



Electrocatalytic oxidation of aliphatic alcohols: Application to the direct alcohol fuel cell (DAFC)[†]

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Abstract

The electrooxidation of some low molecular weight alcohols, such as ethanol, ethylene glycol and *n*-propanol, is discussed in terms of reaction mechanisms and catalytic activity of the anode material. Some examples of a single cell, using a proton exchange membrane (PEM) as electrolyte, are given to illustrate interesting results, particularly for the direct electrooxidation of ethanol. This alcohol may replace methanol in a direct alcohol fuel cell.

1. Introduction

Recently there has been an increasing interest in the development of direct alcohol/air proton exchange membrane fuel cells (PEMFC), particularly those fuelled by methanol to power electric vehicles [1]. Liquid fuels, such as low-molecular weight alcohols, have advantages, compared to pure hydrogen, because they can be easily handled, stored and transported using the present gasoline infrastructure with only slight modifications. Furthermore, their energy densities are comparable to that of gasoline, varying from 6 kWh kg⁻¹ (5 kWh l⁻¹) for methanol to about 10 kWh kg⁻¹ (8 kWh l⁻¹) for heavy alcohols.

The direct oxidation of methanol in a direct methanol fuel cell (DMFC) has been investigated over many years and some prototypes were built in the 1960s by the Shell Research Centre in England [2] and by Hitachi Research Laboratories in Japan [3]. However, these studies were abandoned in the mid-1980s due to low performances (25 mW cm⁻² at best) resulting from the conception of the fuel cell (acid liquid electrolytes). The recent development of PEMFCs gave a new impetus to further investigate DMFCs using a proton exchange membrane (PEM) as solid electrolyte. Many national research programs (in the USA, Japan and Europe) now exist, and the large car companies, such as Daimler–Chrysler, General Motors, Toyota and Nissan, are involved in the development of fuel cells for electric vehicle application using methanol as fuel. Methanol can be converted directly into electricity in

a DMFC or transformed (by steam reforming, partial oxidation or autothermal reforming) into a hydrogen-rich gas to feed an indirect methanol fuel cell (IMFC).

However, methanol has some disadvantages, for example, it is relatively toxic, has a low boiling point (65 °C) and it is not a primary fuel. Therefore other alcohols, particularly those coming from biomass resources, are being considered as alternative fuels. Ethanol is an attractive fuel for electric vehicles, since it can be easily produced in great quantity by fermentation of sugar-containing raw materials. In addition, in some countries (e.g., Brazil) ethanol is already distributed in gas stations for use in conventional cars with internal combustion engines. Other alcohols have also been considered for fuel cells, for example ethylene-glycol [4] or glycerol [5]; some of these have led to prototypes of a few 100 W.

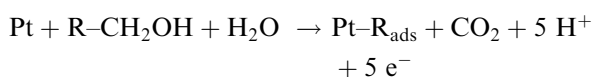
In the first part of this paper, we discuss the complexity of the reaction mechanism of the oxidation of alcohols, which involves several steps, and a number of intermediates and byproducts. Using *in situ* spectroscopic techniques, particularly in the infrared range, and online analytical techniques, such as liquid chromatography (HPLC), some of the reaction mechanisms were elucidated, at least for the oxidation of the lowest alcohols, methanol, ethanol and ethylene-glycol. It appears that the catalytic properties of the electrode material is key to controlling the formation of adsorbed intermediates and thus avoiding the formation of poisoning species, which are recognized to be deleterious for the fuel cell operation. Multimetallic catalysts are necessary to orientate the oxidation reaction selectively in the direction of complete combustion to carbon dioxide.

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In the second part of the paper, we present some recent investigations on direct alcohol fuel cells (single PEMFC) using low molecular weight alcohols, such as ethanol, 1-propanol and 2-propanol.

2. Electrocatalytic oxidation of alcohols

To recover the maximum energy of an alcohol molecule, the oxidation reaction must be complete, that is, it must lead to CO₂. Since the alcoholic group only contains one oxygen atom, the extra oxygen atom must be provided by water, or water adsorbed residues (e.g., adsorbed OH) produced at the cathodic compartment by oxygen reduction. Thus, the general overall reaction of the electrooxidation of a primary alcohol on platinum can be written as follows:

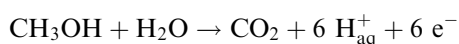


where the adsorbed intermediate species R_{ads} can be further oxidized to CO₂. It turns out that the reaction mechanisms of alcohol oxidation always involve the participation of water, or of its adsorption residue, so that a good catalyst must activate both the alcohol chemisorption and the water molecule. Moreover, the reaction mechanisms are complex involving several adsorbed intermediates and the formation of numerous products and byproducts.

The elucidation of the reaction mechanism thus requires a combination of pure electrochemical methods, such as cyclic voltammetry and rotating disc electrodes, with other physicochemical methods, such as *in situ* spectroscopic methods (infrared [6] and u.v.-visible [7] reflectance spectroscopy) to monitor the adsorbed intermediates and online analytical techniques (chromatographic analysis [8] and mass spectrometry [9]) to analyse quantitatively the reaction products and byproducts.

2.1. Investigation of the reaction mechanisms

The oxidation of methanol has been thoroughly studied over many years [10], so that the reaction mechanism is now well established [11]. The overall oxidation reaction involves six electrons and one water molecule, as follows:



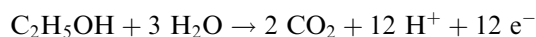
It was first shown by electrochemically modulated infrared reflectance spectroscopy (EMIRS) that the main poisoning species formed during the chemisorption and oxidation of methanol on a platinum electrode is carbon monoxide CO, either linearly bonded, or bridge bonded to the surface [12]. The coverage by

linearly bonded CO can reach 90% on a pure platinum electrode, so that most of the active sites are blocked. In addition, some reactive adsorbed species, such as (•CHO)_{ads} or (•COOH)_{ads}, were identified by infrared reflectance spectroscopy (EMIRS or Fourier transform infrared reflectance spectroscopy) [13].

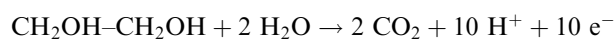
Intermediate reaction products (such as formaldehyde HCHO and formic acid HCOOH) and final product (CO₂) were also analysed quantitatively by liquid or gas chromatography [14]. The reaction mechanism, even for the oxidation of the lightest alcohols involving the smallest number of electrons ($n = 6$ for methanol oxidation), is therefore relatively complex [11]. In this mechanism the adsorbed formyl-like species (•CHO)_{ads} plays a key role and the strategy to develop efficient electrocatalysts will be to favour this reactive adsorbed species, and decrease the amount of poisoning species (CO), either by preventing its formation by blocking neighboring Pt sites, or by oxidizing it at lower potentials. This can be achieved by alloying platinum with some other metal catalysts or promoters, such as ruthenium (see Section 2.2).

The reaction mechanisms of the anodic oxidation of other alcohols are more difficult to elucidate as the number of electrons exchanged greatly increases. The adsorption and oxidation of C₂ alcohols (i.e., ethanol and ethylene glycol) have been thoroughly investigated for two decades.

The complete oxidation of ethanol involves 12 electrons per molecule. That is,



whereas that of ethylene glycol involves 10 electrons:



Thus, many adsorbed intermediates and products are involved.

The electrocatalytic oxidation of ethanol has been investigated on different platinum-based electrodes, including Pt-X alloys (with X = Ru, Sn, Mo, ...), and dispersed particles. Pure platinum electrodes are rapidly poisoned by a strongly adsorbed intermediate (e.g., carbon monoxide) resulting from the dissociative chemisorption of the molecule, as shown by infrared reflectance spectroscopy [15–17]. Other adsorbed species were also identified by infrared spectroscopy, including reaction intermediates, such as acetaldehyde and acetic acid, and other byproducts (Figure 1) [16–18].

Detailed analysis of the reaction products by chromatographic techniques (HPLC, GC) [17] or by DEMS [16, 19, 20] allowed a more detailed reaction mechanism of ethanol oxidation on Pt electrodes in acid medium to be formulated, which involves parallel and consecutive oxidation reactions, as follows:

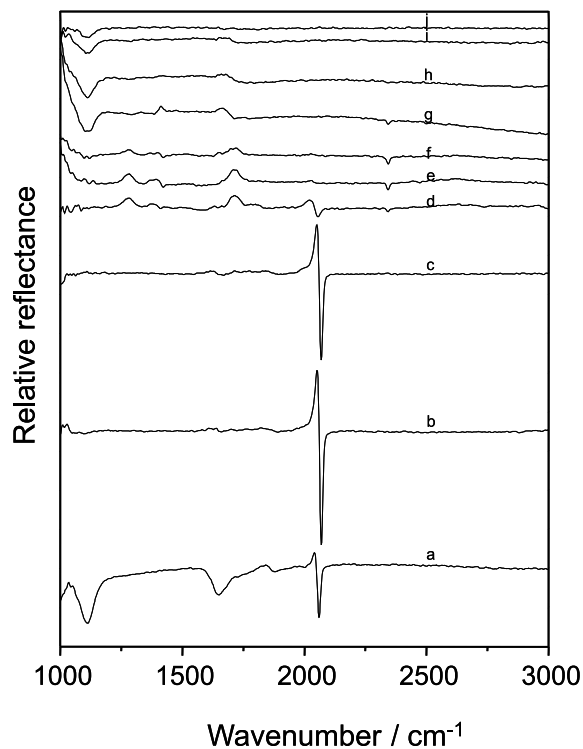
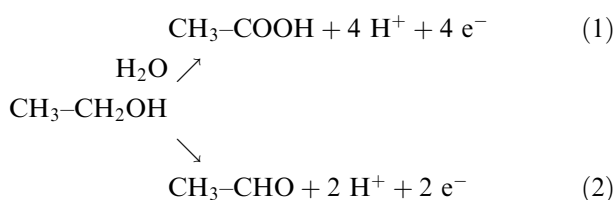
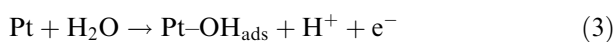


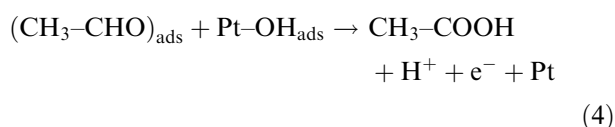
Fig. 1. SNIPTIR Spectra of the species involved in the adsorption and oxidation of ethanol on platinum, as a function of the mean electrode potential (from 0.15 V vs RHE (curve a) to 1.35 V vs RHE (curve j) in steps of 0.1 V). 0.1 M ethanol in 0.5 M H₂SO₄; $\Delta E = 0.3$ V, 'p' polarization.



Reaction 1 occurs mainly at higher electrode potentials ($E > 0.8$ V vs RHE), where the water molecule is activated to form oxygenated species at the platinum surface; Reaction 2 occurs mainly at lower potentials ($E < 0.6$ V vs RHE) [17]. At intermediate potentials (0.6 V vs RHE $\leq E \leq 0.8$ V vs RHE), the dissociative adsorption of water occurs:

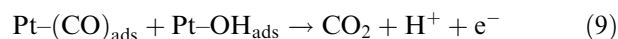
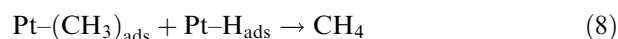
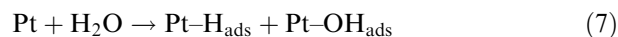
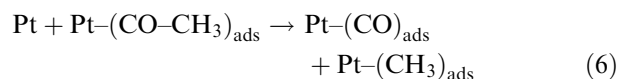
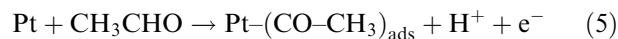


so that the oxidation of adsorbed CH₃-CHO may produce acetic acid, as follows:



Further oxidation to carbon dioxide is usually difficult on pure Pt electrodes at room temperature. However, carbon monoxide acting as a poisoning species, and

CO₂, were clearly observed by infrared reflectance spectroscopy [15] or by DEMS [16], and by gas chromatography [17], respectively, together with some traces of methane at low potential ($E < 0.4$ V vs RHE) [16]. This may be explained by the following mechanisms:



The presence of both poisoning species and intermediate reaction products (which decreases 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 CO at lower potentials, that is, to reduce the oxidation overpotential. As an example, Pt-Sn alloys, either dispersed in a conducting polymer matrix, such as polyaniline [21], or directly deposited on the proton exchange membrane [22], lead to a significant decrease (of at least 200 mV) of the anodic overpotential (Figure 2). Other bimetallic platinum based alloys, such as Pt-Ru, display an enhanced activity for ethanol electrooxidation [19–21], particularly those with the optimum Pt_{0.85}Ru_{0.15} surface atomic composition [19].

Other electrocatalysts have been considered for the electrooxidation of ethanol, for example, rhodium, iridium [23] or gold [24], 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 similar amounts, at relatively low potentials, which transform rapidly to carbon dioxide when the rhodium surface begins to oxidize, at ~ 0.5 – 0.7 V vs RHE [23].

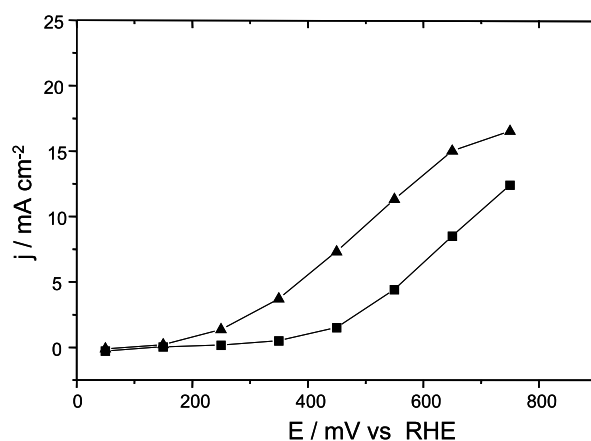
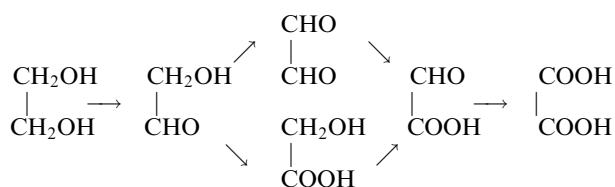


Fig. 2. Stationary j/E curves for the oxidation of ethanol on Pt-Nafion® (■) and Pt-Sn-Nafion® (▲) electrodes.

On gold in acid medium the oxidation reaction is much slower than on Pt, but is highly selective (97%) in the formation of acetaldehyde; in alkaline medium the main reaction product is acetate, with no formation of CO or CO₂ [24].

The electrocatalytic oxidation of ethylene glycol was also thoroughly investigated. This alcohol was considered as an interesting fuel, particularly in alkaline medium, where its electroreactivity at a platinum electrode is very high [25]. Since the overall oxidation reaction involves 10 electrons, the reaction mechanism is relatively complex involving several adsorbed species and intermediate products. Detailed analysis of the reaction mechanism on a Pt electrode by HPLC and FTIRS showed the formation of all C₂ intermediates, such as glycolaldehyde, glyoxal, glycolic acid, glyoxylic acid and oxalic acid. The following reaction mechanism has been postulated [26]:



In addition, some carbon dioxide was detected, presumably coming from the breaking of the C–C bond of

any of the C₂ intermediates. Modification of the platinum surface by lead adatoms allowed the transformation of ethylene glycol to glycolaldehyde with high selectivity (90%) at low electrode potentials (0.6 V vs RHE) [8].

The observation of adsorbed species was also made possible by infrared reflectance spectroscopy (EMIRS and FTIRS). On a platinum electrode, the formation of adsorbed CO and of CO₂ was clearly demonstrated, showing the cleavage of the C–C bond [27]. But at which stage this occurs is still not clear, since the intermediate products (glycol aldehyde and glyoxal) also dissociate on a platinum surface leading to adsorbed CO [28]. Furthermore, in the case of the chemisorption of ethylene glycol the distribution of adsorbed CO, linearly or bridge bonded to the surface, depends on the solution pH; an alkaline medium favors the two kinds of adsorbed species to a similar extent [27].

The molecular structure of the electroreactive species has a great influence on its electroreactivity, particularly on a platinum electrode, as shown by cyclic voltammetry. For example, the current density at the first oxidation peak A (at ~0.8–0.9 V vs RHE), decreases for primary alcohols, from methanol to *n*-butanol, that is, when the number of carbon atoms increases, whereas a second oxidation peak B increases progressively at around 1.3 V vs RHE (Figure 3).

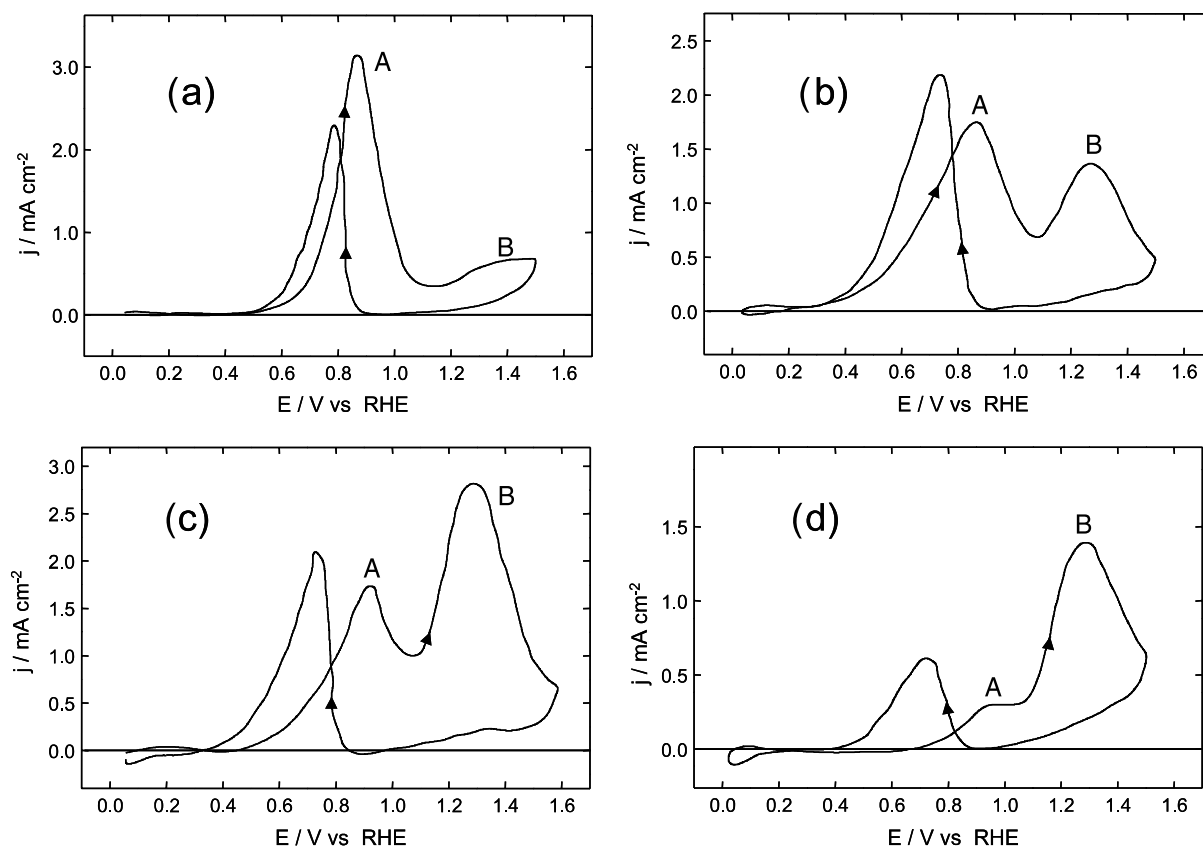
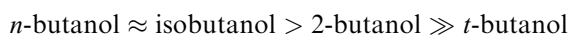


Fig. 3. Voltammograms showing the oxidation of different primary alcohols (0.1 M) in 0.1 M HClO₄ on a platinum electrode (temperature 25 °C, sweep rate 50 mV s⁻¹): (a) methanol, (b) ethanol, (c) *n*-propanol and (d) *n*-butanol.

For the same number of carbon atoms (e.g., for the butanol isomers) the oxidation rate depends greatly on the structure of the alcohol functional group. The current density decreases as follows:



The tertiary butanol is nearly unreactive. This was confirmed by infrared reflectance spectroscopy (EMIRS), which showed that the primary alcohols easily dissociate upon chemisorption leading to adsorbed CO, whereas the tertiary butanol produces no carbon monoxide [29].

To summarize, most alcohols dissociate at platinum electrodes producing different chemisorbed species, among them adsorbed CO, which is always observed at around 2000 cm^{-1} . However, the amount of CO_{ads} decreases when the number of carbon atoms increases [11].

2.2. Catalytic role of the electrode material

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

The chemical nature of the electrode and the pH of the electrolytic solution are the main factors affecting

the electrocatalytic activity. This is illustrated by the electrooxidation of *n*-butanol in alkaline medium on the different noble metals, Pt, Au, Rh and Pd (Figure 4). Gold has the highest electrocatalytic activity in terms of current density, but also has high overpotential (0.7–1.4 V); Pt displays the lowest overvoltage (0.35–1.0 V). Palladium and rhodium are quite inactive under these experimental conditions.

From a practical point of view only platinum is the best electrocatalyst for alcohol fuel cells, particularly in acid medium, where it is the only active and stable noble metal.

Geometric and electronic structures also greatly affect the electrocatalytic activity. This is illustrated by the oxidation of ethanol at different platinum single crystals $\text{Pt}(hkl)$ with low indices (Figure 5). The current densities and the positions of the voltammetric peaks depend greatly on the crystal face [30]. $\text{Pt}(100)$ displays a sharp peak with the highest current (about 6 mA cm^{-2} for 0.1 M ethanol during the first sweep), but also has the highest overvoltage (peak at 0.72 V). During successive sweeps the activity decreased strongly due to the formation of a poisoning species which was identified as linearly bonded CO by infrared reflectance spectroscopy. For the $\text{Pt}(110)$ plane the behavior is relatively similar with the broadest peak, lower current densities (about 4 mA cm^{-2} for the first sweep), and rapid

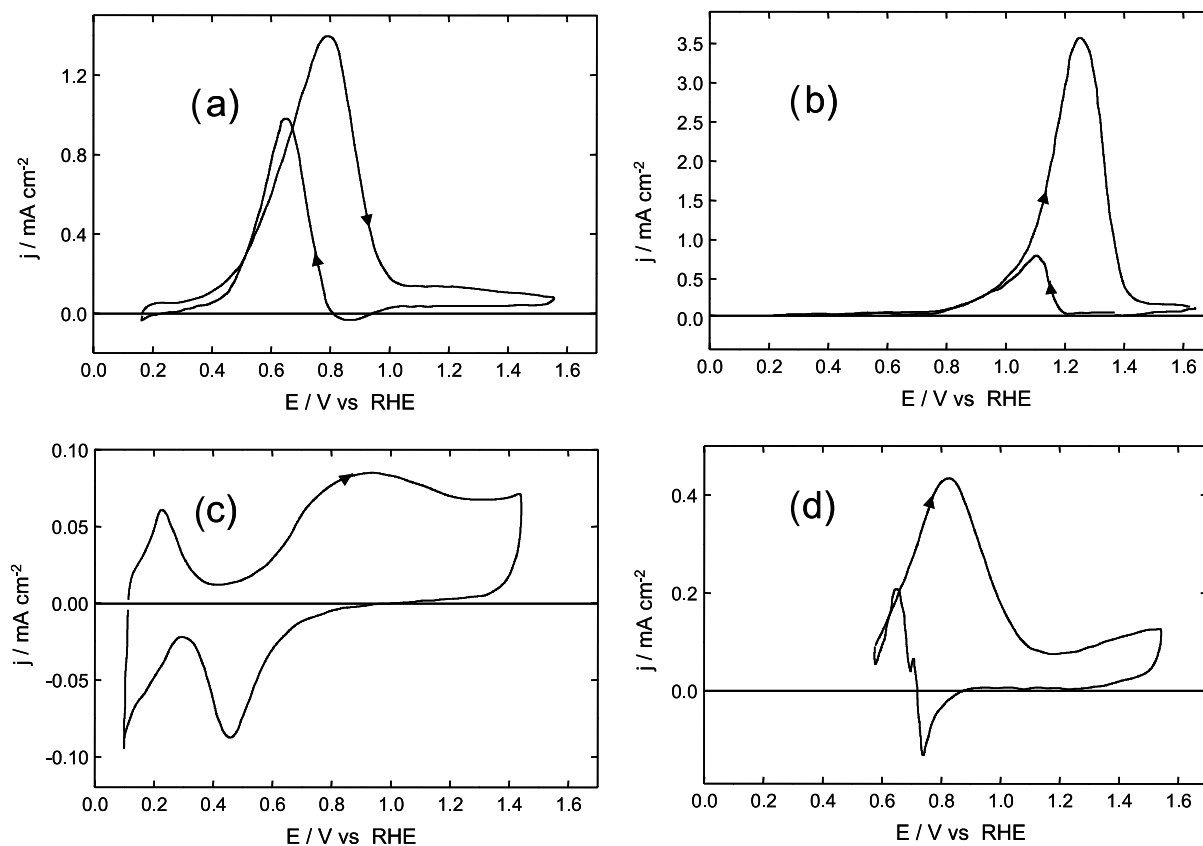


Fig. 4. Voltammograms showing the oxidation of 0.1 M *n*-butanol in 0.1 M NaOH on different noble metal electrodes (temperature $25\text{ }^{\circ}\text{C}$, sweep rate 50 mV s^{-1}): (a) platinum, (b) gold, (c) rhodium and (d) palladium.

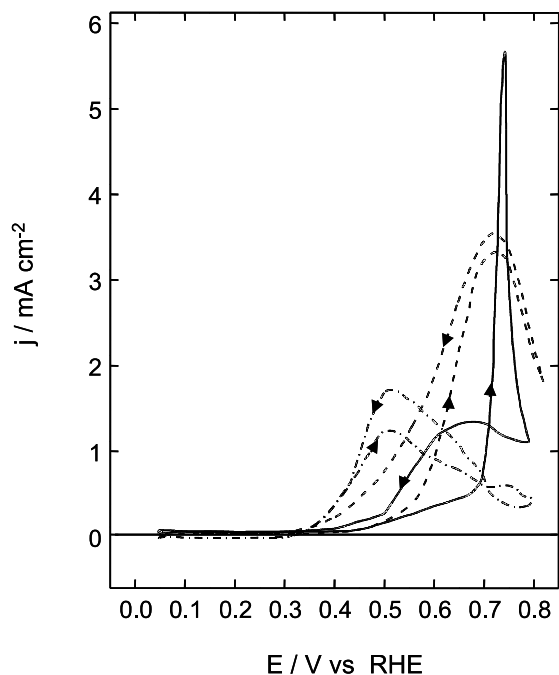


Fig. 5. Voltammograms showing the oxidation of 0.1 M ethanol in 0.1 M HClO₄ on platinum single crystals Pt(*h k l*) (temperature 25 °C, sweep rate 50 mV s⁻¹, first sweep): (—) Pt(1 0 0); (-----) Pt(1 1 0); (- · - · -) Pt(1 1 1).

poisoning of the surface during successive sweeps. The Pt(1 1 1) plane exhibits the smallest current densities (1.5 mA cm⁻²) but at lower overpotentials (peak at 0.51 V vs RHE), and the forward and backward sweeps are nearly superimposed, thus showing the weakest poisoning effect. It is also interesting to compare the behavior of the polycrystalline platinum surface with that of the single crystal faces. The main contribution comes from the Pt(1 1 0) face with some contribution from the Pt(1 0 0) and Pt(1 1 1) faces. Similar results have been obtained with the oxidation of methanol in acid medium on low index Pt single crystal faces [31].

A convenient way to modify the electrocatalytic properties of platinum, and to overcome poisoning by adsorbed CO, is to make alloys with a second, or even a third metal. Many metals were considered for modifying platinum, but only a few have resulted a definite enhancement of the activity for alcohol oxidation. The favourite 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 et al. [32] 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. These OH_{ads} species are necessary to oxidize completely to CO₂ the residue of alcohol chemisorption. They also prevent the accumulation of poisoning species (e.g., CO_{ads}) which are oxidized more rapidly at lower potentials. A Pt/Ru (1/1) atomic ratio gives the best electrocatalytic activity for CO oxidation [33, 34], whereas the optimum ratio for

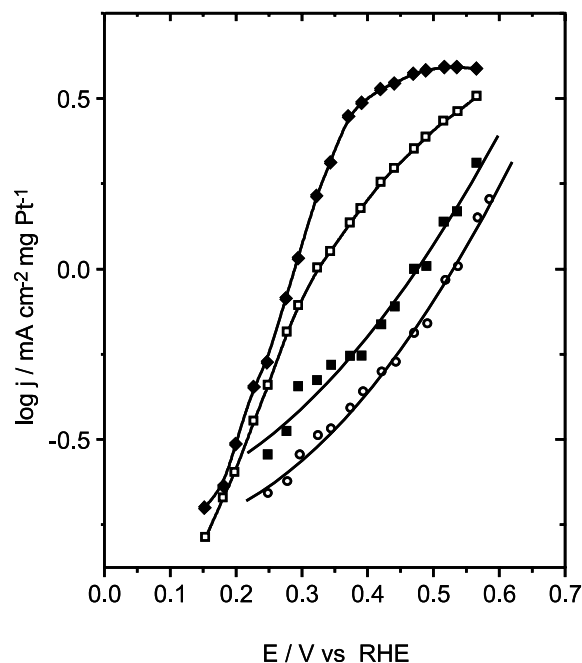


Fig. 6. Tafel-like plots showing the oxidation of 0.1 M ethanol in 0.1 M HClO₄ on pure Pt (600 μg cm⁻²) dispersed in a PANi electron conducting matrix or modified by 60 μg cm⁻² Ru or Sn. Key: (□) Pt-Ru/PANi; (■) Pt-Ru/PANi; (◆) Pt-Sn/PANi; (○) Pt/PANi.

methanol oxidation is still subject to controversy, although some experimental evidence is in favour of a low Ru content, for example, about 20 at % [34, 35]. The best electrocatalyst for the oxidation of other alcohols is not necessarily a Pt-Ru alloy. Other alloys, such as Pt/Ru/Sn and Pt/Sn are very efficient electrocatalysts for the oxidation of ethanol (Figure 6). The oxidation currents are doubled and the overvoltage is decreased by about 0.3 V when using a Pt/Sn alloy dispersed in polyaniline [21].

Very few studies have been devoted to the electrooxidation of other alcohols using platinum alloys or platinum electrodes modified by the underpotential deposition (u.p.d.) of foreign metal adatoms (Ag, Bi, Cd, Cu, Pb, Re, Ru, Sn, Tl,...). The latter is also a convenient way to modify the electrocatalytic activity of platinum based electrodes [36]. A very large effect was found, particularly in alkaline medium, for the oxidation of diols (ethylene glycol, propanediols, butanediols,...). In the case of the oxidation of ethylene glycol on modified platinum electrodes a very large enhancement effect was found with Pb, Bi or Tl adatoms, leading with Pb to current densities about 6 to 15 times as those for pure platinum [37]. A greater enhancement effect was also found for ternary electrocatalysts, such as platinum-gold alloys modified by lead adatoms [38], or with Pt/Pd/Bi or Pt/Pd/Pb alloy electrodes [39]. With higher molecular weight vicinal diols (propanediol 1,2, butanediol,...) similar enhancement effects were also observed due to the presence of Pb, Bi or Tl adatoms leading to high current densities (16–18 mA cm⁻²) and to enhancement factors close to 60 (Pb and Tl). The behavior of Cd

adatoms is different since the peak current is usually decreased, but the peak position is shifted by about 0.2–0.3 V towards the more negative potentials, thus leading to a 0.3 V decrease of the oxidation overpotential [40].

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 reducing 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 $1000 \text{ m}^2 \text{ g}^{-1}$. This allows preparation of active surface areas of $200 \text{ m}^2 \text{ g}^{-1}$ of platinum corresponding to nanoparticles of 1.5 nm [41].

Other supports can be considered, particularly proton exchange membrane (PEM) and electron conducting polymers. Proton exchange membranes are solid electrolytes which are now widely used in PEM fuel cells. 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,...) [42]. This gives very active electrodes for the oxidation of methanol, using Pt–Ru catalysts [43], and of ethanol using Pt–Sn catalysts [22].

Another convenient way to disperse electrocatalytic materials is to use an electron conducting polymer, such as polyaniline (PAni), polypyrrole (PPy) or polythiophene (PTh). These polymers are easily formed by electropolymerization in aqueous 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 vs RHE for PAni). This allows the electrocatalytic material to be dispersed at the molecular level in such a way that the reactive molecules will easily reach the catalytic centres. Very high dispersion levels have been thus achieved, up to a few $\mu\text{g cm}^{-2}$ of platinum based catalysts, which are particularly active for the oxidation of methanol [44] and of ethanol [21].

3. Anodic oxidation of alcohols in a PEMFC

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

The direct anodic oxidation of an alcoholic fuel would allow one to build compact power sources (with no heavy and bulky fuel reformer), fed with a convenient electrochemically reactive and relatively non toxic, as well cheap liquid fuel. Recent progress in the proton exchange membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC) has allowed the conception of a direct alcohol fuel cell (DAFC) based on a PEMFC (Figure 7). In the case of ethanol, for example, an ethanol water mixture (a few percent by weight to make a 1 to 2 M ethanol solution) is circulated through the anodic compartment, while oxygen (air) flows through

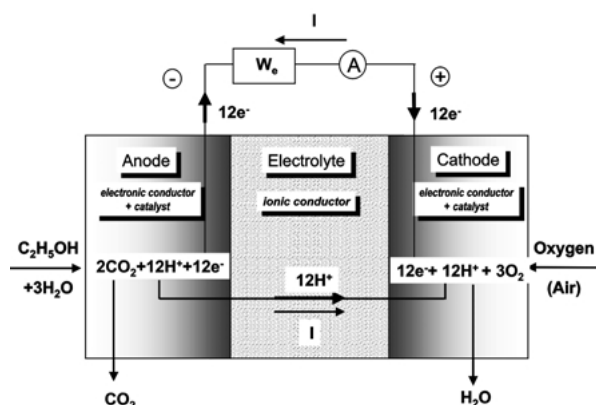
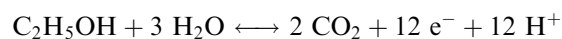


Fig. 7. Schematic principle of a direct ethanol fuel cell.

the cathodic compartment. The anode solution keeps the proton exchange membrane (usually Nafion[®]) wet, particularly for working at higher temperatures (100 to 130 °C). In that case some pressure (2–5 bar) is needed in the anode compartment to keep the alcohol in solution.

3.1.1. Thermodynamic data

The reversible anode potential (under standard equilibrium conditions) can be calculated from thermodynamic data, knowing the overall electrode reaction. For ethanol electrooxidation,



with a Gibbs energy change, calculated from the standard energy of formation ΔG_i^f of reactant (i):

$$\begin{aligned} -\Delta G^- &= 2 \Delta G_{\text{CO}_2}^f - \Delta G_{\text{C}_2\text{H}_5\text{OH}}^f - 3 \Delta G_{\text{H}_2\text{O}}^f \\ -\Delta G^- &= -2 \times 394.4 + 174.8 + 3 \times 237.1 \\ &= 97.3 \text{ kJ mol}^{-1} \end{aligned}$$

This gives the anode potential:

$$E^- = \frac{-\Delta G^-}{12 F} = 0.084 \text{ V vs SHE}$$

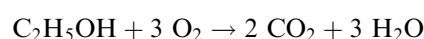
For the cathodic reaction, $\frac{1}{2} \text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- \leftrightarrow \text{H}_2\text{O}$, the electrode potential is

$$E^{\oplus} = 1.229 \text{ V vs SHE}$$

so that the standard electromotive force is

$$E_{\text{emf}} = E^{\oplus} - E^- = 1.229 - 0.084 = 1.145 \text{ V}$$

corresponding to a Gibbs energy change $\Delta G = -1326.7 \text{ kJ mol}^{-1}$ for the overall combustion reaction:



This gives an energy density:

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

Fuel	ΔG^- /kJ mol ⁻¹	E^- /V vs SHE	E_{emf} /V	ΔG /kJ mol ⁻¹	W_e /kWh kg ⁻¹	ΔH /kJ mol ⁻¹	ε_r
CH ₃ OH	-9.3	0.016	1.213	-702.7	6.09	-726.7	0.967
C ₂ H ₅ OH	-97.3	0.084	1.145	-1326.7	8.01	-1367.9	0.970
CH ₂ OH-CH ₂ OH	-4.8	0.005	1.224	-1181.5	5.29	-1190.2	0.992
C ₃ H ₇ OH	-168	0.097	1.132	-1965.3	9.10	-2023.2	0.971
C ₄ H ₉ OH	-243	0.105	1.124	-2602.1	9.77	-2676.8	0.972

$$W_e = \frac{-\Delta G}{3600 M} = 8.01 \text{ kWh kg}^{-1}$$

where $M = 46.07 \text{ g}$ is the molecular weight of ethanol.

The enthalpy change $\Delta H = -1367.9 \text{ kJ mol}^{-1}$ allows calculation of a reversible energy efficiency (at equilibrium potential):

$$\varepsilon_r = \frac{\Delta G}{\Delta H} = \frac{1326.7}{1367.9} = 0.970$$

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

According to Table 1, the alcohols have a very good energy density W_e , comparable to that of hydrocarbons and gasoline (e.g., 10–11 kWh kg⁻¹), so that they are alternative energy carriers for electric vehicles. The cell voltage under equilibrium conditions is about 1.1–1.2 V, that is, very similar to that of a hydrogen/oxygen fuel cell (1.23 V). However, the energy efficiency ε_r , under reversible conditions, is much better than that of a H₂/O₂ fuel cell (which is only 0.83 at 25 °C), approaching unity for the lightest alcohol.

3.1.2. Kinetic data

In spite of these promising thermodynamic data, the kinetics of alcohol oxidation is more difficult, leading to high anodic overvoltages, particularly with a platinum electrode (Figure 8). As a typical example, the overvoltage of ethanol electrooxidation is around 0.6 V at 100 mA cm⁻² on pure platinum, although the development of better electrocatalysts, such as bimetallic Pt–X, or trimetallic Pt–Sn–X platinum based alloys (with X = Ru, Sn, other transition metals) can lower it to 0.1 V for Pt/Ru and to 0.3 V for Pt/Sn (see also Figure 9).

For other alcohols (except methanol) the oxidation kinetics is even more difficult, so that higher overvoltages and lower current densities are obtained. As discussed in Section 2.2, one way to decrease the overvoltage is to look for more active electrocatalysts, bimetallic or multimetallic platinum-based catalysts. Another way to increase the reaction rate, that is, to decrease the overvoltage, is to increase the working temperature above 120 °C. But the usual Nafion[®] membranes cannot work above 120–140 °C, so that other membranes have to be developed. Higher temperatures up to 170 °C were effectively reached using composite polymer membranes, such as silica/Nafion[®] films [45] or a polybenzimidazole (PBI) membrane doped with phosphoric acid [46].

3.2. Realization of a direct alcohol fuel cell

Except for methanol, the direct oxidation of which is now widely studied in a PEMFC [1], and which is considered as a possible fuel for electric vehicles, very few other alcohols have been investigated.

In the late 1970s Siemens Research Laboratories (Germany) investigated a 125 W ethylene glycol/air fuel cell with an alkaline medium [4]. The stack was made with 52 single cells and was able to deliver 28 V at 4.5 A (nominal power output of 125 W) and 16 V at 14 A (225 W peak power at 40 °C). The anode catalyst was a trimetallic alloy Pt/Pd/Bi with a noble metal loading of about 5 mg cm⁻². The specific data were relatively interesting (5 W kg⁻¹, 55 Wh kg⁻¹ with a tank volume of 17 dm³ and a weight of 22 kg), but the electrooxidation of ethylene glycol was far from being complete, giving principally glycolate as product. However, the use of an alkaline medium is not convenient with an organic fuel, since carboxylates and carbonates are produced, which consume the alkaline electrolyte, lowering the performance of the fuel cell. Therefore, only acidic electrolytes

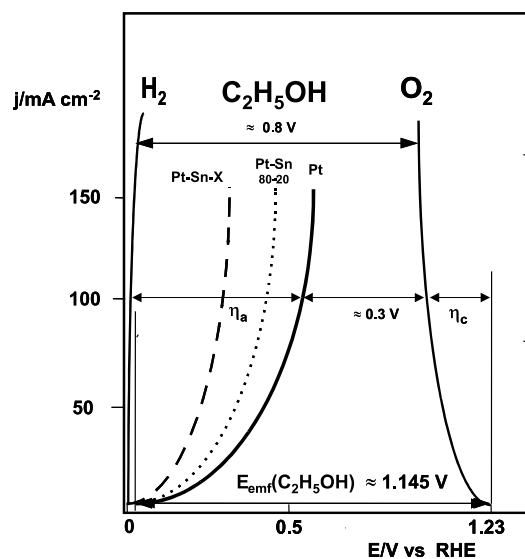


Fig. 8. j/E curves of an ethanol/oxygen fuel cell with different anode platinum-based catalysts (Pt–Sn–X), comparatively to that of a hydrogen/oxygen fuel cell with Pt catalysts.

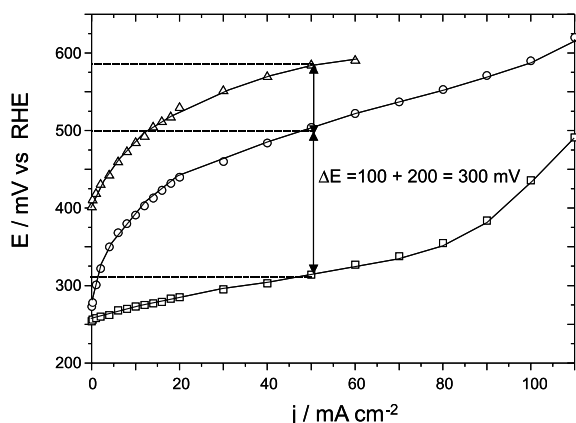


Fig. 9. Comparison of the anode characteristics for the oxidation of ethanol on Pt-X-Nafion[®] electrodes (liquid ethanol/water mixture feed, cell temperature 90 °C, 1 mg cm⁻² anode catalyst, 1 mg Pt cm⁻² cathode catalyst): (Δ) Pt ; (○) Pt-Ru ; (□) Pt-Sn.

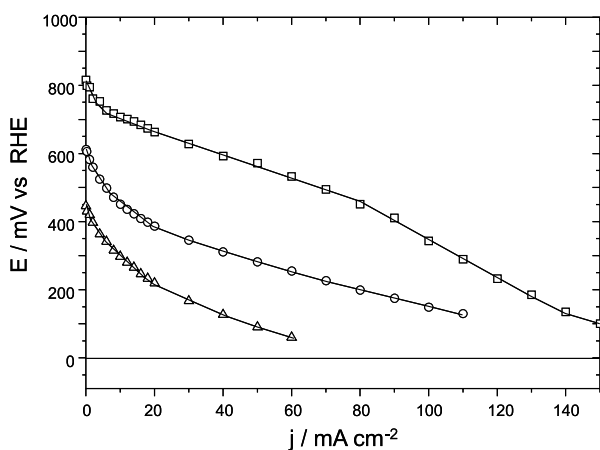


Fig. 10. Comparison of the fuel cell characteristics of a direct ethanol fuel cell with Pt-X-Nafion[®] anodes (liquid ethanol/water mixture feed, cell temperature 90 °C, 1 mg cm⁻² anode catalyst, 1 mg Pt cm⁻² cathode catalyst): (Δ) Pt ; (○) Pt-Ru ; (□) Pt-Sn.

are now considered for the direct alcohol fuel cell, and, due to the great progress made in the hydrogen/air PEMFC, only proton exchange membranes fed with the alcohol-water mixture are now under investigation.

The first attempts were made with ethanol, which seems to be the more 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 were carried out in our Laboratory [47]. Different binary electrocatalysts were investigated; among them Pt/Ru and Pt/Sn were the most active catalysts and less poisoned by strongly adsorbed intermediates (CO) from the dissociation of ethanol.

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 a pure Pt electrode [47]. Using a Nafion[®] 117 membrane, current densities of 60 mA cm⁻² were obtained at 90 °C for a cell voltage of 550 mV with Pt/Sn (i.e., a power density of 33 mW cm⁻²), 250 mV with Pt/Ru and 50 mV with Pt, respectively (Figure 10).

Nevertheless, 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. used a 80 μm thick composite membrane prepared by mixing and heat treating an appropriate amount of Nafion[®] ionomer (5 wt % Aldrich) with 3 wt % silica (Aerosil 200, Degussa) [45]. They used (1/1) Pt/Ru/C as anode catalyst and Pt/C as cathode catalyst with a Pt loading of 2 mg cm⁻² 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 cm⁻² was obtained at 0.32 V and at 350 mA cm⁻², without correcting for the ohmic drop (specific resistance of the membrane electrode assembly $R_e = 0.18 \Omega \text{ cm}^2$), whereas at 0.5 V the current density reached 180 mA cm⁻² (Figure 11). Chromatographic analysis of the anode outlet during steady state measurements (300 mA cm⁻² at 0.35 V) seems to indicate that CO₂ is the main oxidation product (with a yield greater than 90%), together with some small amounts of acetaldehyde (4%) and unreacted ethanol.

Using a phosphoric acid doped polybenzimidazole (PBI) membrane, Savinell et al. were able to work at higher temperatures (170 °C) [46]. They compared the behaviour in a PEMFC of four aliphatic alcohols: methanol, ethanol, 1-propanol and 2-propanol (Figure 12). The PEMFC was operating on pure oxygen at 170 °C with 4 mg cm⁻² Pt/Ru at the anode and 4 mg cm⁻² Pt at the cathode. The cell resistance was 0.42 Ω cm². At a current density of 250 mA cm⁻² the cell voltages were 0.35, 0.30, 0.17 and 0.050 V for methanol, ethanol, 1-propanol and 2-propanol, respectively. The behaviour of ethanol was similar to that of methanol, so that it could advantageously substitute for methanol as a fuel in a PEMFC. On the other hand, even with a Pt/Ru anode catalyst the propanols are not very electro-reactive, particularly 2-propanol. Analysis of the reaction products by online mass spectrometry showed, at variance with the work of Arico et al. [45], that ethanal is the main reaction product of ethanol electrooxidation, while CO₂ is a minor product. This depended on the water/ethanol mole ratio, since the relative amount of CO₂ increased from 20 to 32% when this ratio increased from 2 to 5. With 1-propanol and 2-propanol the electrooxidation reaction yields mainly propanal and acetone, respectively, meaning that the electrooxidation of primary or secondary alcoholic groups proceeds only through the dehydrogenation step (see Equation 2 for ethanol oxidation).

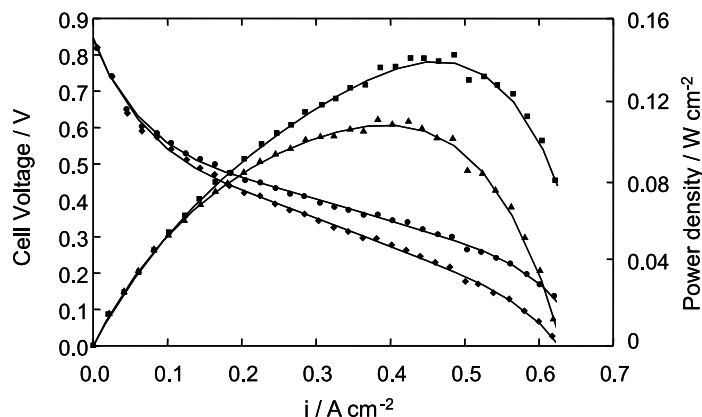


Fig. 11. Polarization curves and power density curves of a direct ethanol fuel cell using a silica/Nafion[®] membrane (1 M ethanol, cell temperature 145 °C, p_{anode} 4 bar, p_{cathode} 5.5 bar, 2 mg cm⁻² (1/1) Pt-Ru/C anode catalyst, 2 mg cm⁻² Pt cathode catalyst). See [44]. Key: (●), (■) raw; (▲), (◆) IR-free.

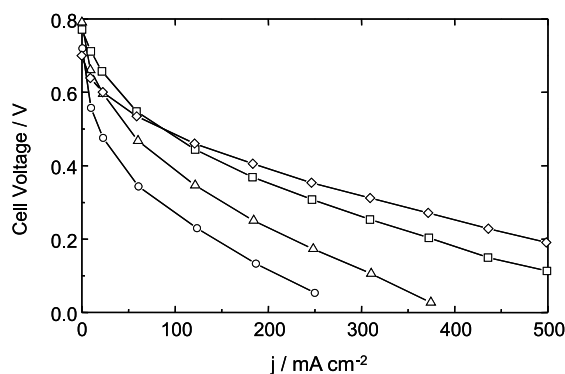


Fig. 12. Comparison of the cell performances of a direct alcohol fuel cell using a PBI membrane doped with H₃PO₄. (cell temperature 170 °C, 4 mg cm⁻² Pt-Ru anode catalyst, 4 mg cm⁻² Pt black cathode catalyst): methanol (◇), ethanol (□), 1-propanol (△) and 2-propanol (○). After [45].

4. Conclusions

The reactivity of ethanol at platinum based electrodes is comparable to that of methanol, but the electrooxidation reaction stops at intermediate steps, producing mainly acetaldehyde and acetic acid, together with some carbon dioxide, depending on the experimental conditions. Pt/Sn appears to be the best electrocatalyst, although the right atomic composition has not yet been definitely established. Investigation of other binary or ternary Pt-based electrocatalysts is necessary to increase the reaction rate and to break the C–C bond for greater selectivity towards the formation of CO₂. This is particularly true for the oxidation of propanols and higher alcohols, the rate of which is still too low even at high temperature (170 °C) to compete with methanol and ethanol.

The j/E characteristics of a PEMFC fed with methanol and ethanol are rather similar, so that ethanol appears to be a good alternative to methanol. Moreover, ethanol is much less toxic than methanol, and its mass

production from the agriculture raw materials may result in a lower price, allowing it to compete economically with methanol.

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