(g)} + Cl _{2(g)} + H ₂ O _(l) → ClCH ₂ CH ₂ OH _(l) + HCl _(aq) (R9)	Pt ^{a,b}	[15]
HClO _{4(aq)}	3H _{2(g)} + C ₆ H _{6(g)} → C ₆ H _{12(l)} (R10)	Pt ^{a,b}	[16]
H ₂ SO _{4(aq)}	O _{2(g)} + 2C ₄ H _{8(g)} → 2CH ₃ COC ₂ H _{5(l)} (R11)	Pt ^{a,b}	[17]
H ₂ SO _{4(aq)}	2C ₂ H ₅ OH + O _{2(g)} → 2CH ₃ CHO + 2H ₂ O _(l) (R12)	Pt-black ^{a,b}	[18]
PEMFC			
	H _{2(g)} + O _{2(g)} → H ₂ O _{2(l)} (R13)	Pt ^a and C ^b	[21–23]
	C ₆ H ₅ NO _{2(l)} + 3H _{2(g)} → C ₆ H ₅ NH _{2(l)} + 2H ₂ O _(l) (R14)	Pt ^{a,b}	[26]
	CH ₂ = CHCH ₂ OH _(l) + H _{2(g)} → CH ₃ CH ₂ CH ₂ OH _(l) (R15)	Pt ^{a,b}	[27]
PAFC			
	C ₂ H _{6(g)} + O* + O _{2(g)} → CH ₃ COOH _(g) + H ₂ O _(g) (R16)	Pt-black ^a and Pd-black + VO(acac) ₂ ^b	[30,31]
	C ₃ H _{8(g)} + O* + (1/2)O ₂ → CH ₃ COCH _{3(g)} + H ₂ O _(g) (R17)	Pt-black ^a and Pd-black + VO(acac) ₂ ^b	[30,31]
	C ₂ H _{4(g)} + CO _(g) + H _{2(g)} → CH ₃ CH ₂ CHO _(g) (R18)	Pt-black ^a and Pt ^b , Na ₃ PO ₄ ^b	[32]
	2C ₂ H _{4(g)} + O _{2(g)} → 2CH ₃ CHO _(g) (R19)	Pd-black ^a and Pt-black ^b	[33,34]
	2C ₃ H _{6(g)} + O _{2(g)} → 2CH ₃ COCH _{3(g)} (R20)	Pd-black ^a and graphite ^b	[33,34]
	2CH ₃ OH _(g) + O _{2(g)} → HCOOCH _{3(g)} + 2H ₂ O _(g) (R21)	Ir ^a and Pt ^b	[36]
	C ₆ H _{6(g)} + O _{2(g)} + H _{2(g)} → PhOH _(g) + H ₂ O _(g) (R22)	Pd-black ^a and Pt-black ^b	[39]
	PhCH _{3(g)} + O _{2(g)} → PhCHO _(g) + H ₂ O _(g) (R23)	Pt-black ^a and Pd-black ^b	[40]
Molten salt FC			
	2C ₂ H ₅ OH _(g) + O _{2(g)} → 2CH ₃ CHO _(g) + 2H ₂ O _(g) (R24)	Transition metal compound ^a and Pt ^b	[43]
SOFC			
	4NH _{3(g)} + 5O _{2(g)} → 4NO _(g) + 6H ₂ O _(g) (R25)	Pt-Rh ^a and Pt ^b	[44]
	2CH _{4(g)} + 2NH _{3(g)} + 3O _{2(g)} → 2HCN _(g) + 6H ₂ O _(g) (R26)	Pt-Rh ^a and Pt ^b	[45,46]
	2H ₂ S _(g) + 3O _{2(g)} → 2SO _{2(g)} + 2H ₂ O _(g) (R27)	Pt ^{a,b}	[47]
	2C ₆ H ₅ -CH ₂ CH _{3(g)} + O _{2(g)} → 2C ₆ H ₅ -CH = CH _{2(g)} + 2H ₂ O _(g) (R28)	Pt ^{a,b}	[48]
	2CH ₃ OH _(g) + O _{2(g)} → 2H ₂ CO _(g) + 2H ₂ O _(g) (R29)	Ag ^{a,b}	[49]
	2CH _{4(g)} + O _{2(g)} → C ₂ H _{4(g)} + 2H ₂ O _(g) (R30)	Ag ^a , Sm ₂ O ₃ -CaO-Ag ^a and Ag ^b	[50]
	4CH _{4(g)} + O _{2(g)} → 2C ₂ H _{6(g)} + 2H ₂ O _(g) (R31)	La _{1.8} Al _{0.2} O ₃ ^a /La _{0.85} Sr _{0.15} MnO ₃ ^b	[51]
	2C ₂ H _{6(g)} + O _{2(g)} → 2C ₂ H _{4(g)} + 2H ₂ O _(g) (R32)	Ag ^{a,b}	[52]
	4C ₃ H _{6(g)} + 3O _{2(g)} → 2C ₆ H _{6(g)} + 6H ₂ O _(g) (R33)	(Bi ₂ O ₃) _{0.85} (La ₂ O ₃) _{0.15} ^{a,b}	[53]
	2CH _{4(g)} + O _{2(g)} → 2CO _(g) + 4H _{2(g)} (R34)	Ni ^a and La _{0.6} Sr _{0.4} CoO ₃ ^b	[54]

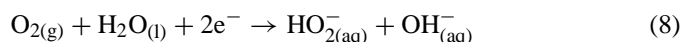
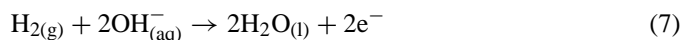
^a Anode electrocatalyst.

^b Cathode electrocatalyst.

Chlorine is reduced at the Rh-on-C cathode, whereas hydrogen is oxidized at the anode. The cell produced 0.51 W cm⁻² with a cell voltage of 0.5 V, and the main source of polarization was the ohmic overpotential.

There is an increasing interest in the applicability of hydrogen peroxide to a wide variety of industrial processes, because of the notable reduction of the environmental impact caused by similar processes with other typical chemical oxidants. Electrogenerated hydrogen peroxide is now employed for bleaching and brightening of chemical pulp in the pulp and paper industry, water and wastewater treatment, food processing and oxidation of organic compounds, among other uses. On the other hand, there is an increasing demand of new electrochemical devices with high efficiency and low cost for on-site hydrogen peroxide production. In this way, we have proposed a novel electrochemical method for on-site production of hydroperoxide ion (HO₂⁻, the basic form of hydrogen peroxide) in an undivided flow alkaline fuel cell (AFC) [11,12]. The electrodes were a H₂-diffusion anode, composed of a carbon cloth covered with a carbon-PTFE

layer and a carbon black layer with 10% Pt, and an O₂-diffusion cathode, in which the carbon cloth was covered by an uncatalyzed carbon-PTFE layer. The electrolyte was KOH, which was circulated to extract the hydroperoxide ion. A scheme of this cell is depicted in Fig. 2, in which the overall reaction in short-circuit through an external load is represented. The anode and cathode reactions were:



giving the overall reaction (R6) in Table 2. The cell can operate either in batch or in continuous mode. Under circulation of HO₂⁻ + KOH solutions in open circuit, the flow AFC behaved as a two-electron reversible system. When the cell was shorted with an external resistance, a quasi-steady behavior was observed when a fresh KOH solution was continuously injected through it, supplying a spontaneous current, while HO₂⁻ was electrogenerated and accumulated in the circulating electrolyte [12].

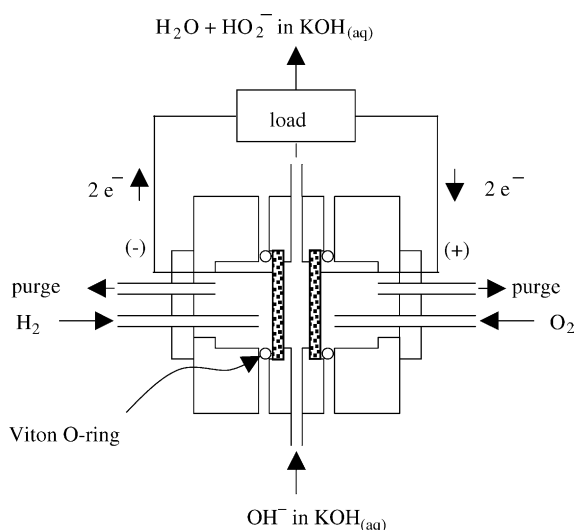
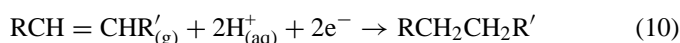


Fig. 2. Scheme of the aqueous alkaline flow fuel cell for on-site production of hydroperoxide ion, the conjugated base of hydrogen peroxide. The anode is a Pt-catalyzed carbon-PTFE hydrogen diffusion electrode, whereas the cathode is an uncatalyzed carbon-PTFE oxygen diffusion electrode. Hydroperoxide ion is produced in the electrolyte and can be collected in the cell outlet. Adapted from Ref. [12].

For example, when using 1.0 mol dm^{-3} KOH with a flow of 20 mL min^{-1} and an external load of 0.10Ω at 25.0°C , the current density through the electrodes of the same section was 0.10 A cm^{-2} and the productivity of hydroperoxide ions was $1.89 \text{ mmol cm}^{-2} \text{ h}^{-1}$. These values increased with temperature: at 45.0°C , a current density of 0.12 A cm^{-2} and a hydroperoxide ion productivity of $2.15 \text{ mmol cm}^{-2} \text{ h}^{-1}$ were obtained. When air was employed instead of pure oxygen, the current density and hydroperoxide ion productivity decreased to 0.06 A cm^{-2} and $1.11 \text{ mmol cm}^{-2} \text{ h}^{-1}$, respectively. The current efficiency for hydroperoxide ion production was close to 97% in all these cases. The main experimental parameter controlling the HO_2^- productivity is the external resistance connected between the electrodes, since it can regulate the voltage and current density supplied by the flow AFC. When $V < 0.200 \text{ V}$ the process was under ohmic-type control, whereas a more complex behavior was found between 0.650 and 0.200 V , which was related to mixed charge transfer plus ohmic-type control of the process.

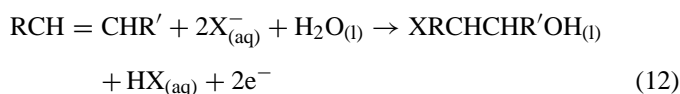
Yamanaka et al. [13] have reported a $\text{H}_2\text{-O}_2$ fuel cell divided by a cation exchange membrane in two sections, each one filled with NaOH, which produced H_2O_2 at 93% selectivity. The anode was fabricated from hot-pressed vapor-grown carbon fiber (VGCF), PTFE[®] and Pt black. The cathode had the same composition, but contained some quantity of carbon black instead of platinum. Using this FC reactor, H_2O_2 was generated at a rate of $2.0 \text{ mmol cm}^{-2} \text{ h}^{-1}$ with a concentration of 7 wt.%. The current density, stabilized by pumping NaOH continuously into the anode compartment, was 0.1 A cm^{-2} , with a current efficiency of 93% after 2 h of operation. However, the cell performance decreased when the cathode was fed with air. Hydrogen peroxide was then formed at $1.3 \text{ mmol cm}^{-2} \text{ h}^{-1}$, with a concentration of 6.5 wt.%, a current density of 0.078 A cm^{-2} , and a current efficiency of 88% after 3 h of operation.

Langer et al. [14–18] have investigated different cogeneration processes involving hydrogenations, dehydrogenations, halogenations and oxidations. For example, the hydrogenation of unsaturated hydrocarbons takes place according to the following anode and cathode reactions [14]:



with the overall reaction (R7) in Table 2. The electrolyte was perchloric acid and both electrodes were porous catalytic Pt black bonded with PTFE. During the FC operation, hydrogen ions have to be transported through the electrolyte.

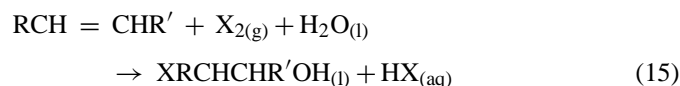
Halogenations are other cogeneration processes with commercial potential interest [15]. In such cells, the reactions at the anode can be:



whereas the cathode reaction is:

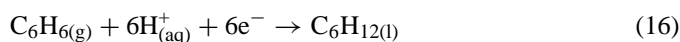


The overall reactions corresponding to reactions (11) and (12) are:



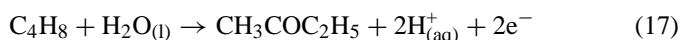
In an ethylene–chlorine fuel cell, with Pt black electrocatalysts as electrodes and aqueous KCl as electrolyte, the corresponding dichloroalkane and chlorohydrin were obtained (reactions (R8) and (R9) in Table 2). The last product was dominant at high cell voltages. In an ethylene–bromine fuel cell, with bromide as electrolyte, the dibromoalkane and bromohydrin were produced. In this case a porous graphite electrode was utilized as the cathode.

Cyclohexane is used mainly in the synthesis of adipic acid for Nylon-6/6 and caprolactam for Nylon-6. Other applications include its use as a solvent (in laboratory, for rubber manufacture and varnishes), insecticides and plasticizers. This chemical can be obtained by the hydrogenation of benzene in a way similar to the unsaturated hydrocarbons, in a cell using a filter paper wetted with $3.0 \text{ M HClO}_{4(\text{aq})}$ as electrolyte. Benzene vapor was fed to the cathode, where it was reduced to cyclohexane [16]. The standard *emf* of the cell is $E^\circ = 0.17 \text{ V}$ (reaction (R10) in Table 2), where the anode reaction is reaction (9) and the cathode reaction is:



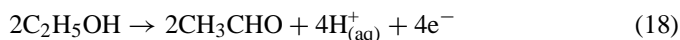
Methyl-ethyl-ketone is a chemical widely used in the manufacture of solvents, resins, artificial leather, rubbers, lacquers,

varnishes and glues. Its production by chemical cogeneration would suppose a reduction in the energy cost of about 25% with respect to the conventional chemical process [17]. The fuel cell reaction involves the oxidation of butene in a porous Pt anode with a hydrophobic backing layer. At the cathode, oxygen can be reduced to water. The electrolyte could be aqueous 10 M sulfuric acid. The anode reaction in the FC can be written as follows:



the cathode reaction is reaction (6) and the overall reaction is (R11) in Table 2 ($E^\circ = 1.16$ V). The ketone can be obtained with a selectivity greater than 90%, with about 50% of the current from oxidation of the butene causing CO_2 formation in the only side reaction. The product is recovered by gas stripping from the circulating electrolyte, where it is accumulated.

Alcohol oxidation to aldehydes and ketones is important because they can be employed in the synthesis of other chemicals. For example, acetaldehyde is applied in silvering of mirrors, leather tanning, fuel, glue, dyes, plastics and synthetic rubbers. The oxidation of ethanol to acetaldehyde can be made in a cell, divided by a cation exchange membrane, with 3.0 M $\text{H}_2\text{SO}_4_{(\text{aq})}$ as electrolyte and porous catalytic Pt black electrodes [18]. The diagram of this cell would be $\text{Pt}|\text{C}_2\text{H}_5\text{OH}, \text{CH}_3\text{CHO}, \text{H}^+, \text{H}_2\text{O}|\text{cation exchange membrane}|\text{H}^+, \text{H}_2\text{O}|\text{O}_2_{(\text{g})}|\text{Pt}$. The corresponding anode reaction is:



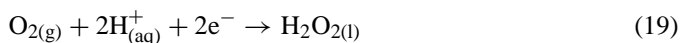
the cathode reaction is reaction (6) and the overall reaction is (R12) in Table 2. Ethanol can be fed dissolved in the electrolyte or contained in a vapor stream. When the cell runs with ethanol vapor (75%) at 38 °C, a molar flow rate of acetaldehyde in the anodic effluent of 59 $\mu\text{mol min}^{-1}$ is obtained (current efficiency of 61%). The electric power delivered was 8.7 mW cm^{-2} .

A particular application of aqueous electrolyte fuel cells result from the fact that they can spontaneously produce strong oxidizing radicals such as $\bullet\text{OH}$ and $\text{HO}_2\bullet$, which can destroy aromatic pollutants [19,20]. In this case, no synthesis is performed, but the aromatic pollutants are mineralized, i.e. they are transformed into CO_2 and inorganic compounds, thus allowing decontamination of wastewaters. The cell contained a Fe anode and an O_2 -fed carbon-PTFE cathode, reason why it is prop-

erly considered a semi-fuel cell, and operated in short-circuit at room temperature and atmospheric pressure. The electrolyte was sodium sulfate set to pH about 3 by addition of sulfuric acid.

2.2. Chemical cogeneration in PEFCs

In acidic medium, Otsuka and Yamanaka have reported a divided fuel cell made with Nafion[®] 117 electrolyte, a proton exchange membrane (PEM), with Pt deposited on one face, where H_2 is oxidized, and graphite or Au-mesh adhered on the other face, where O_2 is reduced to hydrogen peroxide [21]. The structure of the cell is shown in Fig. 3(a). Pure H_2 is fed to deposited Pt whereas O_2 is bubbled through an aqueous HCl solution. For an optimum 0.1 mol dm^{-3} HCl solution in contact with the cathode, a current density over 10–30 mA cm^{-2} was obtained with a current efficiency sharply dropping from 100 to 70% during 3 h of operation. In this case, the anode reaction is reaction (9) and the cathode reaction is:



whereas the overall reaction is (R13) (see Table 2). The maximum H_2O_2 concentration in this system was only 0.2 wt.% (59 mmol dm^{-3}), with final current efficiencies smaller than 10%, due to the acceleration of hydrogen peroxide reduction to water when its concentration increased [22]. This system was improved using an oxygen diffusion cathode made with active carbon (AC), VGCF, and PTFE in the cell represented by the diagram $\text{Pt}|\text{HCl}|\text{Nafion}^{\text{®}}\ 117|\text{HCl}|\text{AC} + \text{VGCF} + \text{PTFE}$. This cell is schematized in Fig. 3(b) and its reactions are the same as in Fig. 3(a), i.e. reactions (9) and (19). After 6 h of operation, a H_2O_2 concentration of 0.32 mol dm^{-3} was accumulated with a current efficiency of 40%.

Another divided fuel cell to obtain hydrogen peroxide was described [23]. It was composed of a polyfluorosulfonic acid ionomer membrane sandwiched between a H_2 -diffusion anode and an O_2 -diffusion cathode with different catalysts, in which a water flow mixed with O_2 was directly injected to the cathode. This system yields hydrogen peroxide concentrations exceeding 0.3 mol dm^{-3} with selectivity up to 70%. Regarding this subject, some new bipolar membranes (acidic in the anode side and

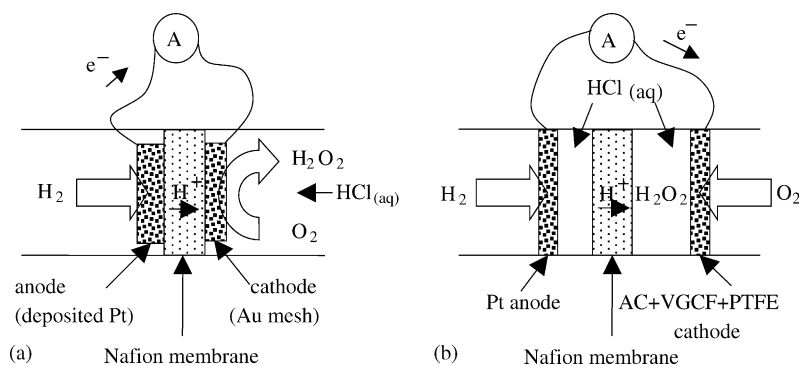


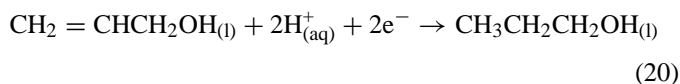
Fig. 3. Fuel cells with acidic electrolyte for H_2O_2 production. (a) The electrolyte is a Nafion membrane with deposited Pt on the left side and with an Au mesh on the right side. (b) The HCl solutions of the anode and the cathode compartment are separated by means of a Nafion membrane. In both cases, H_2O_2 is collected in the electrolyte of the cathode. Adapted from Refs. [21,22].

alkaline in the cathode) have been proposed recently to produce H_2O_2 in a $\text{H}_2|\text{O}_2$ fuel cell [24].

It is possible to directly oxidize some hydrocarbons like ethane (C_2H_6), propane (C_3H_8), and butane (C_4H_{10}) in a PEFC under mild conditions [25]. Such kind of cell can be represented as Pt-on-C|hydrocarbon|Nafion[®] 117| $\text{O}_2(\text{g})$ |Pt-on-C. The membrane electrode assembly (MEA) includes two Pt-on-C catalyzed GDEs and a Nafion[®] 117 membrane. Using ethane as fuel and oxygen as oxidant, with 20% Pt-on-C as catalyst and phosphoric acid treated membrane, the maximum power of the cell at 80 °C and ambient pressure was 0.69 mW cm^{-2} and the maximum current density output was 7.3 mA cm^{-2} . In the case of propane, the maximum power and the maximum current density were 1.47 mW cm^{-2} and 0.016 A cm^{-2} , respectively. Finally, using butane, the maximum power output was 1.33 mW cm^{-2} with a maximum current density of 0.017 A cm^{-2} . With regard to the possible reactions products, as well as CO_2 formation in all reactions, ethane would yield hexane (C_6H_{14}) and octane (C_8H_{18}), propane would yield hexane and butane would yield octane.

Cyclohexylamine is applied as corrosion inhibitor and as metalworking fluid. Selective reduction of nitrobenzene to cyclohexylamine with simultaneous production of electric power has been performed in a PEFC reactor which uses ethanol as solvent and platinum as electrocatalyst [26]. The overall reaction is (R14) shown in Table 2. After 2 h of operation, a selectivity of 57.3% to cyclohexylamine and a selectivity of 28.2% to aniline, with 8.2% conversion of nitrobenzene, were obtained at 70 °C. Changing external loads, the current density varied from 1.6 to 24 mA cm^{-2} , with a maximum power delivered of 1.5 mW cm^{-2} at 15 mA cm^{-2} .

The hydrogenation of allyl alcohol (3-hydroxypropene) to 1-propanol can be done in a PEFC made with two Pt-catalyzed GDEs (1.0 mg cm^{-2} of catalyst loading) and a Nafion[®] 117 membrane as electrolyte [27]. The FC reactor operates in a batch recycle mode. The anode reaction corresponds to reaction (9) and the cathode reaction can be expressed as follows:



The overall reaction is (R15) in Table 2 ($E^\circ = 0.4177 \text{ V}$). In the optimum conditions of anodic H_2 flow at 20 mL min^{-1} and feeding of 2 mol dm^{-3} aqueous allyl alcohol at 3 mL min^{-1} into the cathodic compartment, the FC yield 1.22 mmol (2.04% conversion) of L-propanol with a selectivity of about 100% after 2 h of reaction time at 50 °C. The maximum power density was 5.7 mW cm^{-2} at a current density of 0.064 A cm^{-2} , obtained when the cell was shortened by a copper wire.

In a recent work [28], hydrogenation of several unsaturated alcohols (allyl alcohol, 2-butene-1,4-diol, 2-butyne-1,4-diol and propargyl alcohol) and acids (acrylic, crotonic, acetylene dicarboxylic and maleic acids), were carried out in a conventional PEFC. The fuel cell reactor was built up with commercial Pt catalyzed GDEs (loading of 0.35–0.50 and 4 mg cm^{-2} for the anode and the cathode, respectively) and Nafion[®] 117 membrane as electrolyte. In the anode compartment, hydrogen was humidified

and maintained under a pressure of 0.15 MPa. Aqueous reactants solutions, with a typical concentration of 2.0 mol dm^{-3} , were recirculated through the cathode compartment. The OCV of the cells $\text{H}_2|\text{alcohol}$ or $\text{H}_2|\text{acid}$ investigated were around 0.2 V at room temperature. Maximum current densities between 5 and 40 mA cm^{-2} were reported and power densities of 1 mW cm^{-2} were achieved with allyl alcohol, 2-buten-1,4-diol and acrylic acid at about 0.050 V. In this fuel cell reactor, the electrochemical hydrogenation of olefinic double or triple bonds was made with a high selectivity, because the analysis of the catholyte showed that only the hydrogenated product was obtained. Nevertheless, it seems that current efficiencies less than 100% were due to the hydrogen evolution at the cathode.

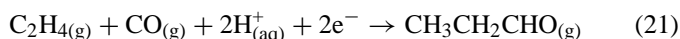
2.3. Chemical cogeneration in PAFCs

Selective oxidation under mild conditions of organic chemicals such as hydrocarbons and benzene-based compounds has a great interest in Green Chemistry. Partial oxidation of propylene to acrolein and acrylic acid was already carried out in a fuel cell using aqueous 25% H_3PO_4 as electrolyte at temperatures in the range 23–80 °C [29]. In this case, the Pt catalyst in the anode of a conventional H_2 – O_2 fuel cell was replaced by a Pd black catalyst, but a poor selectivity to each particular product and a unclear influence of temperature and anode potential on product distribution were found. Afterwards, PAFCs were employed more or less successfully to oxidize light alkanes [30,31], olefins [32–35], methanol [36], cyclohexane [37], benzene [37–39] and toluene [40–42].

Partial oxidation of light alkanes such as methane, ethane and propane during H_2 – O_2 cell reactions at room temperature have been carried out using different cathodes, presumably due to their reaction with reductive activated oxygen O^* [30,31]. The best cathode for the partial oxidation of propane into acetone was the carbon whisker without additives [30]. CO_2 was the only product when using methane, and the main product, together with small amounts of acetaldehyde, when using ethane. In the cell $\text{Pt}|\text{H}_2 + \text{H}_2\text{O}|1.0 \text{ mol dm}^{-3} \text{ H}_3\text{PO}_{4(\text{aq})}$ (silica wool disk)|light alkane + O_2 |Pd + VO(acac)₂ + VGCF [31], methane oxidation also yields only CO_2 . In contrast, ethane and propane oxidation mainly produce acetic acid (raw material for vinyl acetate and cellulose acetate production) and acetone (used as solvent in paints, laboratory, electroplating, etc.), respectively (the exact reaction mechanisms were not clarified, but the probable reactions are given by (R16) and (R17) in Table 2). The rate of the alkane oxidation increases in the order $\text{CH}_4 < \text{C}_2\text{H}_6 < \text{C}_3\text{H}_8$. When operating with ethane at room temperature, the production rate of CH_3COOH was 4.7 $\mu\text{mol cm}^{-2} \text{ h}^{-1}$ (12.2% selectivity) and delivered 0.011 A cm^{-2} . With propane, the production rate of CH_3COCH_3 was 11.5 $\mu\text{mol cm}^{-2} \text{ h}^{-1}$ (25.7% selectivity). However, the maximum oxidation efficiency for the formation of products (acetone, acetic acid and CO_2) from propane was 18%, too low to expect industrial applications.

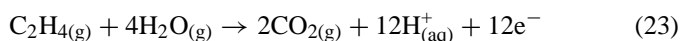
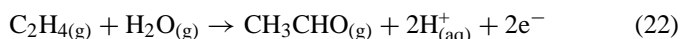
Hydroformylation of olefins, the reaction with synthesis gas being called Oxo process, can be used to cogenerate aldehydes or alcohols. The reaction in the presence of homogeneous catalysts using rhodium and cobalt chlorides is per-

formed at high pressures. However, the same reaction in a FC using H_2PtCl_6 as catalyst could be performed in mild conditions. For example, hydroformylation of ethylene allows synthesizing propionaldehyde [32], which is used in the manufacture of plastics, in the synthesis of rubber chemicals, and as a disinfectant and preservative. The cathode reaction in the cell $\text{Pt-black} + \text{graphite} + \text{PTFE} | \text{H}_2 | \text{H}_3\text{PO}_{4(\text{aq})}$ (silica wool disk) $| \text{C}_2\text{H}_4 + \text{CO} | \text{H}_2\text{PtCl}_6 + \text{graphite} + \text{PTFE}$ is:



the anode reaction is reaction (9) and the overall reaction is (R18) in Table 2. A gas mixture of ethylene and carbon monoxide passed through the cathode, while hydrogen and water vapor passed through the anode. At 80°C , the electrode current density was 1.4 mA cm^{-2} and $\text{CH}_3\text{CH}_2\text{CHO}$ was generated at $1.2 \mu\text{mol cm}^{-2} \text{ h}^{-1}$ with a selectivity of 13.4% and a current efficiency of 4.7% (C_2H_6 was obtained as by-product). This approach is still far from commercial application. Better results could be probably obtained by improving the selectivity and the rate of propionaldehyde formation upon sodium salts addition (especially Na_3PO_4), together with a better preparation of the electrocatalyst and a better design of the electrode-electrolyte system.

Cogeneration of acetaldehyde from ethylene could avoid some disadvantages of the Wacker process [33]. For the cell $\text{Pd} | \text{C}_2\text{H}_4 + \text{H}_2\text{O} | 14.7 \text{ mol dm}^{-3} \text{ H}_3\text{PO}_{4(\text{aq})}$ (silica wool disk) $| \text{O}_2 | \text{Pt}$, schematically shown in Fig. 4(a), the anode electrocatalytic reactions are:



whereas the cathode reaction is reaction (6) and the overall reaction to produce acetaldehyde, with ($E^\circ = 1.04 \text{ V}$ at 80°C), is given by (R19) (see Table 2). Ethylene and water vapor were carried into the anode of the cell with helium, while oxygen was fed into the cathode. The rate of CH_3CHO formation at 100°C was $97 \mu\text{mol cm}^{-2} \text{ h}^{-1}$, with 100% selectivity, a current density of 9 mA cm^{-2} and a current efficiency of 82%. Better results were obtained with the cell $\text{Pd} + \text{VGCF} | \text{C}_2\text{H}_4 + \text{H}_2\text{O} | 14.7 \text{ mol dm}^{-3} \text{ H}_3\text{PO}_{4(\text{aq})} | \text{O}_2 + \text{NO} | \text{VGCF}$ [34], which uses VGCF instead of

graphite (a cathode without metal). NO was added to the O_2 stream in the cathode and current densities and formation rates of CH_3CHO were $45\text{--}55 \text{ mA cm}^{-2}$ and $720\text{--}900 \mu\text{mol cm}^{-2} \text{ h}^{-1}$, respectively, i.e. over 10 times higher than that of the system described above, thus attaining a selectivity greater than 95%. Similarly, the oxidation of propene in a $\text{C}_3\text{H}_6\text{--O}_2$ cell at 80°C yields acrolein ($\text{C}_3\text{H}_4\text{O}$) and a current density of 2 mA cm^{-2} , which increased to 12 mA cm^{-2} using a $\text{C}_3\text{H}_6\text{--}(\text{O}_2 + \text{NO})$ cell. Under these last conditions, however, the product was acetone (reaction (R20) in Table 2), with a production rate of $678 \mu\text{mol cm}^{-2} \text{ h}^{-1}$ (95% selectivity), due to the change in the oxidation state of the Pd of the anode when adding NO to the O_2 stream. Another way to oxidize alkenes in gas phase is the use of a self-shortened fuel cell, which excludes electric parts [35]. This cell is schematized in Fig. 4(b) and consists of a mixed conductor of H^+ and e^- , prepared by impregnating $\text{H}_3\text{PO}_{4(\text{aq})}$ into a carbon-PTFE matrix, which separates the catalyst layers for alkene oxidation and for O_2 reduction. It can be represented by the diagram $\text{Pd} + \text{VGCF} | \text{C}_2\text{H}_4 + \text{H}_2\text{O} | \text{mixed conductor} | \text{O}_2 + \text{NO} | \text{graphite}$, so that, the anode and cathode are shorted through the electron conducting channels of the membrane, whereas protons are transported through the electrolyte channels. This system showed a catalytic activity as good as that of the industrial catalyst and it could be applied to other catalytic reactions such as oxidative dehydrogenation of alcohols, selective hydrogenation of unsaturated compounds, hydroformylation of alkenes, etc.

Methyl formate is utilized as solvent; fumigant and larvicide for tobacco, dried fruits and cereals; as intermediate in organic synthesis, in preparation of antileukemic agents and as a hardener for phenol esters. Selective oxidation of methanol into methyl formate (reaction (R21) in Table 2) and dimethoxymethane had been performed with the gas-phase reactor $\text{Ir} | \text{CH}_3\text{OH} + \text{H}_2\text{O}, \text{HCOOCH}_3, \text{CH}_2(\text{OCH}_3)_2, \text{CO}_2 | \text{H}_3\text{PO}_{4(\text{aq})} | \text{O}_2 + \text{H}_2\text{O} | \text{Pt}$, at $70\text{--}100^\circ\text{C}$ [36]. Methanol and water vapor were carried into the anode compartment of the cell, while a mixture of oxygen and water vapor were fed into the cathode compartment. The best results were obtained with a combination of Ir–Pt electrocatalysts, which is specifically resistant to the methanol cross-over. Working at 80°C , the rate for methyl formate production was $47.7 \mu\text{mol cm}^{-2} \text{ h}^{-1}$, with

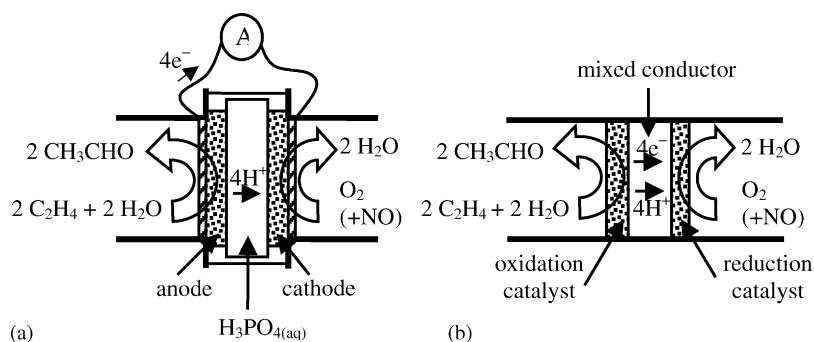
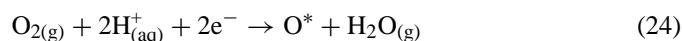


Fig. 4. PAFCs for partial oxidation of alkenes. In plot (a) a Pd + VGCF anode is separated from a VGCF cathode by a silica wool disk containing $14.7 \text{ mol dm}^{-3} \text{ H}_3\text{PO}_{4(\text{aq})}$, and in plot (b) the external circuit is removed due to the use of a mixed conductor of H^+ and e^- , prepared by impregnating $\text{H}_3\text{PO}_{4(\text{aq})}$ into a carbon-PTFE matrix (self-shortened cell). Adapted from Refs. [34,35].

49.7% selectivity and 32% current efficiency. In these conditions, the cell gave 0.016 A cm^{-2} .

Selective oxidation in liquid phase of cyclohexane and benzene, at room temperature and atmospheric pressure, can also be performed at the cathode of a $\text{H}_2\text{-O}_2$ fuel cell with $\text{H}_3\text{PO}_{4(\text{aq})}$ as electrolyte by reductive activated O^* [37,38], in a similar way as for light alkanes in gas phase [30,31]. In this case, oxygen was bubbled through the cathode compartment, which contained the liquid reagents. The anode compartment was fed with a mixture of hydrogen and water vapor. Partial oxidation of cyclohexane [37] was performed in a cell with a powder graphite-PTFE-Pt anode and an oxidized carbon whisker cathode, which was doped with FeCl_3 . Partial direct oxidation of cyclohexane yielded $0.51 \mu\text{mol cm}^{-2} \text{ h}^{-1}$ of cyclohexanol (used as solvent and in wood stains and varnishes) and $1.04 \mu\text{mol cm}^{-2} \text{ h}^{-1}$ of cyclohexanone (utilized in the synthesis of adipic acid and pesticides) with a current density of 6.6 mA cm^{-2} . The oxidation efficiency, defined as the sum of the products with respect to the amount of water produced, was 1.3%. Similarly, benzene was converted in a Pd- FeCl_3 -carbon whisker cathode into phenol (PhOH) in one step [38], following reaction (R22) shown in Table 2, as an alternative method to the Cumene process. Phenol is used in the synthesis of chemicals and drugs, disinfectants and germicidal paints. Partial oxidation of benzene led to $6 \mu\text{mol cm}^{-2} \text{ h}^{-1}$ of phenol, the current density was about 5.9 mA cm^{-2} , and the oxidation efficiency was 13%.

Phenol can also be obtained from gas phase oxidation of benzene in the cathode of a $\text{H}_2\text{-O}_2$ fuel cell, again by reductive activated O^* . The reaction is performed when the electrolyte solution flows constantly through the diaphragm between both electrodes ($1.0 \text{ mol dm}^{-3} \text{ H}_3\text{PO}_4$) and a carbon whisker-PTFE catalyzed by Pd black cathode is employed [39]. Thus, benzene vapor was carried to the cathode compartment with a mixture of O_2 and Ar. A mixture of H_2 and Ar was supplied to the anode compartment. During the FC operation, the cathode reaction was:



Phenol (PhOH) and hydroquinone (HQ) were obtained in a molar ratio 17:1 at 70°C with a phenol formation rate of $4.1 \mu\text{mol cm}^{-2} \text{ h}^{-1}$ (2% current efficiency) and a current density of 0.011 A cm^{-2} .

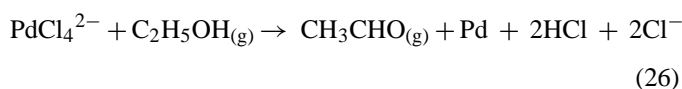
Benzaldehyde (PhCHO) and benzyl alcohol (PhCH₂OH) are used in the manufacture of perfumes, dyes and drugs. These chemicals can be obtained from partial oxidation of toluene in liquid phase also by reaction with reductive activated O^* in the cathode of a $\text{H}_2\text{-O}_2$ fuel cell [41]. Similarly, cresols, which are used in the manufacture of plastics, can be obtained from toluene in one-step [42], thus simplifying the production process. The product distribution depends on the kind of cathode used and the reaction conditions. For example [41], using a carbon whisker cathode, PhCHO, PhCH₂OH and cresols were obtained at 2.0, 0.25 and $0.41 \mu\text{mol cm}^{-2} \text{ h}^{-1}$, respectively. The oxidation efficiency was 11.3%. However, when the cathode was made of carbon whisker, active carbon and FeCl_3 [42], the respective

generation of PhCHO, PhCH₂OH, and cresols was 0.09, 0.08 and $2.1 \mu\text{mol cm}^{-2} \text{ h}^{-1}$. In this case the oxidation efficiency was 9%. Mixtures of carbon whisker with active carbon enhanced the formation of PhCH₂OH.

Catalytic oxidation of toluene with oxygen is difficult to control and selectivity is not satisfactory. This could be improved using a FC. Selective oxidation of toluene (PhCH₃) produced benzaldehyde (PhCHO), as shown in reaction (R23) in Table 2, which finds application in the production of pharmaceutical intermediates, plastic additives, perfumes and flavored drinks, together with benzoic acid (PhCOOH), a raw material in the production of caprolactam, glycol dibenzoate plasticizer esters and food preservatives, when NaCl was added to the anode [40]. Toluene vapor was carried with helium to the anode compartment and oxygen with water vapor was injected to the cathode compartment. During the cell operation a ratio of 9.25:1 of PhCHO to PhCOOH+PhCH₂OH was obtained. CO₂ was negligible. At 70°C , the production rate of PhCHO was $2.4 \mu\text{mol cm}^{-2} \text{ h}^{-1}$ (90% selectivity) and the cell gave 0.5 mA cm^{-2} with a current efficiency of 53.1%. In addition, cyclic shorting an open-circuit operation improved the current efficiency up to 93%. A similar system could be used for π -allyl-type oxidations of olefins. Propylene can thus be converted to acrolein (primarily used in polyurethane manufacture, polyester resins and herbicides), and butene to methyl-vinyl-ketone (used as an intermediate in chemical synthesis, an alkylating agent and a monomer in resins, soil disinfectant and in varnish for automobiles) and crotonaldehyde (utilized as a warning agent in fuel gases, in the preparation of rubber accelerators, in leather tanning and as an alcohol denaturant).

2.4. Chemical cogeneration in molten salt FCs

Partial oxidation of ethanol to produce acetaldehyde is an important chemical reaction that can be carried out in a FC based on the supported molten-salt electrocatalyst (SMSEC) technique (homogeneous liquid-phase catalysis) [43], operating between 57 and 165°C , and around 1.5 atm of pressure. This cell is not a MCFC, but a molten salt is utilized to support the electrocatalyst, which can also be utilized as electrolyte. This technique allowed homogeneous catalysis in FCs for the first time. Different cell configurations are possible. As illustrated in Fig. 5, the anode and cathode can be SMSEC, separated by a Nafion membrane, which is impregnated with a low melting molten salt possessing good protonic conductivity and a low electronic conductivity (such as tetrabutylammonium chloride). The Nafion membrane could also be impregnated with another proton conducting electrolyte such as phosphoric acid. The anode was prepared using a molten salt (tetra-*n*-butylammonium trichlorostannate) containing a dispersed transition metal complex catalyst ($\text{PdCl}_2 + \text{CuCl}_2$), which was coated onto the walls of a porous support such as a carbon cloth or an uncatalyzed GDE. Ethanol or an ethanol-water vapor mixture was carried to the anode with helium and the anode reactions were:



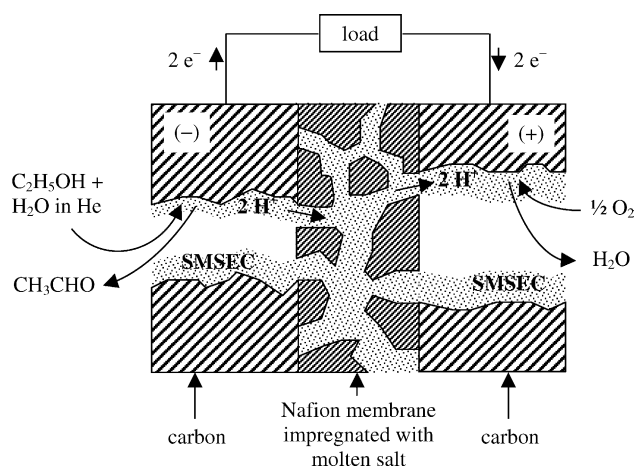
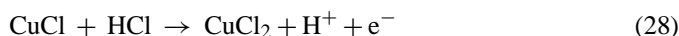
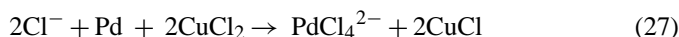
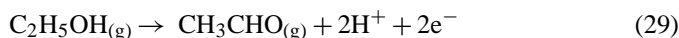


Fig. 5. Schematic diagram of a supported molten-salt electrocatalyst (SMSEC) fuel cell. Reactants and products are transported through the very thin SMSEC film. In this scheme both electrodes are SMSEC, but the cathode can be a conventional GDE with heterogeneous catalyst. Adapted from Ref. [43].



which lead to the following overall anode reaction:



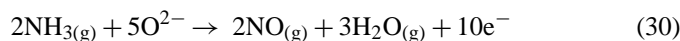
Different cathodes giving reaction (6) were tested and the overall reaction was (R24) shown in Table 2. The best results were obtained using the cell represented by the diagram SMSEC-on-C|CH₃CH₂OH, H₂O|Nafion|O₂|Pt-on-C, in which a conventional carbon supported GDE catalyzed by Pt was employed and the Nafion membrane was impregnated by 5% phosphoric acid. At 90 °C, the power density was 0.35 mW cm⁻² and the product selectivity to acetaldehyde was 83%. With tetrabutylammonium chloride impregnating Nafion at 165 °C, the power density was about 0.26 mW cm⁻². In general, a temperature increase improved the FC output. The current density–voltage curves showed a linear region indicating ohmic control.

2.5. Chemical cogeneration in solid oxide fuel cells (SOFCs)

All the cogeneration systems discussed above operated at low or moderate temperature. However, the use of high temperature has sometimes some advantages: for example the minimization of polarization losses and of the effect of impurities such as H₂S, as well as the possibility of internal reforming. Many chemical cogeneration processes to obtain inorganic [44–47] and organic [48–56] products have been proposed from SOFCs.

The experimental evidence of the chemical cogeneration in SOFCs was firstly shown by Farr and Vayenas [44] with the production of nitric oxide from oxidation of ammonia and recovering part of the emitted energy as electricity. The cell was a high temperature yttria-stabilized zirconia (YSZ) tube FC. The electrodes were porous Pt and the oxygen-ion conducting solid YSZ electrolyte was placed between them. The feeding gas was

NH₃ diluted in He (at a concentration of 4.59%), which flowed through the cell whereas the oxygen cathode was exposed to air. Oxygen is dissociatively adsorbed at the cathode, where it is reduced to oxide ions. The oxide ions pass through the electrolyte to the anode, where they react with NH₃. The cell can be represented by Pt–Rh|NH₃, NO, N₂|ZrO₂(8% Y₂O₃)|air|Pt. Its anode and cathode reactions are:



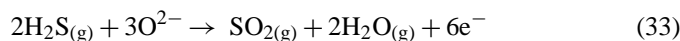
and the corresponding overall reaction is (R25) given in Table 2. The cell currents were in the order of μA cm⁻² and at 727 °C, the main source of polarization was ohmic overpotential. In the temperature range from 427 to 927 °C, NO was the primary anodic product. In optimum operating conditions nitric oxide was obtained with a yield over 60%. Significant amounts of by-product N₂ were also formed due to the catalytic reaction between NH₃ and NO on Pt.

Another process that involves a SOFC is the chemical cogeneration of hydrogen cyanide, used in the synthesis of adiponitrile (for Nylon 6/6), in fumigation, as insecticide, in electroplating, metallurgy and photography [45]. This system utilizes a mixture of methane and ammonia, both diluted in helium, as fuel. The cell was also made with a tube of YSZ enclosed in a quartz tube, containing a porous Pt electrode as the cathode and a porous rhodium and platinum electrode as the anode. The SOFC can then be represented by Pt–Rh|NH₃, CH₄, HCN, CO, N₂|ZrO₂(8% Y₂O₃)|air|Pt, in which the following anode reaction takes place:



the cathode reaction is reaction (31) and the overall reaction is (R26) (see Table 2). The reactor operated in the range 800–1000 °C at an overall pressure of about 1 atm. At these temperatures, the ohmic overpotential is the dominant source of polarization. The product selectivity is a function of the fuel composition, temperature and current density. The cell selectivity to HCN could exceed 75%. For the currents tested, the only by-products formed were CO and N₂ and approximately 0.01 W cm⁻² of power density was delivered. It was found that the cell could operate without external heat supply for the CH₄/NH₃ feed ratio higher than 1.25 [46].

The oxidation reaction of H₂S to SO₂, a basic step of the manufacture of sulfuric acid, has also been carried out successfully in a SOFC [47]. The FC reactor is schematized in Fig. 6, operating at atmospheric pressure and temperatures from 650 to 800 °C, using porous Pt electrodes. Hydrogen sulfide was oxidized on the working electrode, whereas the Pt reference electrode on the opposite side was employed to control the anode potential in the experiments at constant anode current or potential. The diagram of this reactor is Pt|H₂S, (1/2)S₂, SO₂|ZrO₂(8% Y₂O₃)|air|Pt. Hydrogen sulfide, diluted in He, was used as fuel and ambient air was used as oxidant. The respective anode reaction is:



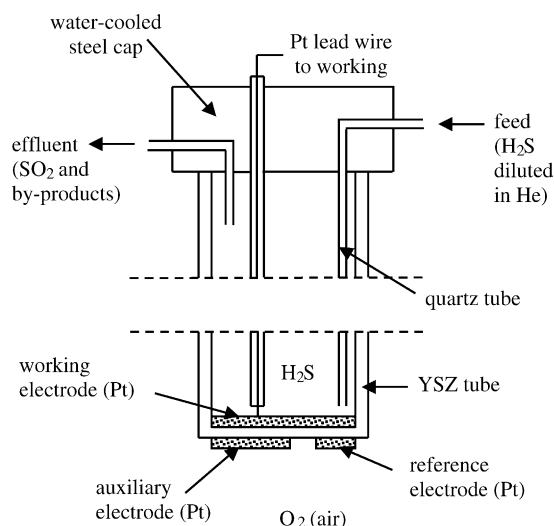
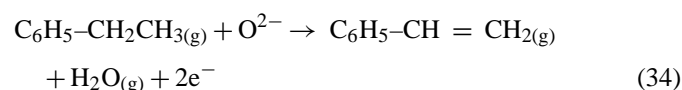


Fig. 6. Schematic diagram of the zirconia SOFC reactor used to produce formaldehyde from methanol. The working, reference and auxiliary electrodes were made of porous deposited Pt. Adapted from Refs. [47,49].

while the cathode reaction is the same as reaction (31) and the overall reaction is (R27) given in Table 2. At low current densities ($<10 \text{ mA cm}^{-2}$) the selectivity to SO_2 remains below 15% and elemental sulfur, $(1/2)\text{S}_2(\text{g})$, is the main product. However, at high current densities ($>40 \text{ mA cm}^{-2}$), the product selectivity to SO_2 increases over 90%. The current density at 730°C at the maximum power density delivered by the FC (about 2.6 mW cm^{-2}) was 6 mA cm^{-2} . Fuel cell stability increased with the ratio of the flow of O^{2-} anion with respect to H_2S .

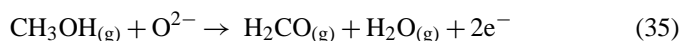
Considering the formation of organic compounds, styrene can be obtained by electrochemical oxidative dehydrogenation of ethylbenzene in the SOFC [48] represented by the diagram $\text{Pt}|\text{C}_8\text{H}_{10}, \text{C}_8\text{H}_8, \text{H}_2\text{O}|\text{ZrO}_2(\text{Y}_2\text{O}_3)|\text{air}|\text{Pt}$, with the following anode reactions:



The cathode reaction is again reaction (31). This cell operates in the range $575\text{--}600^\circ\text{C}$ with porous Pt electrodes and YSZ as electrolyte with the overall reaction (R28) shown in Table 2. Ethylbenzene is diluted with helium, and styrene, water, and other by-products (mainly CO_2) are formed. However, although dehydrogenation rates increased with anodic current, total conversion was limited to 15% or less.

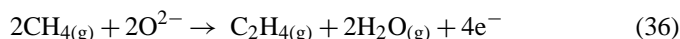
The partial oxidation of methanol to formaldehyde (applied as fertilizer, dyes, disinfectants, germicides and preservatives) is another important industrial reaction that has been reproduced successfully in a SOFC with the diagram $\text{Ag}|\text{CH}_3\text{OH}, \text{H}_2\text{CO}, \text{CO}_2, \text{H}_2, \text{H}_2\text{O}|\text{ZrO}_2(8\% \text{ Y}_2\text{O}_3)|\text{air}|\text{Ag}$ [49]. The experimental cell was similar to that shown in Fig. 6. In this case, porous Ag was deposited on both sides of the bottom of the YSZ tube and the system was introduced in a furnace to operate at atmospheric pressure and temperatures in the range $547\text{--}697^\circ\text{C}$. Methanol vapor diluted in high-purity He was introduced in the inner part of the YSZ tube through the feed. The Ag electrode in the inner

part, i.e. the working electrode of the three-electrode system, was the anode for the methanol oxidation:



One of the electrodes in the external part, the auxiliary electrode, was the cathode for O_2 reduction from reaction (31), whereas the second electrode in the external part was the reference electrode, used to measure the anode overpotential. The overall reaction is (R29) in Table 2, with $E^\circ = 1.091 \text{ V}$ at 923 K . Typical power density outputs obtained were about 1 mW cm^{-2} . The two main contributions to polarization were activation and ohmic overpotential, at low and high current densities, respectively. The methanol conversion was above 30%, with selectivity to formaldehyde of 85–92%. The main by-products were CO and CO_2 .

Oxidation coupling of methane or reforming reaction represents an effective chemical use of natural gas. The oxidative dimerization of methane to ethylene and C_2 hydrocarbons leads to a yield values up to 85 and 88%, respectively, for methane conversion up to 97% at 800°C [50] when it was carried out in a SOFC with a $\text{ZrO}_2(8\% \text{ Y}_2\text{O}_3)$ tube. Two types of anodes were used: a porous Ag film and a porous cermet consisting of Sm_2O_3 doped with CaO and Ag. Methane diluted in helium was used as fuel. Oxygen was fed into a porous Ag cathode. During the cell operation, ethylene, ethane, CO_2 and H_2O were the only detectable products. The anode reaction was:



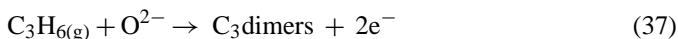
and the cathode reaction was reaction (31), giving rise to the overall reaction (R30) (see Table 2).

On the other hand, a bifunctional reaction system was proposed [51]. This reactor can be represented by $\text{La}_{1.8}\text{Al}_{0.2}\text{O}_3|\text{CH}_4, \text{C}_2\text{H}_4, \text{C}_2\text{H}_6, \text{CO}, \text{CO}_2|\text{ZrO}_2(8\% \text{ Y}_2\text{O}_3)|\text{air}|\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$. The SOFC operated between 700 and 1000°C at atmospheric pressure and converted methane into C_2H_6 according to reaction (R31) (see Table 2), with high selectivity.

Ethane oxidative dehydrogenation on boron oxides supported on YSZ lead to ethylene in the cell $\text{Ag}|\text{C}_2\text{H}_6, \text{C}_2\text{H}_4|\text{B}_2\text{O}_3(\text{YSZ})|\text{O}_2|\text{Ag}$ operating at 550°C and atmospheric pressure balanced with He [52]. In this case, the overall reaction is (R32) (see Table 2).

Other solid electrolytes are used in high temperature FCs to obtain chemicals. For example, the oxidative dehydrogenation of propylene to 1,5-hexadiene and benzene (used in gasoline, inks, oils, paints, plastics, and rubber, manufacture of detergents, explosives, pharmaceuticals, and dyes among others) has been reported in a SOFC, which uses a variety of bismuth oxide-based catalysts and a solid oxide ion conductor as $(\text{Bi}_2\text{O}_3)_{0.85}(\text{La}_2\text{O}_3)_{0.15}$ in the form of a metal oxide disk [53]. A mixture of 20% of propylene in helium was used as fuel, while air was passed through the cathode of the FC reactor. The cell operated at 600°C and atmospheric pressure. The selectivity for the production of 1,5-hexadiene and benzene was 77% at 3.2% conversion. The cell can be represented as $\text{C}_3\text{H}_6, \text{C}_6\text{H}_{10}, \text{C}_6\text{H}_6,$

CO₂, CO, CH₄|(Bi₂O₃)_{0.85}(La₂O₃)_{0.15}|air. Its anode reaction is:



and its cathode reaction corresponds to reaction (31). Production of benzene takes place according to reaction (R33) given in Table 2.

SOFCs can be used as cogenerators to produce intermediates of further products. In this way, partial oxidation of methane to synthesis gas can be achieved in a high temperature FC type reactor [54] (reaction (R34) in Table 2). The resulting synthesis gas is the most useful for hydrocarbon and methanol manufacture. The FC reactor consists of a single planar type SOFC. The electrolyte is a LaGaO₃-based oxide. La_{0.6}Sr_{0.4}CoO₃ and Ni were used as the cathode and the anode, respectively. A gaseous mixture of CH₄ and N₂ was employed as the fuel, while O₂ was used as the oxidant. The FC gave at 1000 °C a maximum power density of 526 mW cm⁻², which could be higher depending on doping, if the oxide ion conductivity was increased in this form. The yield of synthesis gas was around 20% in all the cases studied.

On the other hand, the effect called nonfaradaic electrochemical modification of catalytic activity (NEMCA) can enhance activity and selectivity of catalyst surfaces in SOFC, so the reactor can then operate at temperatures as low as 200 °C and extend economic potential of cogeneration to a large number of reactions [55,56]. It is accomplished when a porous metal catalyst film is deposited on one side of a solid electrolyte and a small voltage or current density of a few μA cm⁻² is applied between the catalyst and an auxiliary electrode deposited on the other side. NEMCA effects in different catalytic reactions have been found when the catalyst is the positive terminal and also when it is the negative terminal. Ions of the solid electrolyte migrate (spill over) onto the catalyst surface (positive current) or there is a negative ion removal from the catalyst surface (negative current), but the metal work function changes and the catalytic properties of the metal vary dramatically in a reversible manner. There is an increase in the catalytic activity accompanied by changes in product selectivity. Although some energy is sacrificed, there is no significant electrolysis and the conversion of the reactants is due to a heterogeneous chemical reaction. Therefore, the cost of the energy required to induce NEMCA is negligible in comparison with the values of the chemicals produced. From a practical viewpoint, a SOFC-type reactor consumes a very small electrical energy to operate and product generation is not limited by Faraday's law. This type of catalytic reactions has also been studied using the reactor shown in Fig. 6, where a potentiostat–galvanostat is employed in this case. A typical example with very high NEMCA effect is the production of CO₂ from ethylene and O₂ on the Pt catalyst using the YSZ electrolyte and temperatures in the range 260–450 °C.

3. Economic evaluation of electrocogeneration processes

The most part of the papers found in the literature dealing with electrocogeneration in fuel cells, summarized here, illus-

trate the feasibility of the process in which electrical energy and useful products are produced together, but they do not aim to evaluate their economic aspects. Accordingly, no effort is generally made to optimize the fuel cell reactor and the working conditions, to scale-up the fuel cell, or to determine sources of electrical inefficiency. Fuel cells are recently being tentatively introduced in the market because they appear as important alternative for meeting future energy requirements. The commercial progress of fuel cells has been very slow, mainly due to the fact that energy is being obtained at smaller cost with conventional technologies. It is not then strange that electrocogeneration in fuel cells covering both, scientific and economic aspects has been the object of only limited number of studies. In this section, the attempts made in the literature to evaluate the economic aspects of electrocogeneration processes are reviewed.

Only a few economic models have been developed [57–59], although with interesting results. Spillman et al. [57] used simplified expressions for power and chemical production in electrochemical cells, obtaining the following ratio between the theoretical operating current density $j_{\text{th,max}}$ and the current density related to the maximum power output j_P (which gives the maximum profitability):

$$\frac{j_{\text{th,max}}}{j_P} = 1 + \left\{ \left(\frac{M}{-\Delta G^\circ} \right) \times \left(\frac{K_P - K_{RM}}{K_E} \right) \right\} = 1 + \frac{1}{\lambda_{\text{th}}} \quad (38)$$

where M is the molecular weight of the chemical product, K_E the unit electrical energy price in \$kW h⁻¹, K_P the unit price for the chemical product in \$ (as it emerges from the cell), and K_{RM} the unit price for the raw material in \$kg⁻¹. The term $S = 1 + 1/\lambda_{\text{th}}$ is a dimensionless ratio of the net chemical product value ($K_P - K_{RM}$) to the electrical energy value ($-K_E \Delta G^\circ/M$) and it is very sensitive to the relative value of chemicals to power. According to this model, the value of S determines in which mode the electrogeneration plant can most profitably be operated: reverse electrolysis for $S \leq 1$, fuel cell for $-1 < S < 0$, cogenerator for $-1 < S < 1$, and forward electrolysis for $S > 1$. None of the reactions that they analyzed gave S values clearly in the cogeneration range. Their main conclusion was that as long as chemicals continue to be more valuable than their electrical energy equivalent, cogeneration will be less attractive than direct electrolysis. However, changes in the prices of chemicals and electricity could make electrocogeneration interesting, in particular for low molecular weight species and for reactions with ΔG° highly negative, when the difference in raw material and product values is low and the power rates are high. In fact, it is necessary that thermodynamic requirements are favorable, although kinetics requirements, most of all related to the catalysts, ultimately decide the outcome. This would be the case of those processes based in the use of precious metals as catalysts, in which the type and quantity affect the cost of the overall process [60].

On the other hand, Vayenas et al. [58] examined within the context of differential economic analysis, the relative profitability of a cogeneration SOFC in relation to a chemical reactor of the same capacity giving the same product composition. The

model derived showed that such a relative profitability depends, mainly, on the value of the dimensionless number, ν , defined as follows:

$$\nu = \left[\frac{24\alpha(K_E - K_H)t_C}{\alpha C_C - C_R} \right] \quad (39)$$

where K_E is again the unit electrical energy price (in \$ kW h⁻¹), K_H the price per thermal unit produced in (\$ kW h⁻¹), t_C the cogenerative FC useful lifetime (in days), C_C the cogenerative fuel cell capital investment per unit installed power (in \$ kW⁻¹), C_R the chemical reactor capital investment per unit installed capacity (in \$ day kW⁻¹) and α is a conversion factor given in the economical model. Thus, a cogeneration fuel cell is more advantageous than a chemical reactor if $\nu > 1$. From these primary considerations, it is concluded that only exothermic reactions with inexpensive raw materials and products are good candidates for electrocogeneration. The results of this economic model were encouraging for H₂SO₄ and possibly, for HNO₃ cogeneration, but not for the ethylene oxide production nor for the methanol conversion to formaldehyde.

Other studies show that cogeneration could represent an energy saving respect to the conventional chemical process in methyl-ethyl-ketone production in a low temperature fuel cell [17] and that methane oxidation coupling to produce ethylene gives acceptable economic results [59].

The models presented here provide general conclusions from several assumptions about prices of chemicals, electric power and reaction characteristics. Prices depend on time (due to the economy and to the energy resources) and on the place of the world, and thus, the profitability of a cogeneration FC can be different along time and location. This presupposes that a detailed analysis for each process is needed in each particular condition.

Fuel cells are recently being introduced in the market to generate energy as the main product, especially for transportation and in remote sites, because the natural resources used in the conventional energy production are not infinite. It is then expected that advances in fuel cell technology will allow adapting electrocogeneration plants to market demands in the future. In this sense it appears that small scale plants for on-site production will be very promising.

4. Conclusions

This review shows the ability of fuel cell systems to convert chemical energy in useful chemicals and electric power. The limited number of scientific studies on electrocogeneration appearing in the literature, indicate that this topic has to be still considered in its primary stages. However, it is an emergent field related to the recent commercial development of fuel cells. Economic studies, which are also in its first stages, show that exothermic reactions involving inexpensive raw materials and products with respect to the cost of electricity are good candidates for electrocogeneration. Attempts to assess the economics of electrocogeneration are simple and show the need for a more detailed analysis. Different electrocogeneration processes have been identified to be interesting from a commercial point of view. Further studies in such fields are desirable because many

different electrocogeneration processes appear to be possible in practice, with adequate current efficiency and product selectivity, and depending on the relative value of chemicals to power of the historical moment, with probable better profitability than in chemical or electrolytic reactors.

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