

Recent advances in the development of direct alcohol fuel cells (DAFC)

Claude Lamy^{*}, Alexandre Lima, Véronique LeRhun, Fabien Delime, Christophe Coutanceau, Jean-Michel Léger

Laboratory of Electrocatalysis, UMR CNRS No. 6503, University of Poitiers, 40, Avenue du Recteur Pineau, 86022 Poitiers, France

Abstract

Recent developments into technology of proton exchange membrane fuel cells (PEMFC) now allow serious consideration to be given to a direct alcohol fuel cell (DAFC) based on a PEMFC, in which alcohol is used directly as the fuel. This is particularly advantageous for mobile applications, since this will avoid the use of a bulky and expensive reformer. However, the relatively complex reaction mechanism, leading to a low electroactivity of most alcohols, even methanol, needs the investigation of new platinum-based electrocatalysts, particularly active for breaking the C–C bond when alcohols other than methanol are to be used. Moreover, in order to overcome the deleterious effect of alcohol crossover through the proton exchange membrane, it is necessary to develop new oxygen reduction electrocatalysts insensitive to the presence of alcohols. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

During the past 10 years, there has been an increasing interest in the development of direct alcohol/air proton exchange membrane fuel cells (PEMFC), particularly for applications to the electric vehicle [1]. Among the different possible alcohols, methanol is the most promising organic fuel because its use as a fuel has several advantages in comparison to hydrogen: high solubility in aqueous electrolytes, liquid fuel available at low cost, easily handled, transported and stored, high theoretical density of energy (6 kWh/kg) comparable to that of gasoline (10–11 kWh/kg). Other alcohols, such as ethanol, ethylene glycol, propanol, etc. have also been considered for use in a fuel cell, but until now very few direct alcohol fuel cells (DAFC) have been demonstrated, the most advanced system being the direct methanol fuel cell (DMFC) [2].

The electro-oxidation of methanol in a DMFC has been studied for more than three decades [2–4]. But little progress was made in the past, due to fundamental problems inherent in the fuel cell design (liquid electrolyte, such as sulphuric acid, to reject CO₂, the reaction product of total oxidation, and conventional carbon supported platinum-based metal

catalysts). Twenty years ago, Shell Research Center in Great Britain [5] and Hitachi Research Laboratories [6] in Japan built relatively large stacks (up to 5 kW for Hitachi), but the performances were low, e.g. 20–30 mW/cm² for a relatively large platinum loading (≈ 10 mg/cm², which corresponds to 2–3 W/g of platinum catalysts). Only recently has the concept of PEMFC been applied to the DMFC leading to a great improvement in the electrical characteristics: 200–400 mA/cm² at 0.5 V, i.e. 100–200 mW/cm² depending on the working conditions of temperature and pressure [7,8]. But these performances are still limited because of several problems: (i) the low activity of the state-of-the-art electrocatalysts, which can only be enhanced by increasing the operating temperature, (ii) anode poisoning by strongly adsorbed intermediates (mainly CO) formed during methanol oxidation, and (iii) the high extent of methanol cross-over through the Nafion[®] type membranes, which depolarizes the air cathode.

Moreover, methanol has some particular disadvantages, e.g. it is relatively toxic, inflammable with a low boiling point (65 °C), and it is not a primary fuel, nor a renewable fuel. Therefore, other alcohols, particularly those coming from biomass resources, begin to be considered as alternative fuels. Ethanol is an attractive fuel for the electric vehicle, since it can be easily produced in great quantity by the fermentation of sugar-containing raw materials from agriculture. In addition, in some countries like Brazil,

^{*} Corresponding author. Tel.: +33-5-49-45-36-28;

fax: +33-5-49-45-35-80.

E-mail address: claude.lamy@univ-poitiers.fr (C. Lamy).

ethanol is already distributed through the gas station network to fuel the thermal engine cars. Other alcohols have also been considered as interesting fuels for fuel cells, some of them having led to prototype production, such as ethylene-glycol [9], or glycerol [10].

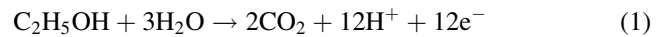
This paper aims to review the more recent advances made in the development of the DAFC, using the PEMFC configuration. In particular, we will present recent progress made in the understanding of the mechanisms of the oxidation reaction, leading to the conception and realization of plurimetalllic catalysts for alcohol oxidation. Moreover, new oxygen reduction catalysts insensitive to the presence of alcohol will be discussed as a convenient way to avoid the cathode depolarization which arises as a consequence of alcohol crossover through the polymeric membrane (usually Nafion[®] membranes).

2. Principle of a direct alcohol fuel cell (DAFC)

The direct anodic oxidation of an alcohol fuel other than methanol would allow building compact power sources (with no heavy and bulky fuel reformer), fed with a convenient electrochemically reactive and relatively non-toxic and cheap liquid fuel. Recent progress in the PEMFC and the DMFC allow us to conceive a DAFC based on a PEMFC. In the case of ethanol, taken as a typical example (Fig. 1), an anode mixture of ethanol dissolved in water (a few percent in weight to make a 1–2 M ethanol solution) is circulated through the anodic compartment, and oxygen (air) flows through the cathodic compartment. The anode/water mixture allows hydration of the proton exchange membrane (usually Nafion[®]) particularly for working at higher temperatures (100–130 °C). In this case, some increase in pressure (2–5 bars) of the anode compartment is needed to keep the alcohol solution liquid.

2.1. Thermodynamic data

The direct electrochemical oxidation of ethanol occurs at the anode, according to the following overall reaction:



corresponding to an anode potential $E_1^\circ = 0.084 \text{ V}$ versus SHE, as calculated from thermodynamic data, knowing the standard energy of formation ΔG_i^f of reactant (i):

$$-\Delta G_1^\circ = 2\Delta G_{\text{CO}_2}^f - \Delta G_{\text{C}_2\text{H}_5\text{OH}}^f - 3\Delta G_{\text{H}_2\text{O}}^f$$

or

$$-\Delta G_1^\circ (\text{kJ/mol}) = -2 \times 394.4 + 174.8 + 3 \times 237.1 = 97.3$$

leading to the anode potential: $E_1^\circ = -\Delta G_1^\circ / 12F = 97.3 \times 10^3 / 12 \times 96485 = 0.084 \text{ V}$ versus SHE.

The reaction product (carbon dioxide), which evolves in the anodic compartment, must be separated from the alcohol flow. The protons, which are simultaneously produced, migrate through the proton exchange membrane (acid electrolyte) and reach the cathodic compartment, where the electroreduction of oxygen occurs:



corresponding to the cathode potential $E_2^\circ = -\Delta G_2^\circ / 2F = 237.1 \times 10^3 / 2 \times 96485 = 1.229 \text{ V}$ versus SHE.

The electrical balance corresponds to the complete combustion reaction of ethanol in pure oxygen:



with $\Delta G^\circ (\text{kJ/mol}) = 6\Delta G_2^\circ - \Delta G_1^\circ = -1325$ and $\Delta H^\circ = -1367 \text{ kJ/mol}$, from which the equilibrium standard electromotive force (emf) can be calculated:

$$\begin{aligned} E_{\text{eq}}^\circ (\text{V}) &= -\frac{\Delta G^\circ}{nF} = \frac{1325 \times 10^3}{12 \times 96485} \\ &= E_2^\circ - E_1^\circ = 1.229 - 0.084 = 1.145 \end{aligned}$$

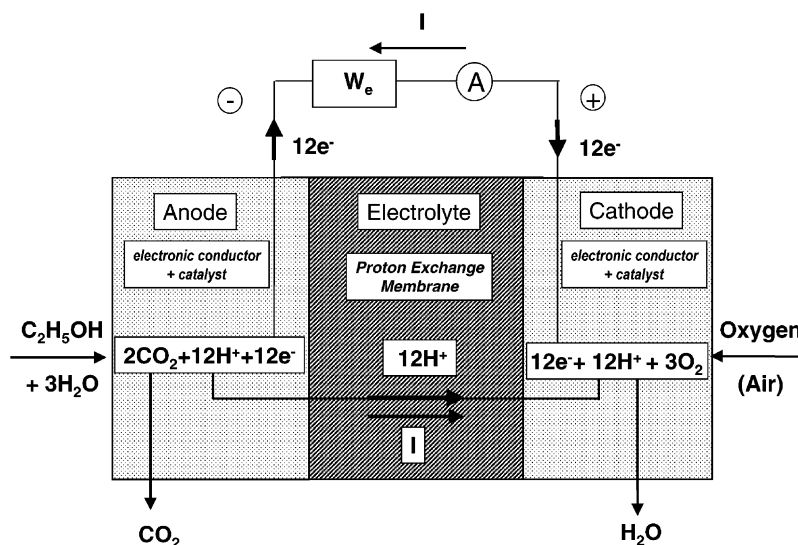


Fig. 1. Schematic principle of a direct ethanol fuel cell.

Table 1
Thermodynamic data associated with the electrochemical oxidation of some alcohols (under standard conditions)

Fuel	ΔG_1° (kJ/mol)	E_1° (V vs. SHE)	ΔG° (kJ/mol)	E_{cell}° (V)	W_e (kWh/kg)	ΔH° (kJ/mol)	ϵ_{rev}
CH ₃ OH	-9.3	0.016	-702	1.213	6.09	-726	0.967
C ₂ H ₅ OH	-97.3	0.084	-1325	1.145	8.00	-1367	0.969
C ₃ H ₇ OH	-281	0.162	-1853	1.067	8.58	-2021	0.916
C ₄ H ₉ OH	-464	0.200	-2381	1.029	8.93	-2676	0.890

The specific energy can, thus, be evaluated as follows:

$$W_e \text{ (kWh/kg)} = \frac{-\Delta G^\circ}{3600 \times M} = \frac{1325 \times 10^3}{3600 \times 0.046} \approx 8.00$$

with M the alcohol molecular mass.

The enthalpy change $\Delta H^\circ = -1367$ kJ/mol allows us to calculate a reversible energy efficiency (at equilibrium potential):

$$\epsilon_{\text{rev}} = \frac{\Delta G^\circ}{\Delta H^\circ} = \frac{1325}{1367} = 0.969$$

Such a system, which does not follow the Carnot's theorem, can produce electricity with a high energy efficiency ($\epsilon_{\text{rev}} \approx 97\%$ under reversible conditions and $\epsilon = \epsilon_{\text{rev}} \epsilon_E \approx 40\%$, with a potential efficiency $\epsilon_E = E_{\text{cell}}/E_{\text{eq}} \approx 41\%$, at a working emf $E_{\text{cell}} = 0.5$ V, with complete oxidation of the alcohol). If the oxidation reaction is not complete (e.g. if it stops at some intermediate stage), the overall efficiency will be proportionally reduced due to a lower Faradaic efficiency ($\epsilon_F = n_{\text{exp}}/n_{\text{th}}$ with n_{exp} the number of electrons effectively observed for the overall reaction, and n_{th} the theoretical number of electrons corresponding to the complete oxidation of the alcohol to carbon dioxide).

For the oxidation of other alcohols similar thermodynamic calculations can be made under standard conditions (25 °C, liquid phase). The results are given in Table 1.

According to Table 1, alcohols have a very good energy density W_e , close to that of hydrocarbons and gasoline (e.g. 10–11 kWh/kg), so that they appear as a reasonable alternative energy carrier for the electric vehicle. The equilibrium electromotive force under standard conditions is around 1.1–1.2 V, i.e. very close to that of a hydrogen/oxygen fuel cell (1.23 V). But the reversible energy efficiency ϵ_{rev} is much better than that of an H₂/O₂ fuel cell (which is only 0.83 at 25 °C), approaching unity for the lightest alcohols.

2.2. Kinetics data

In contrast to these promising thermodynamic data, the kinetics of alcohol oxidation is more difficult, leading to high anodic overvoltages (Fig. 2) particularly for the heaviest alcohols. As a typical example, the overvoltage of methanol electro-oxidation reaches 0.5 V at 200 mA/cm² on pure platinum, although the development of better

electrocatalysts (Pt-based alloys) allows this to be greatly decreased it, e.g. by 0.2 V (Pt_{0.50}/Ru_{0.50}) to 0.3 V (Pt_{0.80}/Ru_{0.20}), see Fig. 2.

For other alcohols, the oxidation kinetics is much more slower, so that higher overvoltages at lower current densities are obtained. This results from complex reaction mechanisms involving multielectron transfers. Only a detailed knowledge of the adsorbed species and intermediate products, of the reaction paths and their rate constants, and of the rate determining step, will allow any increase in the overall reaction rate, and thus, a decrease in the overvoltage. One way to do this, is to look for more active electrocatalysts, (e.g. bimetallic or multimetallic platinum-based catalysts). Another way to increase the reaction rate, i.e. to decrease the overvoltage, is to increase the working temperature above 120 °C. However, the usual Nafion[®] membranes cannot work above 120–140 °C, so that other membranes have to be found and to be developed. Higher temperatures, up to 170 °C, have been reached using composite polymer membranes, such as silica/Nafion films [11] or a polybenzimidazole (PBI) membrane doped with phosphoric acid [12].

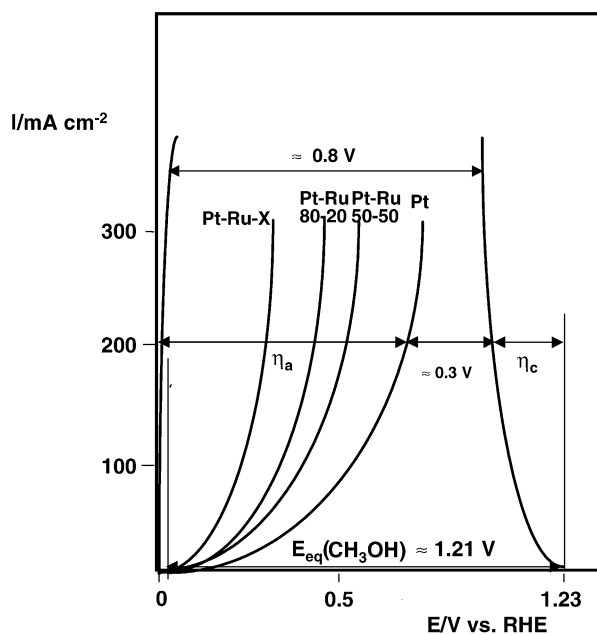
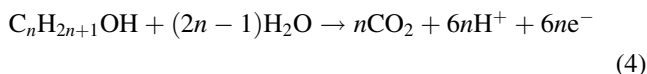


Fig. 2. Current density vs. potential curves of a methanol/oxygen fuel cell, compared with that of a hydrogen/oxygen fuel cell.

3. Investigation of the reaction mechanism of alcohol oxidation

Since an alcoholic group only contains one oxygen atom, the complete oxidation of a (primary) alcohol to CO_2 needs an extra oxygen atom. This atom must be provided by water, or by water adsorbed residue (adsorbed OH). Thus, the general overall electro-oxidation reaction of a primary alcohol can be written as follows:



It turns out that the reaction mechanisms of alcohol oxidation always involve the participation of water, or of its adsorption residue, so that a good electrocatalyst must activate both the alcohol chemisorption and the water molecule. Moreover, the reaction mechanisms are complex involving several adsorbed intermediates and the formation of numerous products and by-products.

The elucidation of the reaction mechanism, thus, needs to combine pure electrochemical methods (cyclic voltammetry, rotating disc electrodes, etc.) with other physicochemical methods, such as “in situ” spectroscopic methods (infrared [13] and UV–VIS [14] reflectance spectroscopy) to monitor the adsorbed intermediates and “on line” chromatographic techniques [15] to analyze quantitatively the reaction products and by-products.

The oxidation of methanol has been thoroughly studied for many years, so that the reaction mechanism is now well established [16]. The overall oxidation reaction involves six electrons, and one water molecule, as follows:

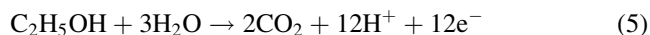


It was first shown by electrochemically modulated infrared reflectance spectroscopy (EMIRS) that the main

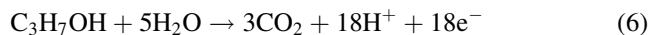
poisoning species formed during the chemisorption and oxidation of methanol on a platinum electrode is carbon monoxide CO, either linearly bonded, or bridge bonded to the surface [17]. The coverage degree of by linearly bonded CO can reach 90% on a pure platinum electrode, so that most of the active sites are blocked. Besides, some other adsorbed species, such as $(\bullet\text{CHO})_{\text{ads}}$ or $(\bullet\text{COOH})_{\text{ads}}$, were identified by infrared reflectance spectroscopy (EMIRS or Fourier transform infrared reflectance spectroscopy) [18–20] (Fig. 3).

Intermediate reaction products, like formaldehyde HCHO and formic acid HCOOH, and final product (CO_2) were also analyzed quantitatively by liquid or gas chromatography [21]. The reaction mechanism, even for the oxidation of the lightest alcohols involving the smallest number of electrons ($n = 6$ for methanol oxidation), is therefore, relatively complex (Fig. 4) [16]. In this mechanism, the adsorbed formyl-like species $(\bullet\text{CHO})_{\text{ads}}$ plays a key role and the strategy to develop efficient electrocatalysts will be to favor this adsorbed species, and to avoid the subsequent formation of adsorbed CO, either to prevent its formation by blocking neighboring Pt sites, or to oxidize it at lower potentials.

The reaction mechanisms of the anodic oxidation of other alcohols is more difficult to elucidate since the number of electrons exchanged greatly increases and the activation of the C–C bond is relatively difficult at moderate temperatures (50–150 °C). The complete oxidation of ethanol involves 12 electrons per molecule, i.e.



whereas that of *n*-propanol involves 18 electrons:



so that the reaction mechanism involves many adsorbed intermediates and by-products.

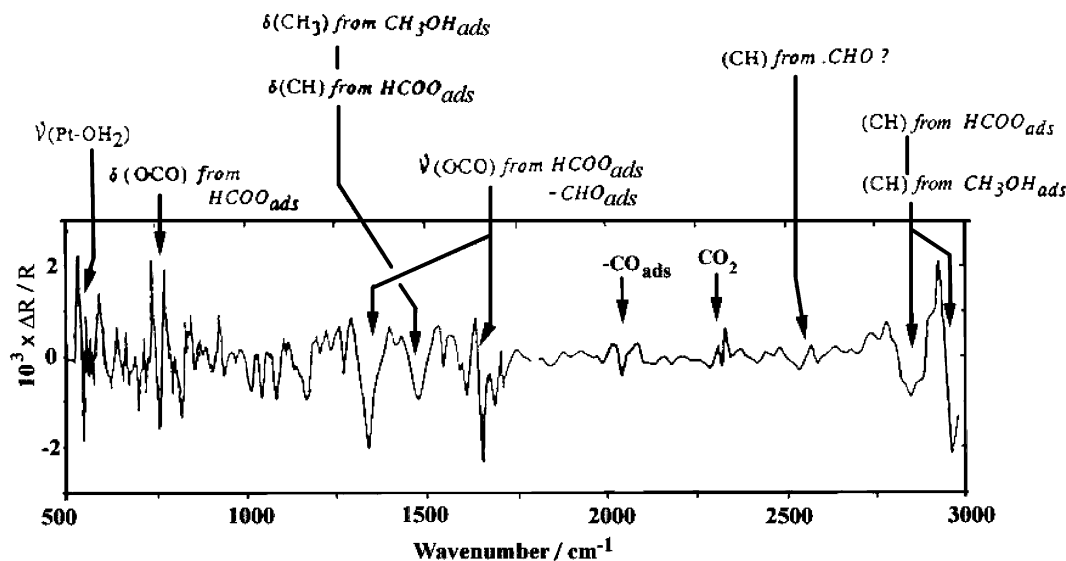


Fig. 3. Infrared reflectance spectra (EMIRS) of the adsorbates resulting from the chemisorption of methanol on a platinum polycrystalline electrode in acid medium (10^{-3} M CH_3OH in 0.5 M HClO_4 , room temperature).

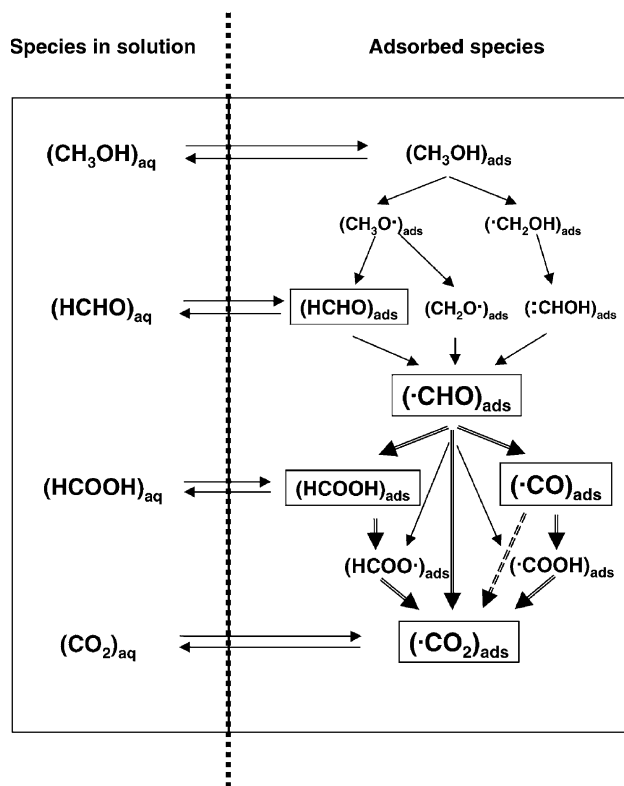
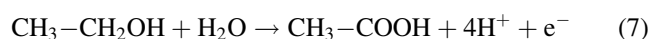


Fig. 4. Detailed reaction mechanism of the oxidation of methanol on a platinum electrode.

The electrocatalytic oxidation of ethanol has been investigated for several years on different platinum-based electrodes, including Pt/X alloys (with $X = \text{Ru, Sn, Mo, etc.}$), and dispersed particles. Pure platinum electrodes are rapidly poisoned by some strongly adsorbed intermediates, such as carbon monoxide, resulting from the dissociative chemisorption of the molecule, as shown by infrared reflectance spectroscopy [22–24]. Both adsorbed CO, either linearly-bonded or bridge-bonded to the platinum surface, are observed. Besides, other adsorbed species have been identified by IR reflectance spectroscopy, including reaction intermediates, such as acetaldehyde and acetic acid, and other by-products (Fig. 5) [23–25].

Detailed analysis of the reaction products by chromatographic techniques (HPLC, GC) [24] or by DEMS [23] allows us to write a more detailed reaction mechanism of ethanol oxidation on Pt electrodes in acid medium, involving parallel and consecutive oxidation reactions, as follows:



Reaction (7) mainly occurs at higher electrode potentials ($E > 0.8 \text{ V/RHE}$), where the water molecule is activated to form oxygenated species at the platinum surface, whereas reaction (8) occurs mainly at lower potentials ($E < 0.6 \text{ V/}$

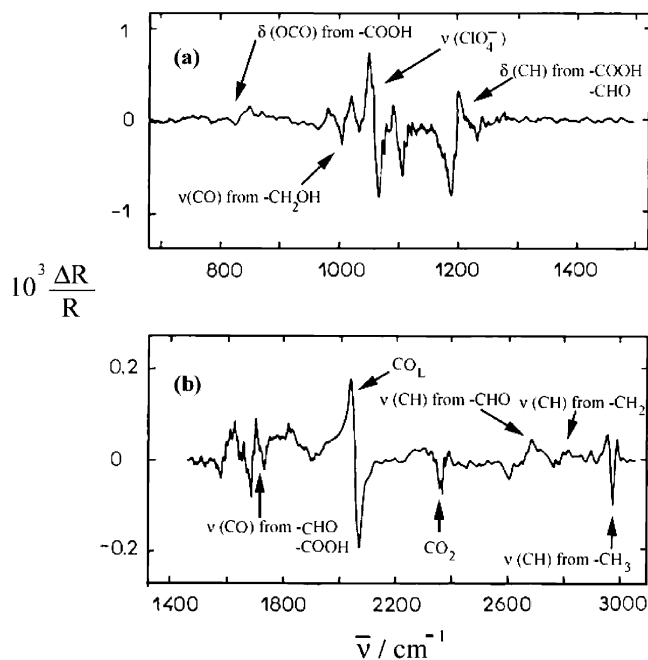
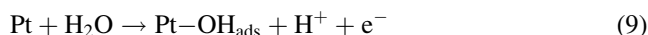
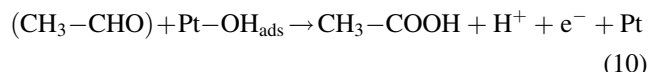


Fig. 5. Infrared reflectance spectra (EMIRS) of the adsorbates resulting from the chemisorption of ethanol on a platinum polycrystalline electrode in acid medium (0.5 M HClO_4 , room temperature). (a) $10^{-3} \text{ M C}_2\text{H}_5\text{OH}$; (b): $10^{-1} \text{ M C}_2\text{H}_5\text{OH}$.

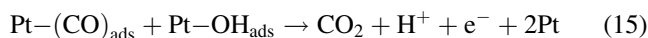
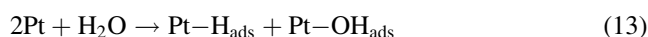
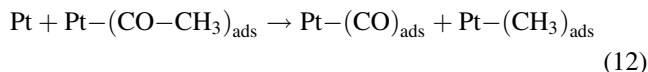
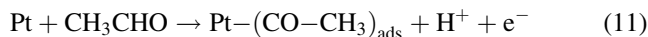
RHE) [24]. At intermediate potentials ($0.6 \leq E \leq 0.8 \text{ V/RHE}$), the dissociative adsorption of water occurs:



so that the oxidation of adsorbed $\text{CH}_3\text{-CHO}$ may produce acetic acid, as follows:



Further oxidation to carbon dioxide is usually difficult on pure Pt electrodes at room temperature. However, carbon monoxide acting as a poisoning species, and CO_2 , were clearly observed by infrared reflectance spectroscopy [22] or by DEMS [23], and by gas chromatography, respectively, together with some traces of methane at low potential ($E < 0.4 \text{ V/RHE}$) [23]. This may be explained by the following mechanism:



The presence of both poisoning species and intermediate reaction products (which decreases correspondingly the useful energy density of the fuel), requires the development

of new electrocatalysts able to break the C–C bond at low temperatures and to oxidize adsorbed CO at lower potentials, i.e. to reduce the oxidation overpotential.

Other electrocatalysts were considered for the electro-oxidation of ethanol, such as rhodium, iridium [26] or gold [27], leading to similar results in acid medium. The oxidation of ethanol on rhodium proceeds mainly through the formation of acetic acid and carbon monoxide. Two types of adsorbed CO are formed, i.e. linearly-bonded and bridge-bonded, in a similar amount, at relatively low potentials, then leading rapidly to carbon dioxide when the rhodium surface begins to oxidize, at 0.5–0.7 V/RHE [26]. On gold in acid medium the oxidation reaction leads mainly to the formation of acetaldehyde [27].

The oxidation of higher alcohols always produces some amounts of adsorbed carbon monoxide, as the result of the adsorption of the molecule. This is confirmed by infrared reflectance spectroscopy, showing that the primary alcohols easily dissociate upon chemisorption leading to adsorbed CO, whereas the tertiary alcohols do not produce any carbon monoxide [16].

To summarize, most alcohols dissociate at platinum electrodes producing different chemisorbed species, among them adsorbed CO is always observed by infrared spectroscopy at around 2000 cm^{-1} . These poisoning species block the electrode active sites leading to a decrease with time of the fuel cell performance. It was also shown that the amount of CO_{ads} decreases when the number of carbon atoms increases [16].

4. Catalytic role of the electrode material

4.1. Electrocatalytic materials for the oxidation of alcohols

The nature and the structure of the electrode material play a key role in the adsorption and electro-oxidation of most organic fuels, particularly aliphatic alcohols.

On the other hand the use of a proton exchange membrane as acid electrolyte induces pH limitations, and therefore, in such a strong acid environment, the only stable and active catalyst for the electrooxidation of alcohols is platinum. Even if some attempts have been made to develop other electrocatalysts, such as tungsten compounds, only platinum seems to be able to adsorb alcohols and to break the C–H bonds. Unfortunately, the dissociative chemisorption of an alcohol leads to the formation of strongly poisoning species (adsorbed CO), which block the electroactive sites of the catalysts. This results in the high overpotentials observed in the electro-oxidation of alcohols. However, fundamental work has shown that the CO poisoning is less important on highly dispersed platinum than on smooth platinum and that it decreases when increasing the roughness factor [28]. Furthermore, the tremendous development of the H_2/O_2 PEMFC during the last decade has also shown that it is now possible to conceive catalytic electrodes, which are very

active for hydrogen oxidation, with a platinum loading as low as 0.1 mg/cm^2 . Unfortunately, it is clear that, as least in the near future, such a small loading is not suitable for the electro-oxidation of alcohols, even if the electrode poisoning of such highly dispersed platinum catalysts is weaker.

The challenge remains then to reduce or to avoid the formation of strongly adsorbed CO species or to favor their oxidation at low potentials. This can be obtained only by modifying the superficial electrode structure in order to change the kinetics of adsorption and oxidation of species linked at the electrode surface.

A convenient way to modify the electrocatalytic properties of platinum, and to decrease the poisoning of its surface by adsorbed CO, is to make alloys with a second metal, or even a third metal. The components added to platinum should have several properties, which restrict greatly their choice. The pH of the membrane leads to the necessity to have a metal, stable in acid media, but sufficiently oxidizable to increase the concentration of adsorbed OH species, which participates directly in the electro-oxidation of CO [29]. Many metals were considered to modify platinum, but only a few of them lead to a definite enhancement of the electrocatalytic activity for alcohol oxidation. The favorite metal is ruthenium which was shown to increase greatly the rate of oxidation of many alcohols at a platinum surface, particularly that of methanol. Watanabe and Motoo [30] postulated a bifunctional mechanism to explain this synergistic effect: platinum dissociates methanol by chemisorption, whereas ruthenium activates water and provides preferential sites for OH adsorption at low potentials (around 0.2 V/RHE). These OH_{ads} species are necessary to oxidize completely to CO_2 the adsorption residue of alcohol chemisorption. They also prevent the accumulation of poisoning species, e.g. CO_{ads} , which are oxidized more rapidly at lower potentials. “In situ” IR reflectance spectroscopic experiments showed that with a Pt/Ru electrode the oxidation of adsorbed CO species does occur at potentials at least 200 mV below those observed with pure platinum [31].

A Pt/Ru (1/1) atomic ratio gives the best electrocatalyst for CO oxidation [32], whereas the optimum ratio for methanol oxidation is still a subject of controversy, although some experimental evidences are in favor of a low Ru content, e.g. about 20 at.% [31,33]. This can be explained by considering the number of Pt atoms necessary to activate the adsorption of methanol (three–five according to the different species present at the electrode surface) and the number of Ru atoms to activate water (one atom usually).

Among the other possible metals suitable to increase the activity of platinum, tin has often been considered [34,35]. The main advantage of using tin is the low potential at which tin is partially covered by OH species. The electro-oxidation of methanol, which needs adsorbed OH to be present in order to be transformed into carbon dioxide, is thus, possible at lower potentials. However, it seems that the conditions of preparation of Pt/Sn bimetallic electrodes are very particular, the difficulty being to maintain Sn in a metallic state.

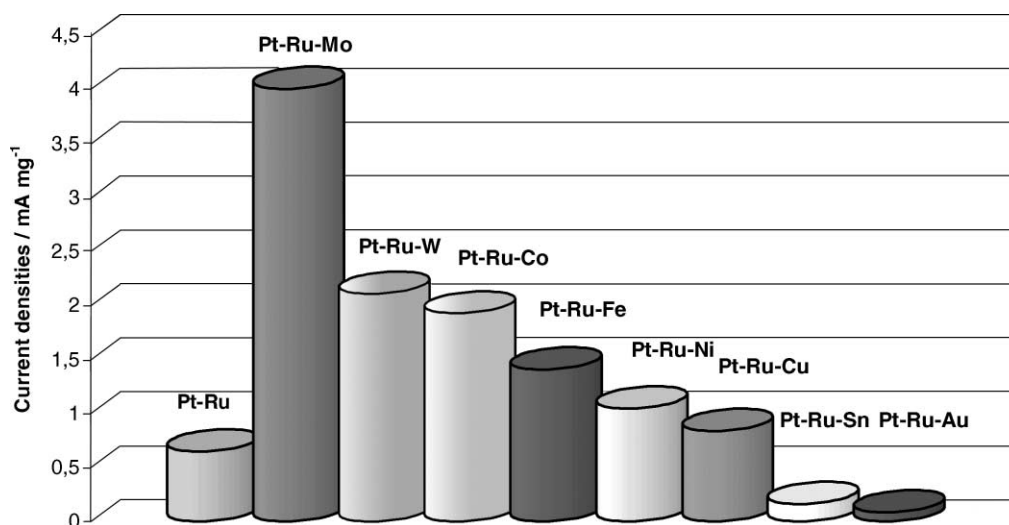


Fig. 6. Oxidation of 1.0 M methanol in 0.1 M perchloric acid at room temperature and at different platinum-based ternary electrocatalysts dispersed in a polyaniline film. Current taken after 30 min at 450 mV vs. RHE.

Recent new results with Pt/Sn dispersed into a conducting polymer have shown that this bimetallic catalyst leads to a negative shift of the electro-oxidation potential of methanol [34]. Moreover, these Pt/Sn electrodes greatly enhance the electro-oxidation of gaseous CO, to a larger extent than Pt/Ru alloys. Finally, trimetallic Pt/Ru/Sn catalysts have also been considered, and even if their preparation is more difficult, they give an electrocatalytic activity slightly improved in comparison to Pt/Ru catalysts [34].

Other trimetallic catalysts for the electrooxidation of methanol were recently screened in our Laboratory. Among the eight ternary catalysts investigated, the Pt/Ru/Mo system gives the best results (Fig. 6).

For the oxidation of other alcohols, the best electrocatalyst is not necessarily a Pt/Ru alloy. Other alloys, such as Pt/Ru/Sn and above all Pt/Sn are very efficient electrocatalysts for the oxidation of ethanol (Fig. 7). The oxidation currents are multiplied by 2 times and the overvoltage is decreased by ca. 0.3 V when using a Pt/Sn alloy dispersed in polyaniline [36].

For practical applications in a direct alcohol fuel cell, the catalytic material needs to be dispersed in a convenient substrate, both to stabilize the catalyst nanoparticles and to reduce the amount of precious metal used, thus, to reduce the anode cost. To achieve a very high dispersion of the electrocatalyst, high surface area electrically conducting substrates are chosen, particularly carbon-based materials, such as graphite, carbon blacks and activated carbons, with specific surface area up to 1000 m²/g. This allows the preparation of an active surface area of 200 m²/g of platinum corresponding to nanoparticles of 1.5 nm [37].

Other supports can be considered, particularly the proton exchange membrane (PEM) itself or electron conducting polymers. Platinum-based electrocatalysts are relatively easily deposited on a Nafion[®] membrane, first by chemical deposition of Pt, then by electrodeposition of the second

metal (Ru, Sn, Ir, Mo, etc.) [38]. This gives very active electrodes for the oxidation of methanol, with Pt/Ru catalysts [39], and of ethanol with Pt/Sn catalysts [40], leading to a significant decrease (of at least 200 mV) of the anode overpotential (Fig. 8).

On the other hand, an electron-conducting polymer, such as polyaniline (PAni), polypyrrole (PPy) or polythiophene (PTh), also allows dispersing electrocatalytic materials at the molecular level in such a way that the reactive molecules will easily reach the catalytic centers [41]. These polymers are easily formed by electropolymerization in aqueous

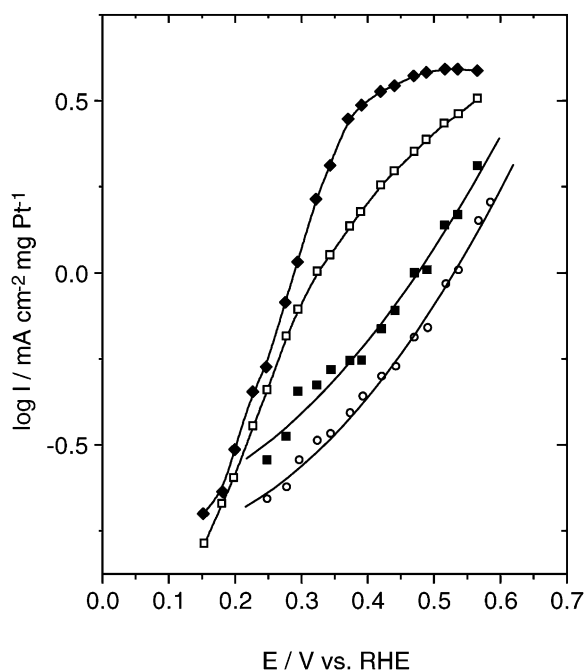


Fig. 7. Tafel-like plots showing the oxidation of 0.1 M ethanol in 0.1 M HClO₄ on pure Pt (600 μg/cm²) dispersed in PAni electrodes or modified by 60 μg/cm² Ru or Sn: (○) Pt; (■) Pt/Ru; (◆) Pt/Sn; (□) Pt/Ru/Sn.

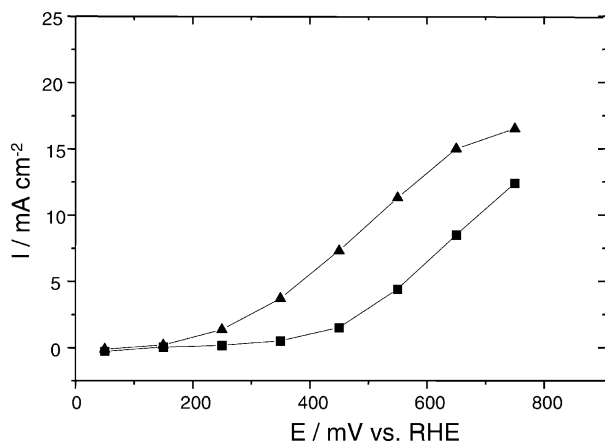


Fig. 8. Stationary I/E curves for the oxidation of ethanol on Pt/Nafion and Pt/Sn/Nafion electrodes. (■) Pt/Nafion; (▲) Pt/Sn/Nafion.

medium leading to a few μm thick films, stable under acidic conditions and electron conducting in a relatively large potential window (from 0.1 to 0.9 V/RHE for PANi). Very high dispersion levels were thus achieved, i.e. up to a few $\mu\text{g}/\text{cm}^2$ of platinum-based catalysts, which are particularly active for the oxidation of methanol [34] and of ethanol [36].

4.2. Electrocatalysts for oxygen reduction

One way to circumvent the effect of methanol leakage through the ionomeric membrane and to avoid the platinum cathode depolarization, which reduces the cell voltage by ca. 0.1–0.2 V, is to replace platinum catalysts by transition metal compounds, such as macrocycles or chalcogenides, which are inactive towards the oxidation of methanol.

This is effectively the case of cobalt and/or iron porphyrins and phthalocyanines. These macrocycles are well known as good oxygen reduction electrocatalysts [42]. However, these compounds are not completely stable under strong acidic and/or oxidizing environments, particularly at medium temperatures (60–100 °C) [43], so that their use in a practical system is still questionable. Usually such macrocycles are dispersed on an active carbon substrate, such as Vulcan XC 72, and pyrolyzed at 700–800 °C, before being used as an oxygen cathode. Such treatments improve the electrode activity and stability, but destroy the molecular structure of the macrocycle. Another strategy is to prepare highly dispersed macrocycle oxygen electrodes by intercalation into an electron conductive polymer (polyaniline PANi, or polypyrrole PPy) of a macrocyclic catalyst, either as a tetrasulphonated counter ion, incorporated in the film during the electropolymerization process [44], or linked by a chemical bond to an electropolymerizable monomer [45].

The results obtained with the first method are very interesting since a PPy or a PANi film containing iron tetrasulphonated phthalocyanine behaves similarly to a platinum electrode for oxygen reduction, but is quite inactive for methanol oxidation. However, the stability of these electrode materials is relatively limited, since the counter anions can be expelled from the matrix at low potentials.

The second method consists of the direct electropolymerization of a functionalized transition metal macrocycle, such as cobalt 4,4',4'',4'''-tetraaminophthalocyanine (CoTAPc) or cobalt tetra(*o*-aminophenyl)porphyrin (CoTAPP) to form the electrocatalysts. This leads to interesting results for the electroreduction of oxygen, as shown in Fig. 9, where the polarization curve for a bare platinum electrode is also given for the sake of comparison. Moreover, it was checked

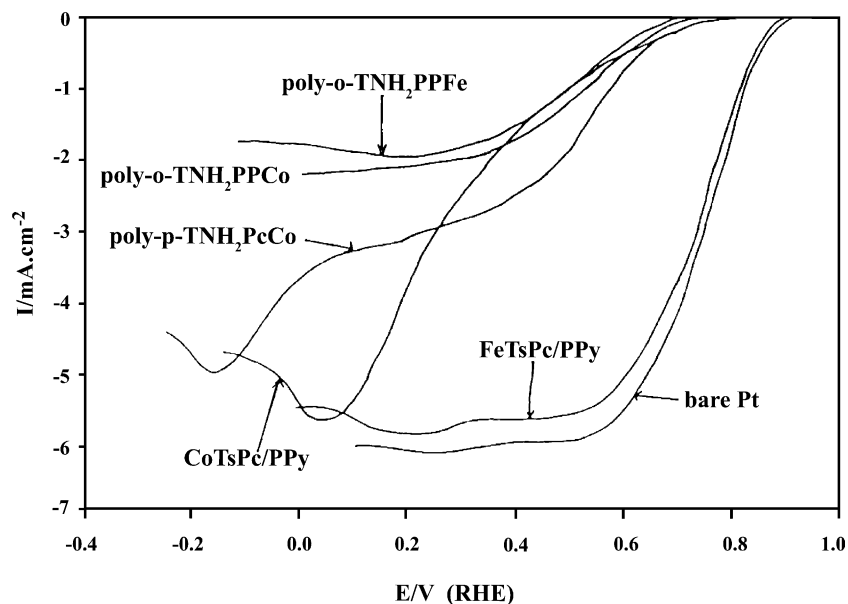


Fig. 9. Oxygen electroreduction at a vitreous carbon rotating-disc electrode covered with various electropolymerized modified macrocycle films (0.5 M H_2SO_4 saturated with oxygen, room temperature, rotating speed 2500 rpm). The polarization curve for a bare platinum electrode is given for the sake of comparison.

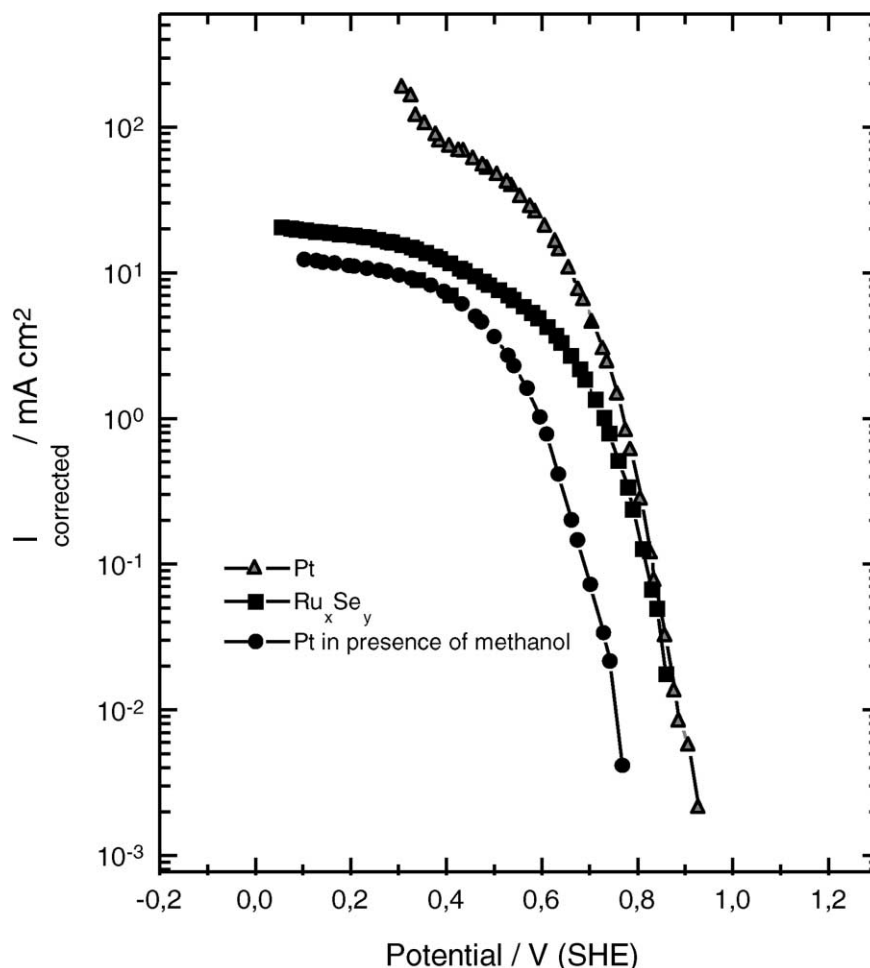


Fig. 10. Tafel plot of the electroreduction of oxygen in sulphuric acid on a platinum and a Ru_xSe_y electrodes in the presence or not of methanol: (Δ) Pt; (\blacksquare) Ru_xSe_y ; (\bullet) Pt in presence of methanol.

that, either poly(H_2TAPP), where the transition metal ion is replaced by hydrogen, or a vitreous carbon electrode, is quite inactive for the electroreduction of oxygen, showing that the catalytic sites are associated with the transition metal. A Koutecky–Levich plot of the inverse of the oxygen reduction current density versus the inverse of the rotating rate of a rotating disc electrode allowed us to determine the number of electrons involved in the electroreduction process. However, only the cobalt phthalocyanine polymer, poly-(CoTAPc), like Pt, leads to a four-electron process per oxygen molecule, i.e. to water, but at lower potentials (between 0.25 and -0.25 V versus RHE).

Other kinds of electrocatalysts could be used for oxygen electroreduction, such as transition metal chalcogenides [46], which seem to be more stable at higher temperature. The comparative behavior of Ru_xSe_y and Pt, using a rotating disk electrode, for the electroreduction of oxygen, is shown in Fig. 10. Even if the performances of the chalcogenide compound are slightly weaker than those of platinum electrocatalysts, the most important difference is the behavior of these electrodes in the presence and in the absence of methanol, which is added to the electrolytic solution to

simulate a crossover in the fuel cell. Under these conditions, the electroactivity of Ru_xSe_y is not changed in the presence of methanol, in contrast to the case of platinum for which a potential shift of 120 to 150 mV in the negative direction is clearly visible. A similar behavior was observed when the electrocatalyst material was embedded in a polymeric matrix, such as polyaniline [47]. These results prove that the chalcogenide of Ru is insensitive to the presence of methanol, in contrast to platinum.

Preliminary experiments using Ru_xSe_y catalysts deposited on a carbon powder (Vulcan XC72) were carried out in a DMFC single cell. They showed clearly that the ruthenium selenide catalyst is active enough for the electroreduction of oxygen and is a possible alternative to platinum as cathode in a DMFC (Fig. 11). The performances achieved are close to those obtained, with a Pt E-TEK cathode. The overall internal resistance of the cell with a Ru_xSe_y electrode seems to be higher than that with an E-TEK electrode, but it should be noted also that the preparation of fuel cell electrodes with Ru_xSe_y is not yet optimized. The amount of catalyst, the thickness of the active layer, the presence of Nafion[®], etc. are parameters which need to be carefully optimized and it

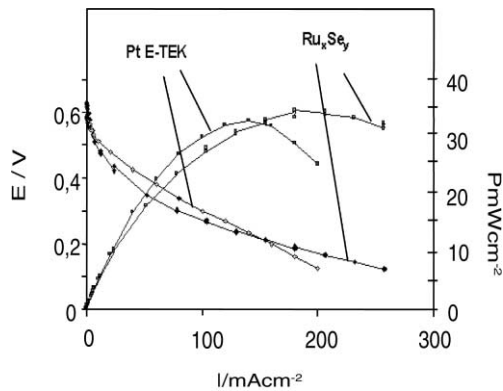


Fig. 11. Comparison of the behavior of a Ru_xSe_y (2 mg/cm^2) cathode and a Pt E-TEK (2 mg/cm^2) electrode in a DMFC. $T = 90^\circ\text{C}$.

is only after this step that the real behavior of this novel cathode catalyst will be known for replacing Pt in a DMFC cathode.

5. Realization of a direct alcohol fuel cell

5.1. Direct methanol fuel cell (DMFC)

Due to the large progresses made in the development of electrocatalysts and proton exchange membranes, different DMFC systems have been built by several research laboratories and industrial companies (IFC, JPL, LANL, etc. in the USA, and Siemens, University of Newcastle, University of Poitiers, ITAE Messina, etc. in Europe). Typically, the anode catalyst used consists of Pt/Ru particles deposited on a carbon powder (e.g. Vulcan XC72), and is hot pressed on the surface of a proton exchange membrane (e.g. Nafion[®]). Methanol can be fed, either as liquid or as gas, and different research groups tested these two feeding techniques of the cell.

Surampudi et al. [48], at Jet Propulsion Laboratory (JPL), investigated a DMFC working with liquid feed of methanol in pure water with concentrations varying from 0.5 to 4.0 M, at working temperatures in the range 60–90 °C. Catalysts for the anode side are Pt/Ru alloys dispersed on a carbon powder with loadings ranging from 0.5 to 5 mg/cm^2 . According to these authors, the liquid methanol feed offers an advantage, in comparison to the gas methanol feed, by eliminating complex water and thermal managements. But, the working temperature is limited under these conditions. However, the authors claimed interesting results (250 mA/cm^2 at 0.5 V), under the following conditions: 88 °C, 5 mg/cm^2 of catalyst, and 2.0 M methanol concentration. The problem of methanol crossover through the membrane remains nevertheless a critical point, which prevents the use of higher temperatures or higher methanol concentrations.

Gottesfeld et al. at Los Alamos National Laboratory (LANL) constructed and tested several liquid feed DMFCs working under different conditions. Several protonic membranes were used, including Nafion[®] 117, 115 and 112 (of

175, 125 and 50 μm thickness, respectively). The best performances were obtained at high temperatures (130 °C), i.e. 670 mA/cm^2 at 0.5 V with Nafion[®] 112 and 2.2 mg/cm^2 of Pt/Ru (1/1 atomic ratio), with 5 atm of oxygen [7]. Methanol was fed from a 1 M aqueous solution with a flow of $2 \text{ cm}^3/\text{min}$ under a pressure of 1.8 atm. A peak power of 400 mW/cm^2 was claimed by this group with pure oxygen under 5 atm and 250 mW/cm^2 with air under 3 atm.

DMFCs operating under less severe conditions of temperature (60–100 °C) and pressure (close to atmospheric air pressure) were recently demonstrated, particularly for portable power sources. At 90 °C with 20 psig air pressure the performance attained by JPL was 0.44 V at 300 mA/cm^2 [49]. At a lower temperature (60 °C) and 1 atm air pressure, using electrodes of 25 cm^2 active surface area and containing 4 mg/cm^2 of platinum-based catalysts, they obtained a voltage of 0.4 V at 150 mA/cm^2 . At LANL a 50 cm^2 , 2 mm thick DMFC single cell containing an overall Pt loading of 2.6 mg/cm^2 , and operating at 60 °C with ambient air pressure, also gave good performances (0.4 V at 200 mA/cm^2). The cell can operate for >2000 h at 100 °C with >90% of fuel utilization and a power density of 150 mW/cm^2 without loss of performance [50] (Fig. 12).

More recent developments at Siemens led to the construction of small DMFC stacks (300 W) and larger stacks

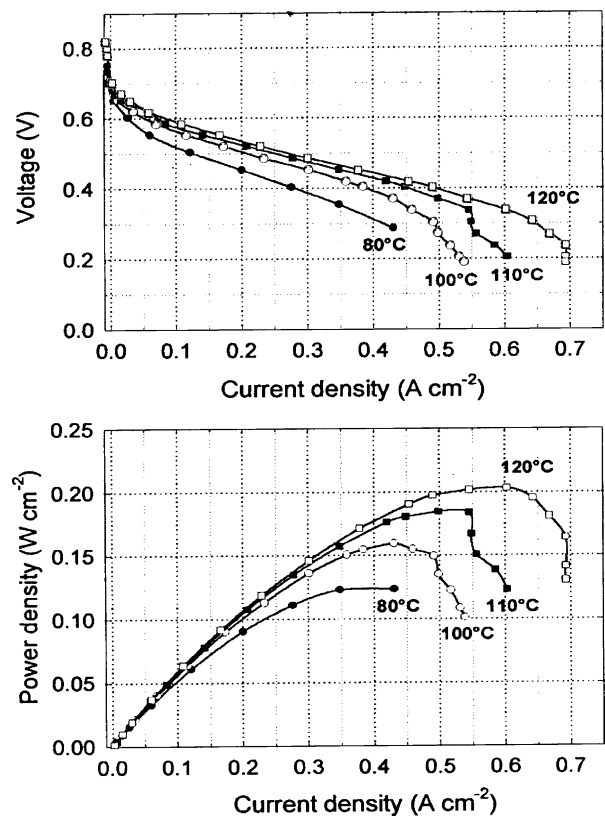


Fig. 12. Voltage and power density as a function of current density for a DMFC single cell. Overall Pt loading of 2.6 mg/cm^2 , anode feed of 1 M methanol, cathode feed of 30 psig air (after [50]).

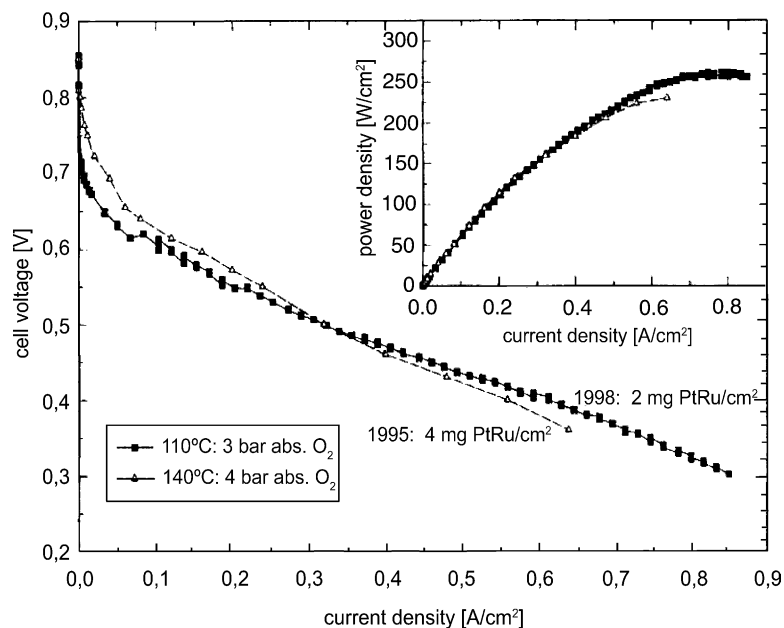


Fig. 13. Cell voltage and power density vs. current density plots for a single cell of a small DMFC stack at Siemens (after [8]).

(1 kW) with improved characteristics: 250 mW/cm^2 at 0.6 A/cm^2 , 110°C , 3 bar (absolute) oxygen and $2 \text{ mg Pt/Ru per cm}^2$ (Fig. 13). This was mainly due to the development of new more active Pt/Ru electrocatalysts and the optimization of the electrode structure. Further improvements allowed running the DMFC at lower temperatures and lower pressures with air, and lower catalyst loadings ($1 \text{ mg Pt/Ru per cm}^2$). Under these conditions a small 3-cell stack delivered 77 W at 1.4 V , at 80°C and 1.5 bar (absolute) air pressure [8].

In order to improve the performance of the anodic oxidation of methanol, a possibility is to feed the cell with gaseous methanol instead of liquid methanol. The immediate advantage of this technique is the possibility to increase the working temperature much above the boiling point of methanol (65°C), without pressurization. It is then possible to develop a system similar to that used in an H_2/O_2 PEMFC, with an electrode membrane assembly separating two gaseous compartments. However, under these experimental conditions, limitations due to the membranes appears clearly, related to the water management, which is much more critical at temperatures higher than 100°C . The water concentration inside the membrane needs to be maintained constant, and this can be achieved by adding water vapor to the methanol vapor, which in addition is necessary to oxidize the methanol chemisorption oxygenated residue to carbon dioxide.

Different gaseous DMFCs were tested during the last few years and this demonstrated that such a concept is valid even if numerous improvements are necessary in order to reach performances convenient for powering an electric car [51]. Shukla et al. [52] proposed a gas-feed DMFC constructed with a Nafion[®] 117 membrane and Pt/Ru impregnated

carbon catalysts for methanol oxidation. Under 1 atm pressure at 98°C , with 5 mg/cm^2 of platinum, the open circuit potential is typically around 0.9 V , and a cell voltage of 0.55 V at 75 mA/cm^2 is obtained with a gaseous composition of 1% in methanol, and a fuel utilization coefficient of 0.56. But, even if they do not reach higher levels of performance, these authors concluded that a power of 0.2 W/cm^2 is attainable, with improved electrocatalysts.

5.2. Other direct alcohol fuel cells (DAFC)

Except methanol, the direct oxidation of which is now widely studied in a PEMFC, and which is considered as a possible fuel for the electric vehicle, very few other alcohols have been investigated. Due to the great progress made in the hydrogen/air PEMFC, only proton exchange membranes fed with the alcohol/water mixture are now under investigations, because they allow to be rejected the carbon dioxide produced.

Ethanol seems to be the most convenient and the more reactive alcohol after methanol. Half cell studies and single cell studies using a Nafion[®] 117 membrane directly covered with the anode catalytic material have been carried out in our Laboratory [53]. Different binary electrocatalysts were investigated, among them Pt/Ru and Pt/Sn were the more active and the less poisoned ones (Fig. 14).

The optimization of the composition (80/20 at.% Pt/Sn) and of the structure of a Pt/Sn catalyst leads to a very active ethanol anode, much better than a Pt/Ru electrode, and above all better than a pure Pt electrode [53]. Using a Nafion[®] 117 membrane, current densities of 60 mA/cm^2 are obtained at 90°C for a cell voltage of 550 mV , i.e. a power density of 33 mW/cm^2 (Fig. 15).

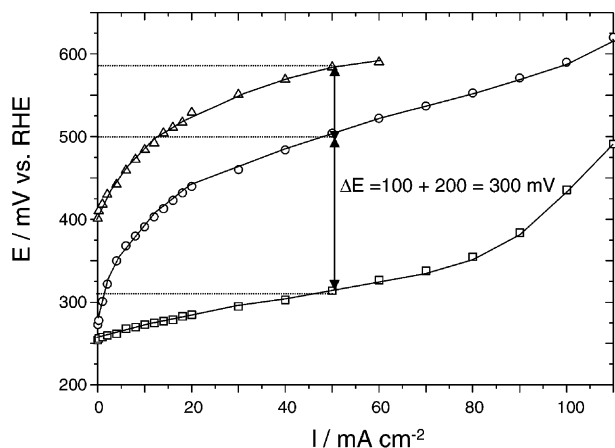


Fig. 14. Comparison of the anode characteristics for the oxidation of ethanol on Pt/X/Nafion electrodes (liquid ethanol/water mixture feed, cell temperature 90 °C, anode catalysts 1 mg/cm², oxygen catalyst 1 mg Pt/cm²): (△) Pt; (○) Pt/Ru; (□) Pt/Sn.

However, the reactivity of ethanol is rather low at the working temperature (120 °C) of a PEMFC based on a Nafion[®] membrane, so that recent attempts were made with high-temperature-resistant membranes. Arico et al. [11] prepared a 80 μm thick composite membrane by mixing and heat treating an appropriate amount of Nafion ionomer (5% w/w, Aldrich) with 3% w/w silica (Aerosil 200, Degussa). They used (1/1) Pt/Ru/C as anode catalyst and Pt/C as cathode catalyst with a Pt loading of 2 mg/cm² in each electrode. A 1 M ethanol solution under 4.0 bar (absolute) was fed to the anodic compartment and pure O₂ under 5.5 bar to the cathodic compartment. At a working temperature of 145 °C the electrochemical characteristics of the single fuel cell were interesting: a maximum power density

of 110 mW/cm² is obtained at 0.32 V and 350 mA/cm², without correcting for the ohmic drop (specific resistance $R_e = 0.18 \Omega \text{ cm}^2$), whereas at 0.5 V the current density reaches 180 mA/cm² (Fig. 16). Chromatographic analysis of the anode outlet during stationary measurements (300 mA/cm² at 0.35 V) seems to indicate that CO₂ is the main oxidation product (with a yield >90%), together with some small amounts of acetaldehyde (4%) and unreacted ethanol.

Using a phosphoric acid doped polybenzimidazole (PBI) membrane, Wang et al. were able to work at higher temperatures [12]. They compared the behavior in a PEMFC of 4 aliphatic alcohols: methanol, ethanol, 1-propanol and 2-propanol (Fig. 17). The PEMFC was operated on pure oxygen at 170 °C with 4 mg/cm² Pt/Ru at the anode and 4 mg/cm² Pt at the cathode. At a current density of 250 mA/cm² the cell voltages are 0.35, 0.30, 0.17 and 0.050 V for methanol, ethanol, 1-propanol and 2-propanol, respectively. The behavior of ethanol is close to that of methanol, so that it could advantageously substitute for methanol as a fuel in a PEMFC, whereas even with a Pt/Ru anode catalyst the propanols are not so electroreactive, particularly 2-propanol. Analysis of the reaction products by on-line mass spectrometry showed, at variance with the work of Arico et al. [11], that acetaldehyde is the main reaction product of ethanol electro-oxidation, while CO₂ is a minor product. This depends on the water/ethanol mole ratio, since the CO₂ amount increases from 20 to 32% when this ratio increases from 2 to 5. With 1-propanol and 2-propanol the electro-oxidation reaction yields mainly propanal and acetone, respectively, meaning that the primary or secondary alcoholic group proceeds only through the dehydrogenation step, see Eq. (8) for ethanol oxidation.

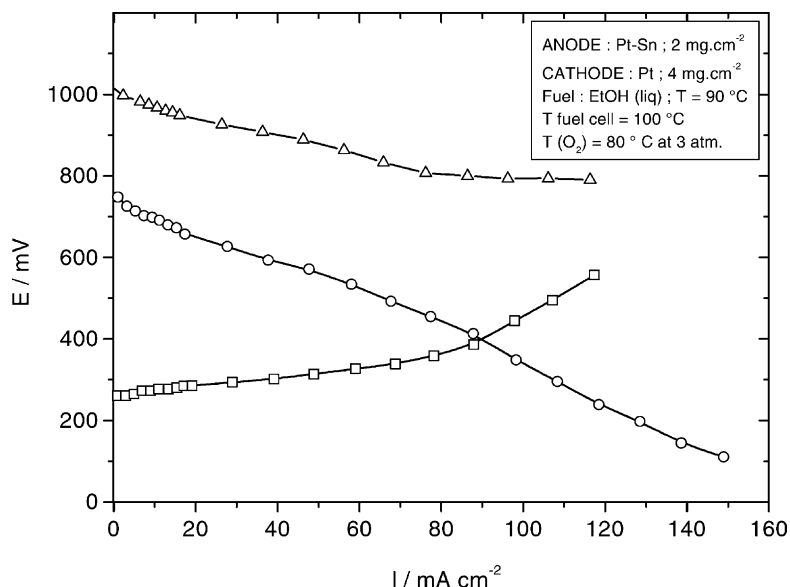


Fig. 15. Anodic (□) and cathodic (△) polarization curves, and I/E cell voltage curve (○) of the ethanol-oxygen fuel cell with a Pt/Sn/C anode.

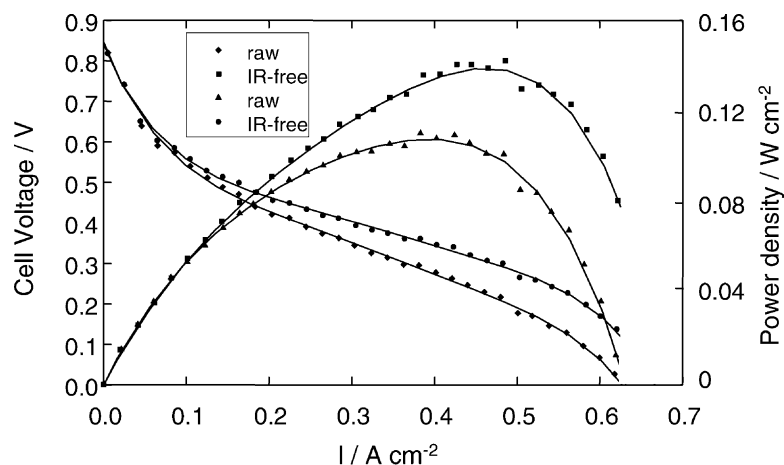


Fig. 16. Polarization curves and power density of a direct ethanol fuel cell with a silica/Nafion membrane (1 M ethanol; cell temperature, 145 °C; p_{anode} , 4 bar; p_{cathode} , 5.5 bar; anode catalyst, 2 mg/cm² (1/1) Pt/Ru/C cathode catalyst, 2 mg cm⁻² Pt).

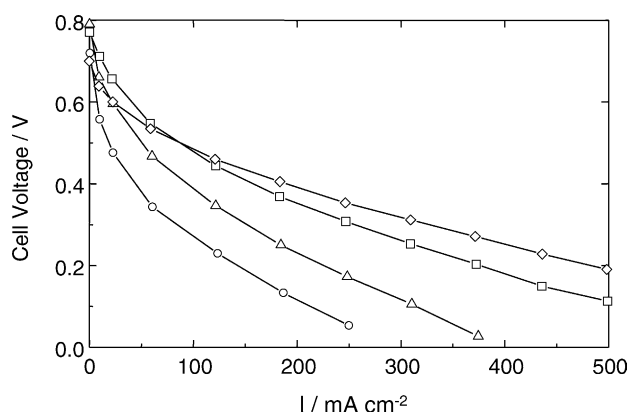


Fig. 17. Comparison of the cell performances of a direct alcohol fuel cell using a PBI membrane doped with H₃PO₄ (cell temperature, 170 °C; Pt/Ru anode catalyst, 4 mg/cm²; Pt black cathode catalyst, 4 mg/cm²): methanol (◇); ethanol (□); 1-propanol (△); 2-propanol (○).

6. Conclusions

The current density vs. cell potential characteristics of a PEMFC fed with methanol or ethanol are rather similar at high temperatures (170 °C), so that ethanol appears as an alternative fuel to methanol. Moreover, ethanol is much less toxic than methanol, and its mass production from agriculture may decrease its price, so that it may compete economically with methanol. However, the electro-oxidation reaction stops at intermediates steps (production mainly of acetaldehyde and acetic acid), together with a small amount of carbon dioxide, depending on the experimental conditions. Pt/Sn is actually one of the best electrocatalysts, although the right atomic composition is not yet definitely established. Investigation of other binary or ternary Pt-based electrocatalysts is necessary to increase the reaction rate and to activate the breaking of the C–C bond at lower temperatures in order to increase the reaction selectivity towards the formation of CO₂, and thus the Faradaic efficiency.

This is particularly true for the oxidation of the propanols and of higher alcohols, the rate of which is still too low even at high temperature (170 °C) to compete with methanol and ethanol.

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