

# Methoxy methane (dimethyl ether) as an alternative fuel for direct fuel cells

G. Kerangueven, C. Coutanceau\*, E. Sibert, J.-M. Léger, C. Lamy

UMR-CNRS 6503, Université de Poitiers, Equipe Electrocatalse, 40 Avenue du Recteur Pineau, 86022 Poitiers Cedex, France

Received 24 May 2005; received in revised form 21 June 2005; accepted 22 July 2005

Available online 19 October 2005

## Abstract

The electrooxidation of methoxy methane (dimethyl ether) was studied at different Pt-based electrocatalysts in a standard three-electrode electrochemical cell. It was shown that alloying platinum with ruthenium or tin leads to shift the onset of the oxidation wave towards lower potentials. On the other hand, the maximum current density achieved was lower with a bimetallic catalyst compared to that obtained with a Pt catalyst. The direct oxidation of dimethoxy methane in a fuel cell was carried out with Pt/C, PtRu/C and PtSn/C catalysts. When Pt/C catalyst is used in the anode, it was shown that the pressure of the fuel and the temperature of the cell played important roles to enhance the fuel cell electrical performance. An increase of the pressure from 1 to 3 bar leads to multiply by two times the maximum achieved power density. An increase of the temperature from 90 to 110 °C has the same effect. When PtRu/C catalyst is used in the anode, it was shown that the electrical performance of the cell was only a little bit enhanced. The maximum power density only increased from 50 to 60 mW cm<sup>-2</sup> at 110 °C using a Pt/C anode and a Pt<sub>0.8</sub>Ru<sub>0.2</sub>/C anode, respectively. But, the maximum power density is achieved at lower current densities, i.e. higher cell voltages. The addition of ruthenium to platinum has other effect: it introduces a large potential drop at relatively low current densities. With the Pt<sub>0.5</sub>Ru<sub>0.5</sub>/C anode, it has not been possible to applied current densities higher than 20 mA cm<sup>-2</sup> under fuel cell operating conditions, whereas 250 and almost 400 mA cm<sup>-2</sup> were achieved with Pt<sub>0.8</sub>Ru<sub>0.2</sub>/C and Pt/C anodes. The Pt<sub>0.9</sub>Sn<sub>0.1</sub>/C anode leads to higher power densities at low current densities and to the same maximum power density as the Pt/C anode.

© 2005 Elsevier B.V. All rights reserved.

**Keywords:** Fuel cell; Electrooxidation; Methoxymethane; Platinum ruthenium tin catalysts

## 1. Introduction

In the field of fuel cells working at low temperatures, the proton exchange membrane fuel cells (PEMFCs) [1–5], direct methanol fuel cells (DMFCs) [6–10] and direct ethanol fuel cells (DEFCs) [11–15] are the most studied. But each of them displays some limitations due to either storage, safety issue, toxicity, reactivity, etc., of the fuel. DME (dimethyl ether or methoxy methane—CH<sub>3</sub>OCH<sub>3</sub>—) can be an alternative fuel for such applications. It is the simplest ether. It is stable in liquid and gas phases, with a boiling point of –25.1 °C under atmospheric pressure. It is then easier to store under pressure than hydrogen. Some advantages for its use as fuel in fuel cells are the followings:

1. No C–C bond to break as for ethanol electrooxidation, which can make easier a complete oxidation of DME into CO<sub>2</sub>.
2. The lower dipolar momentum of DME compared with that of methanol, and ethanol (1.3 D versus 1.7 D and 1.69 D, respectively) may decrease the crossover effect.
3. Conversely to methanol, DME has a low toxicity when ingested or in contact with skin.
4. Its ignition point is high (235 °C), it displays a low inflammability and a relatively high explosive limit [16].

According to the thermodynamic data related to this compound (Table 1) [17], the Gibbs energy of the combustion reaction of DME into oxygen at 25 °C is 1362 kJ mol<sup>-1</sup>, which corresponds to an equilibrium potential for the combustion reaction of DME leading to CO<sub>2</sub> of

$$\Delta G_r^\circ + nFE_{eq}^\circ = 0 \quad (1)$$

\* Corresponding author. Tel.: +33 5 49 45 48 95; fax: +33 5 49 45 35 80.  
E-mail address: [christophe.coutanceau@univ-poitiers.fr](mailto:christophe.coutanceau@univ-poitiers.fr) (C. Coutanceau).

Table 1  
Thermodynamic data related to DME at 298K, in gas phase

Phase	Gas
$n$	12
$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	-1328.3
$\Delta G^\circ$ (kJ mol <sup>-1</sup> )	-1362
$\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> )	111.3

$$E_{\text{eq}}^\circ = -\frac{\Delta G_r^\circ}{nF} = \frac{1362 \times 10^3}{12 \times 96500} = 1.176 \text{ V} \quad (2)$$

with  $n=12$  electrons in the complete oxidation of DME into CO<sub>2</sub> and the Faraday constant  $F=96500 \text{ F mol}^{-1}$ .

This value of equilibrium potential makes DME a good alternative as a fuel in fuel cells when compared to that for hydrogen/oxygen (1.23 V), methanol/oxygen (1.21 V) or ethanol/oxygen (1.145 V). The reversible energy efficiency at 25 °C is

$$\varepsilon_{\text{rev}} = -\frac{nFE_{\text{eq}}^\circ}{\Delta H_r^\circ} = \frac{\Delta G_r^\circ}{\Delta H_r^\circ} = \frac{1362}{1328} = 103\% \quad (3)$$

In fact, because the variation of entropy  $\Delta S$  is positive, the reversible energy efficiency is a little higher than 100%. However,  $\varepsilon_{\text{rev}}$  is calculated from thermodynamic data under standard conditions, i.e. at equilibrium potential with zero current. Under operating conditions, the actual efficiency is

$$\varepsilon = \frac{n_{\text{exp}} FE(j)}{-\Delta H_r^\circ} = -\frac{nFE_{\text{eq}}^\circ E(j) n_{\text{exp}}}{\Delta H_r^\circ E_{\text{eq}}^\circ n} = \varepsilon_{\text{rev}} \varepsilon_E \varepsilon_F \quad (4)$$

where

$$E(j) = E_2 - E_1 = E_{\text{eq}}^\circ - (|\eta_a| + |\eta_c| + |\eta_{\text{Xover}}| + R_i j) \quad (5)$$

$\eta_a$  is the anodic overpotential,  $\eta_c$  the cathodic overpotential,  $\eta_{\text{Xover}}$  the overpotential due to the crossing of DME through the membrane from the anodic compartment towards the cathodic compartment,  $j$  the current density,  $R_i$  the internal resistance of the cell,  $n_{\text{exp}}$  the experimental number of exchanged electrons and  $n$  is the theoretical number of exchanged electrons ( $n=12$  electrons for a complete oxidation of DME into CO<sub>2</sub>). As might be expected from Eq. (5), the voltage efficiency,  $\varepsilon_E$ , and the Faradaic efficiency,  $\varepsilon_F$ , are strongly depending on electrocatalyst performance: activity at low potentials and selectivity towards CO<sub>2</sub> production for DME oxidation and activity at high potentials, selectivity towards H<sub>2</sub>O formation and high tolerance towards the presence of DME for oxygen reduction.

In the present paper, the activity of platinum-based electrocatalysts towards DME oxidation are compared. Results on the performance of direct DME fuel cell are reported and discussed according to the catalyst composition.

## 2. Experimental

### 2.1. Electrochemical measurements

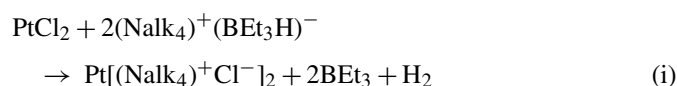
The electrochemical set-up consists of a Voltalab PGZ 402 potentiostat controlled by a computer.

The solutions were prepared from H<sub>2</sub>SO<sub>4</sub> 96% (Suprapur, Merck) in ultrapure water (MilliQ, Millipore 18 MΩ cm). The electrochemical experiments were carried out at 20 °C using a conventional thermostated standard three-electrode electrochemical cell. The desired concentrations of DME in the electrolyte were obtained by addition of a given volume of a saturated DME solution in a known volume of the N<sub>2</sub>-purged solution in the cell. The working electrode was a rotating glassy carbon disc (0.071 cm<sup>2</sup> geometric surface area) on which the catalytic powder was deposited, the counter electrode was a platinum grid and the reference electrode was a mercury mercurous sulphate electrode (MSE), but all potentials are related to the reversible hydrogen electrode (RHE).

### 2.2. Preparation of catalysts and electrodes

The preparation method of the Pt-based catalysts dispersed on carbon powder (Vulcan XC72) is based on the synthesis of colloidal precursors using the procedure described by Bönemann et al. [18], slightly modified.

The preparation method was described elsewhere [19,20]. Briefly, the synthesis method is as follows. The first step consisted in the synthesis of the reducing agent by mixing a stoichiometric amount of tetraalkylammonium bromide (Nalk<sub>4</sub>)<sup>+</sup>Br<sup>-</sup> and potassium triethylhydroborate K<sup>+</sup>(BEt<sub>3</sub>H)<sup>-</sup> in tetrahydrofuran as solvent (THF). After elimination of the precipitated KBr, a solution of tetraalkylammonium triethylhydroborate (Nalk<sub>4</sub>)<sup>+</sup>(BEt<sub>3</sub>H)<sup>-</sup> was obtained which reduced the platinum, ruthenium or tin salts according to the following reaction, written in the case of platinum as



In this way, the platinum nanoparticles were stabilized by (Nalk<sub>4</sub>)<sup>+</sup>Cl<sup>-</sup>, which acts as a surfactant protecting the metal particles by its long alkyl chain.

The colloid particles were adsorbed on Vulcan XC72, previously treated for four hours at 400 °C under nitrogen to clean it, in order to obtain a catalyst loading of 60 wt.% based on the metal content. Before using them as electrocatalysts, the organic surfactant shell of the supported colloid catalysts must be removed by a thermal treatment under air atmosphere at 300 °C. The physicochemical characterisations of such catalysts were described elsewhere [20,21].

The dispersed catalysts were deposited on vitreous carbon according to a method developed by Gloaguen et al. [22]. Twenty-five milligrams of carbon supported catalyst powder is added to 0.5 mL de Nafion<sup>®</sup> 5% (from Aldrich) in 2.5 mL ultrapure water (Millipore MilliQ, 18 MΩ cm), which leads to a Nafion<sup>®</sup>/catalyst powder ratio close to 40 wt.%. After ultrasonic homogenisation of the PtX/XC72-Nafion<sup>®</sup> ink, 3 μL of ink is deposited from a syringe onto a fresh polished glassy carbon substrate yielding a catalyst loading of 0.21 mg cm<sup>-2</sup>, i.e. 0.35 mg cm<sup>-2</sup> catalytic powder PtX/XC72 loading. The solvent is then evaporated in a stream of ultrapure nitrogen at room temperature.

### 2.3. Fuel cell tests

The fuel cell tests in a single cell with a  $5\text{ cm}^2$  geometric surface area were carried out with a Globe Tech test bench. The  $E$  versus  $j$  and  $P$  versus  $j$  curves were recorded using a high power potentiostat (Wenking model HP 88) interfaced with a PC to apply constant current sequences and to store the data, and a variable resistance in order to fix the current applied to the cell.

A water solution was saturated with DME by bubbling. The concentration of DME was close to  $1.65\text{ mol L}^{-1}$  [23]. The fuel cell was fed with the DME solution without pre-heating. Back pressure valves allow controlling DME and oxygen pressure in the cell.

Anodes for fuel cell tests were prepared from an ink consisting of a mixture of  $100\text{ }\mu\text{L}$  of Nafion<sup>®</sup> (5 wt.% from Aldrich) solution,  $1\text{ mL}$  of isopropanol and  $17\text{ mg}$  of catalytic powder, brushed on a carbon gas diffusion electrode. Carbon gas diffusion electrodes were home-made using a carbon cloth from Electrochem Inc. on which was brushed an ink made of Vulcan XC72 carbon powder and a PTFE/water emulsion in isopropanol. The gas diffusion electrodes were loaded with  $4\text{ mg cm}^{-2}$  of a mixture of carbon powder and 15 wt.% PTFE. Prior to the preparation of the membrane electrode assembly (MEA), the electrodes were heated at  $150\text{ }^\circ\text{C}$  to recast the Nafion<sup>®</sup> film. The metal loading of the electrodes was close to  $2\text{ mg cm}^{-2}$  and the Nafion<sup>®</sup> loading of the electrode was  $0.8\text{ mg cm}^{-2}$ . The MEAs were prepared, by hot pressing at  $130\text{ }^\circ\text{C}$  for  $90\text{ s}$  under a pressure of  $35\text{ kg cm}^{-2}$ , a pretreated Nafion<sup>®</sup>117 membrane with an E-TEK cathode ( $2.0\text{ mg cm}^{-2}$  Pt loading, 40% metal/C, 40% PTFE,  $0.8\text{ mg cm}^{-2}$  Nafion<sup>®</sup>) and with the homemade anodes. The Nafion<sup>®</sup> membranes were preliminary treated according to a standard method described by Büchi and Srinivasan [24].

## 3. Results and discussion

### 3.1. DME electrooxidation on dispersed Pt/C, PtRu/C, and PtSn/C electrodes

In a previous study at a platinum sphere electrode it was shown that the activation of molecules of water is needed to complete the oxidation of DME into  $\text{CO}_2$  or  $\text{HCOOH}$  [25]. It is well known, in the case of methanol electrooxidation that ruthenium alloyed with platinum leads to enhance the oxidation reaction at lower potentials, because ruthenium is able to activate water at lower potentials than platinum [26,27]. The same is also true for CO oxidation [28–30] and ethanol oxidation [31–33] at PtSn alloys. The behaviour of such catalyst towards DME electrooxidation was then studied and compared. In order to compare the results obtained in the electrochemical half cell to those obtained in the direct DME fuel cell, the catalysts were prepared as fuel cell catalysts. The method of Bönemann is adapted to our purpose: to prepare different PtX catalysts ( $X = \text{Ru, Sn, } \dots$ ) nanodispersed on carbon with different bulk atomic ratios [19,20]. The voltammograms are represented in Fig. 1a–d for Pt/C, Pt<sub>0.5</sub>Ru<sub>0.5</sub>, Pt<sub>0.8</sub>Ru<sub>0.2</sub> and Pt<sub>0.9</sub>Sn<sub>0.1</sub>/C, respectively. The different ratios were chosen with respect to the atomic ratio clas-

sically used for methanol oxidation and ethanol oxidation. First, nanodispersed platinum catalyst leads to an onset on the oxidation peak at a potential close to  $0.5\text{ V}$  versus RHE. Second, the addition of Ru or Sn to platinum leads to decrease the onset potential of the oxidation peaks from  $0.5\text{ V}$  versus RHE for Pt/C to  $0.4\text{ V}$  versus RHE for Pt<sub>0.8</sub>Ru<sub>0.2</sub>/C and Pt<sub>0.9</sub>Sn<sub>0.1</sub>/C catalysts, i.e. leads to increase the catalytic activity at low potentials. However, the highest activity in terms of maximum current densities achieved for the electrooxidation of DME is obtained at a Pt/C catalyst with  $42\text{ }\mu\text{A cm}^{-2}$  at  $0.72\text{ V}$  versus RHE, i.e. 1.5 times higher than at a Pt<sub>0.8</sub>Ru<sub>0.2</sub>/C catalyst and a Pt<sub>0.9</sub>Sn<sub>0.1</sub>/C catalyst (close to  $26\text{ }\mu\text{A cm}^{-2}$  at  $0.68\text{ V}$  versus RHE and  $33\text{ }\mu\text{A cm}^{-2}$  at  $0.7\text{ V}$  versus RHE, respectively). Third, it is interesting to note that the ruthenium rich catalyst displays the worst activity of the bimetallic catalyst, as it is the case for methanol oxidation [19,20,34,35], the onset of the oxidation peak being close to  $0.42\text{ V}$  versus RHE and the maximum current density of  $18\text{ }\mu\text{A cm}^{-2}$  at a potential close to  $0.65\text{ V}$  versus RHE. This fact can be due to the dehydrogenation mechanism of DME, which could need the presence of three adjacent platinum atoms or sites to lead to a adsorbed CHO or CO species [23,36] as for methanol electrooxidation [37,38]. In fact, it appears that the adsorption of DME only occurs at platinum, since the addition of an alloy component leads to decrease the maximum activity of the catalyst, i.e. the number of adsorbed molecules. The role of the alloying component may be either to favour the DME adsorption at platinum (ligand effect) and/or to activate water at lower potentials than platinum alone and complete the oxidation reaction (bi-functional mechanism). Both these effects have already been pointed out in studies about methanol [39] and ethanol [15] electrooxidation at bimetallic platinum-based catalysts.

### 3.2. Fuel cell tests with a platinum anode

The electrooxidation of DME was also studied in a  $5\text{ cm}^2$  fuel cell. Fuel cell tests with DME are often carried out in gas phase. DME is hydrated at temperature close to  $80\text{ }^\circ\text{C}$  by bubbling in hot water before feeding the anodic compartment of the cell [16,36]. But, because the management of liquid fuel is easier than gaseous fuel (in term of storage), a water solution saturated with DME at  $20\text{ }^\circ\text{C}$  has also been used to feed the anodic compartment. Fuel cell tests were carried out with a feed in DME either under gas phase after hydration by bubbling in hot water ( $90\text{ }^\circ\text{C}$ ) or in liquid phase after saturation of water. At  $90\text{ }^\circ\text{C}$ , the best results obtained were given in Fig. 2. Under the same conditions excepted the physical state of DME, the best performance in terms of maximum power density was achieved with the liquid feed, with  $16\text{ mW cm}^{-2}$  instead of  $7\text{ mW cm}^{-2}$  when the fuel cell is fed with gas phase DME. The open circuit voltage (OCV) between  $0.75$  and  $0.80\text{ V}$  is in agreement with that obtained by other authors at platinum or platinum–ruthenium electrodes with hydrated gaseous DME [16,36]. However, the OCVs of the cells are very close in both cases. But, as soon as the cell starts to deliver low current density, the potential drop is higher with the DME in gas phase than in liquid phase. According to the invariance of the OCV with the physical state of DME,

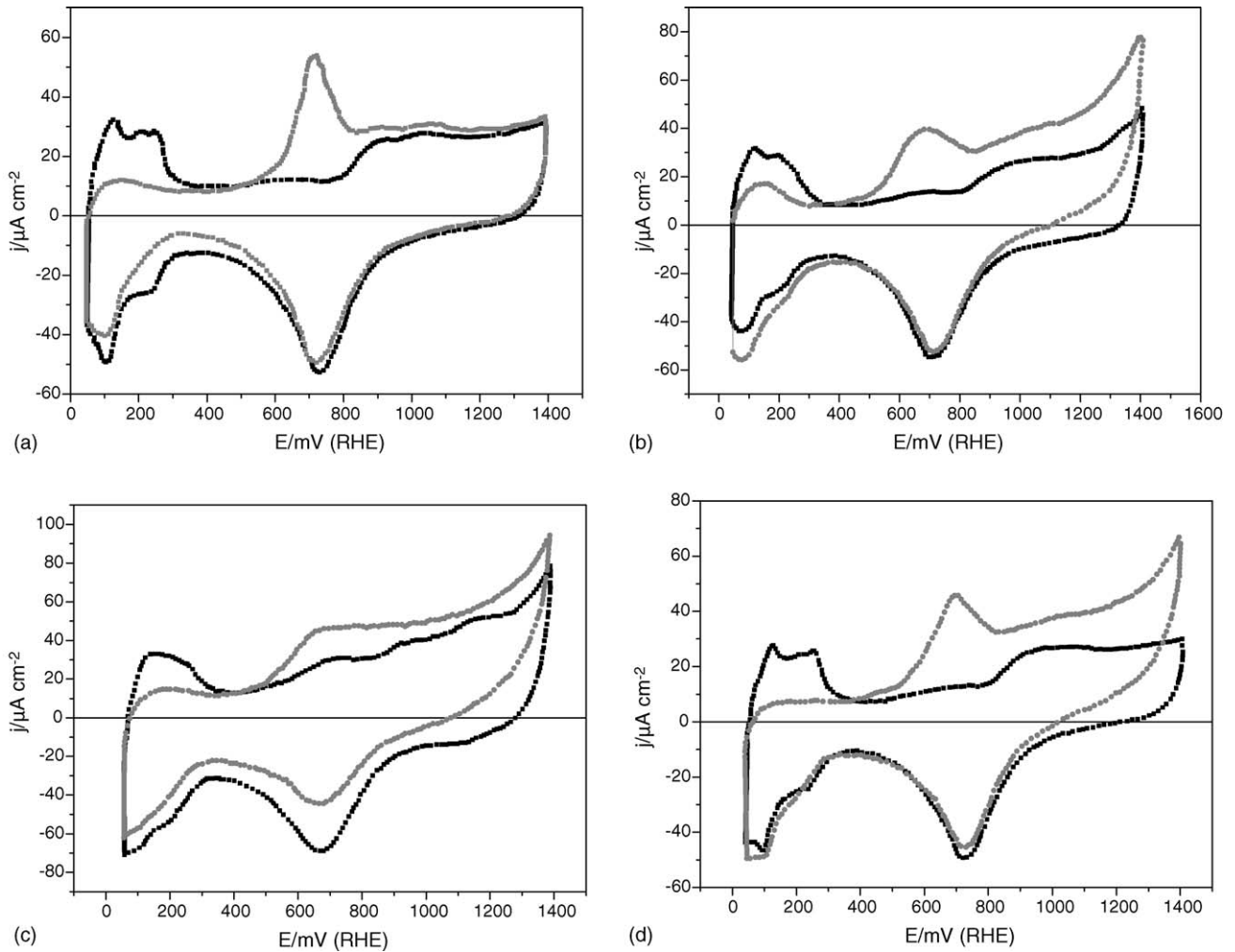


Fig. 1. Voltammograms of (a) Pt/C, (b) Pt<sub>0.8</sub>Ru<sub>0.2</sub>/C, (c) Pt<sub>0.5</sub>Ru<sub>0.5</sub>/C and (d) Pt<sub>0.9</sub>Sn<sub>0.1</sub>/C catalysts recorded in N<sub>2</sub> purged 0.1 M H<sub>2</sub>SO<sub>4</sub> electrolyte ( $T=20\text{ }^{\circ}\text{C}$ ,  $v=20\text{ mV s}^{-1}$ ,  $\Omega=2500\text{ rpm}$ ). Black line: without DME; grey line: with of 0.6 M DME.

it can be proposed that the DME crossover is not responsible of this effect. Therefore, the reactivity of DME in gas phase is lower than in aqueous phase. In a previous work, we proposed that the good reactivity of DME at platinum electrode was due to the possibility of the hydrolysis of DME [25]. Therefore, the pres-

ence of water molecules around DME is important to oxidize it at relatively low potentials. In gas phase, the lack of water molecules around DME may lead to decrease the kinetics of DME hydrolysis and may be responsible of the decrease of the activity in fuel cell operating conditions. Because of this, further fuel cell experiments will be performed from DME saturating water solutions (DME concentration of  $1.65\text{ mol L}^{-1}$ ).

The  $E(j)$  polarisation curves obtained with a Pt/C catalysts at the anode were given as a function of the temperature in Fig. 3 and of the pressure in Fig. 4. The increase of the cell temperature leads to increase drastically the performances of the cell. This indicates the difficulty to activate the DME oxidation at low temperatures and the important work to do in the field of electrocatalysis. At low temperature ( $50\text{ }^{\circ}\text{C}$ ), the maximum power density is very low (below  $2\text{ mW cm}^{-2}$ ). But, increasing the temperature from  $50$  to  $90\text{ }^{\circ}\text{C}$  leads to increase the power density almost by a factor 10 ( $16\text{ mW cm}^{-2}$  at  $90\text{ }^{\circ}\text{C}$ ). The pressure of the reactants is also very important. In Fig. 4, the fuel cell performances are given for different O<sub>2</sub> and DME pressure. The increase of the pressures leads also to increase drastically the performance of the fuel cell. For example, at a fuel cell temperature of  $90\text{ }^{\circ}\text{C}$ , increasing the pressure of DME

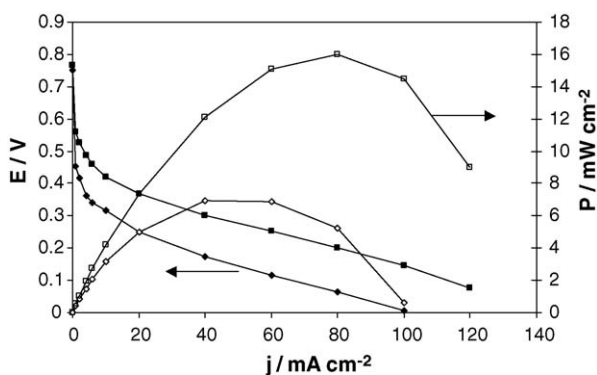


Fig. 2. Cell voltage  $E$  and power density  $P$  vs. current density  $j$  curves in a single  $5\text{ cm}^2$  surface area FC with a Pt/C anode at  $90\text{ }^{\circ}\text{C}$  (Nafion® 117 membrane); (◇ and ◆) DME under gas phase; (□ and ■)  $1.65\text{ M}$  DME in water.  $P_{\text{O}_2}=2\text{ bar}$ ;  $P_{\text{DME}}=1\text{ bar}$ .



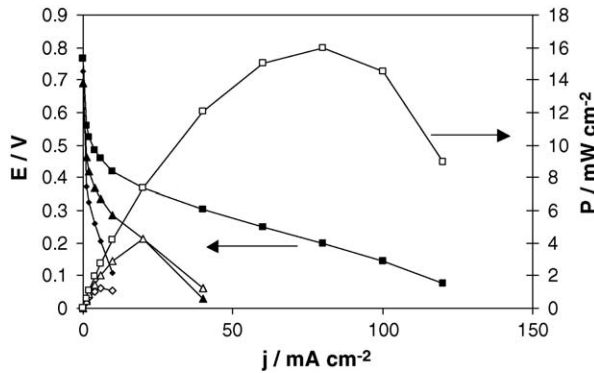


Fig. 3. Cell voltage  $E$  and power density  $P$  vs. current density  $j$  curves in a single  $5 \text{ cm}^2$  surface area FC with a Pt/C anode at different temperatures (1.65 M DME in water, Nafion<sup>®</sup> 117 membrane;  $P_{\text{O}_2} = 2 \text{ bar}$ ;  $P_{\text{DME}} = 1 \text{ bar}$ ); (◆ and ◇)  $50 \text{ }^\circ\text{C}$ ; (▲ and △)  $70 \text{ }^\circ\text{C}$ ; (■ and □)  $90 \text{ }^\circ\text{C}$ .

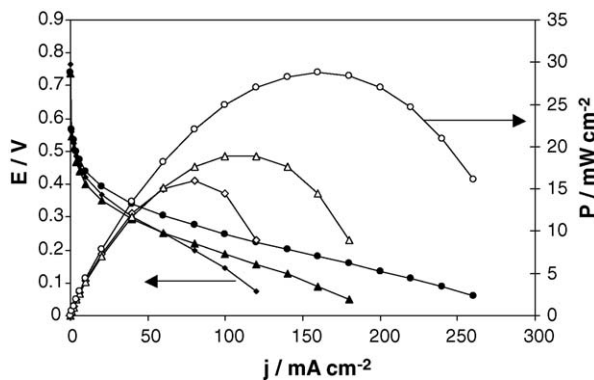


Fig. 4. Cell voltage  $E$  and power density  $P$  vs. current density  $j$  curves in a single  $5 \text{ cm}^2$  surface area FC with a Pt/C anode at  $90 \text{ }^\circ\text{C}$  under different DME pressures (1.65 M DME in water, Nafion<sup>®</sup> 117 membrane;  $P_{\text{O}_2} = 2 \text{ bar}$ ); (◆ and ◇);  $P_{\text{DME}} = 1 \text{ bar}$ ; (▲ and △)  $P_{\text{DME}} = 2 \text{ bar}$ ; (● and ○)  $P_{\text{DME}} = 3 \text{ bar}$ .

from 1 to 3 bars leads to increase the maximum power density from 16 to  $30 \text{ mW cm}^{-2}$ . For DME and  $\text{O}_2$  pressure of 3 and 2 bars, respectively, the increase of the temperature from 90 to  $110 \text{ }^\circ\text{C}$  leads to increase the maximum power density from 30 to  $50 \text{ mW cm}^{-2}$  (Fig. 5). If increasing the temperature leads to enhance the activation of the DME electrooxidation at a platinum catalyst, increasing the DME pressure seems to favour the

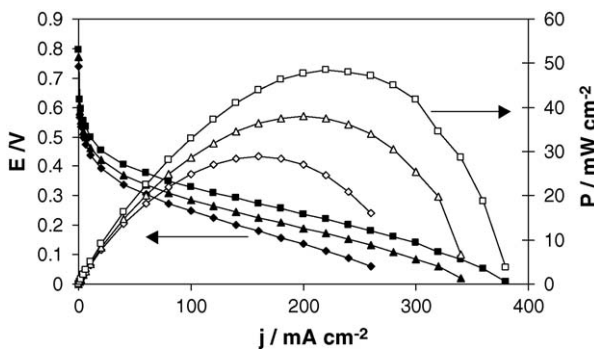


Fig. 5. Cell voltage  $E$  and power density  $P$  vs. current density  $j$  curves in a single  $5 \text{ cm}^2$  surface area FC with a Pt/C anode at different temperatures (1.65 M DME in water, Nafion<sup>®</sup> 117 membrane;  $P_{\text{O}_2} = 2 \text{ bar}$ ;  $P_{\text{DME}} = 3 \text{ bar}$ ); (◆ and ◇)  $90 \text{ }^\circ\text{C}$ ; (▲ and △)  $100 \text{ }^\circ\text{C}$ ; (■ and □)  $110 \text{ }^\circ\text{C}$ .

adsorption of DME at platinum and hence to enhance the DME electrooxidation.

### 3.3. Fuel cell tests with PtRu and PtSn anodes

The effect of the addition of ruthenium or tin to platinum for DME electrooxidation in a Fuel Cell is represented in Fig. 6a. The presence of tin or ruthenium does not have a great effect on the OCV, which remains always around 0.8 V. This behaviour is rather surprising when comparing with electrochemical half cell results, where a shift towards lower potentials of the onset of the DME electrooxidation was observed. Müller et al. [23] explained this behaviour by considering that the crossover of DME through the Nafion<sup>®</sup> membrane does not affect the Pt/C cathode catalyst, because at the cathode potentials, DME is not adsorbed or oxidised at platinum. Then, the constancy of the OCV may indicate that the adsorption of DME at platinum occurs at very close potentials, alloyed or not with Ru or Sn. Ru and Sn appear then to have no ligand effect conversely to what happens in the case of methanol adsorption on PtRu alloys [39] and ethanol adsorption on PtSn alloys [15]. On the other hand, the PtRu and PtSn catalysts lead to higher cell voltages in the low current density region than the Pt catalyst does (Fig. 6b). The performance of the fuel cell working with  $\text{Pt}_{0.5}\text{Ru}_{0.5}$ ,  $\text{Pt}_{0.8}\text{Ru}_{0.2}$  and  $\text{Pt}_{0.9}\text{Sn}_{0.1}$  catalysts are higher than that with the Pt catalyst up to a current density of 20, 250 and  $180 \text{ mA cm}^{-2}$ , respectively. This result is in agreement with those obtained in an electrochemical half cell, where the electrooxidation of DME was shown to start at lower potentials at the PtRu and PtSn catalysts than at a Pt catalyst. This can be explained by the bi-functional mechanism, in which Ru and Sn are able to activate water molecules at lower potentials than Pt does, bringing the missing oxygen atom to complete the oxidation reaction of DME either into  $\text{CO}_2$  and/or  $\text{HCOOH}$ .

Alloying platinum with tin (10% atomic ratio) leads to higher power densities at low current densities than with Pt/C and PtRu/C anodes (Fig. 6b). In this region, the behaviour of the polarisation curves is mainly controlled by the electrocatalytic activity of the catalysts [40–42]. Since platinum cathodes used in all experiments were the same (commercial from E-TEK), coming from the same batch, it can be assumed that the improvement of the electrical performance in this current density range is due to the PtSn catalyst. However, in the high current density region, the electrical performance become lower than that obtained at  $\text{Pt}_{0.8}\text{Ru}_{0.2}$  catalyst, due to the higher slope of the polarisation curve. This can result from the formation of Sn oxides, which are non-catalytic and non-conductive compounds [43].

The  $\text{Pt}_{0.8}\text{Ru}_{0.2}/\text{C}$  anode appears to be the most active one at  $110 \text{ }^\circ\text{C}$  since the highest power density is achieved with it ( $60 \text{ mW cm}^{-2}$ ) at a current density of  $200 \text{ mA cm}^{-2}$  and a cell voltage of 0.3 V, while with the Pt/C catalyst, a maximum power density of  $50 \text{ mW cm}^{-2}$  is achieved at a current density of  $250 \text{ mA cm}^{-2}$  and a cell voltage of 0.2 V. This makes the  $\text{Pt}_{0.8}\text{Ru}_{0.2}/\text{C}$  catalyst more interesting for direct DME fuel cells application. However, the presence of ruthenium has an unexpected effect: for high current densities, i.e. cell voltages below 0.2 V, the voltage of the cell is not stable and decreases

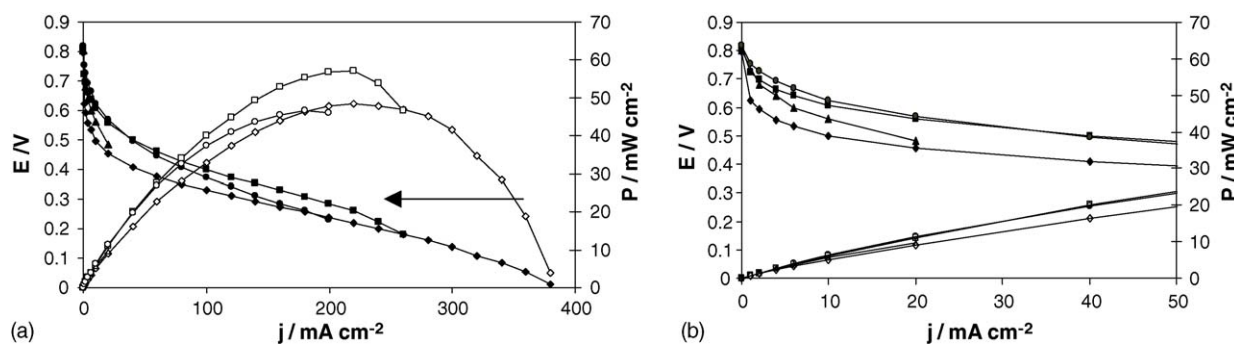


Fig. 6. (a) Cell voltage  $E$  and power density  $P$  vs. current density  $j$  curves in a single  $5\text{ cm}^2$  surface area. (b) Cell voltage  $E$  and power density  $P$  for current density  $j$  curves for current densities lower than  $50\text{ mA cm}^{-2}$  in a single  $5\text{ cm}^2$  surface area FC. Pt/C ( $\blacklozenge$  and  $\diamond$ ); Pt<sub>0.5</sub>Ru<sub>0.5</sub>/C ( $\blacktriangle$  and  $\triangle$ ); Pt<sub>0.8</sub>Ru<sub>0.2</sub>/C ( $\blacksquare$  and  $\square$ ); Pt<sub>0.9</sub>Sn<sub>0.1</sub>/C ( $\bullet$  and  $\circ$ ) anodes at  $110^\circ\text{C}$  (1.65 M DME in water, Nafion<sup>®</sup> 117 membrane;  $P_{\text{O}_2} = 2\text{ bar}$ ;  $P_{\text{DME}} = 3\text{ bar}$ ).

rapidly towards 0, whatever the cell temperatures and the reactants flow rates and pressures are. Moreover, this phenomenon is amplified with higher ruthenium content in the catalyst. For the Pt<sub>0.5</sub>Ru<sub>0.5</sub>/C catalyst, these instability and drastic decrease of the cell voltage take place at 0.45 V, which corresponds to a current density between 40 and  $50\text{ mA cm}^{-2}$ . This general behaviour of PtRu catalysts in presence of DME was already described by Tsutsumi et al. [17], but no explanation was given. However, it can be proposed that the adsorption of DME at platinum needs several adjacent sites to occur and that increasing the ruthenium content in the catalyst leads to dilute the platinum adsorption sites and to decrease the accessibility of DME. Therefore, at a given current density, the voltage decreases drastically. And indeed, in previous investigations on DME adsorption at platinum catalyst [25], the calculation of the number of electron per adsorption site needed to oxidize the adsorbed species coming from DME and further the calculation of the number of adsorbed molecule per platinum site led to propose that bridge bonded CO was a reaction intermediate of the DME oxidation. This was confirmed in the same study by in situ IR reflectance spectroscopy measurements on bulk platinum, where, bridge and linearly bonded adsorbed CO species were detected at very low potentials (close to 0.1 V versus RHE). But, to elucidate this behaviour of PtRu catalysts in a direct DME fuel cell, some spectroelectrochemical experiments have to be done and could give some answer to that problem.

The comparison of the electrical performances of fuel cells fed with DME and methanol was carried out. The  $E(j)$  and  $P(j)$  curves obtained at a cell temperature of  $110^\circ\text{C}$  are given in Fig. 7. Even if the working conditions are slightly different, methanol leads to a power density twice higher than DME,  $120\text{ mW cm}^{-2}$  against  $60\text{ mW cm}^{-2}$ . But it has to be noted that the anode catalyst used in these experiments was optimised for methanol electrooxidation [19,20]. It is likely that the formulation of the optimised anode catalyst for DME electrooxidation is different, as it is the case for ethanol oxidation [28,29]. However, the results obtained with non-optimised electrodes are rather encouraging. This indicates the necessity to investigate further the DME electrooxidation in order to determine the mechanism at platinum electrodes and to propose electrode formulation leading to enhance the activity and selectivity towards CO<sub>2</sub> formation.

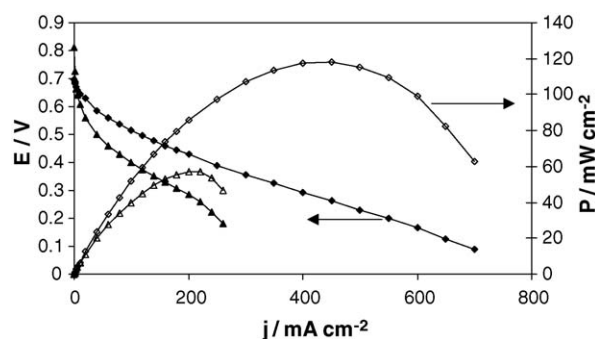


Fig. 7. Cell voltage  $E$  and power density  $P$  vs. current density  $j$  curves in a single  $5\text{ cm}^2$  surface area FC with a Pt<sub>0.8</sub>Ru<sub>0.2</sub>/C at  $110^\circ\text{C}$  (Nafion<sup>®</sup> 117 membrane); ( $\blacklozenge$  and  $\diamond$ ) MeOH 2.0 M,  $P_{\text{O}_2} = 3\text{ bar}$ ;  $P_{\text{MeOH}} = 2\text{ bar}$ ; ( $\blacktriangle$  and  $\triangle$ ) DME 1.65 M,  $P_{\text{O}_2} = 2\text{ bar}$ ;  $P_{\text{DME}} = 3\text{ bar}$ .

#### 4. Conclusion

Platinum is active for DME electrooxidation, but fuel cell performance remains relatively low. The role of electrocatalysis is important. It was shown that alloying platinum with either ruthenium or tin leads to increase the activity at low potentials in a standard half electrochemical cell. However, in DDMEFC the behaviour of PtRu electrodes is rather unexpected: the more the content of ruthenium, the less the stability under operating conditions. It seems that the presence of ruthenium decreases the ability of platinum to adsorb DME by diluting the adsorption sites. But, for low ruthenium content, the fuel cell performance was increased compared with that obtained at a pure platinum catalyst. Ruthenium leads to increase the role of the bi-functional mechanism in the whole process, but conversely to what happens with methanol, it displays no ligand effect for DME adsorption. In fact, the addition of ruthenium or tin does not influence the OCV of the cell, i.e. the poisoning of the electrode at low anodic overpotential. This indicates the hard work to do in order to develop a new electrocatalyst more active towards DME electrooxidation and less poisoned by species coming from the dissociative adsorption of DME. The electrical performance of a fuel cell fed with liquid DME is half lower than that obtained with a DMFC, but remains encouraging considering that the anode catalyst was optimised for DMFC but not for DME electrooxidation.

## References

- [1] F.N. Büchi, S. Srinivasan, *J. Electrochem. Soc.* 144 (1997) 2767.
- [2] A. Fischer, J. Jindra, H. Wendt, *J. Appl. Electrochem.* 28 (1998) 277.
- [3] K.A. Starz, E. Auer, Th. Lehmann, R. Zuber, *J. Power Sources* 84 (1999) 167.
- [4] J. Shim, D.-Y. Yoo, J.-S. Lee, *Electrochim. Acta* 45 (2000) 1943.
- [5] D. Chu, R. Jiang, C. Walker, *J. Appl. Electrochem.* 30 (2000) 365.
- [6] M.K. Ravikumar, A.K. Shukla, *J. Electrochem. Soc.* 143 (1996) 2601.
- [7] X. Ren, M.S. Wilson, S. Gottesfeld, *J. Electrochem. Soc.* 143 (1996) 12.
- [8] M. Straumann, M. Dupont, D. Buttin, J.-C. Dubois, *Fuel Cells Bull.* 3 (2000) 11.
- [9] A.K. Shukla, C.L. Jackson, K. Scott, R.K. Raman, *Electrochim. Acta* 47 (2002) 3401.
- [10] C. Coutanceau, A.F. Rakotondrainibe, A. Lima, E. Garnier, S. Pronier, J.-M. Léger, C. Lamy, *J. Appl. Electrochem.* 34 (2004) 61.
- [11] W. Zhou, Z. Zhou, S. Song, W. Li, G. Sun, P. Tsiakaras, Q. Xin, *Appl. Catal. B: Environ.* 46 (2003) 273.
- [12] C. Lamy, S. Rousseau, E.M. Belgsir, C. Coutanceau, J.-M. Léger, *Electrochim. Acta* 49 (2004) 3901.
- [13] F. Vigier, C. Coutanceau, A. Perrard, E.M. Belgsir, C. Lamy, *J. Appl. Electrochem.* 34 (2004) 439.
- [14] W. Zhou, W. Li, S. Song, Z. Zhou, L. Jiang, G. Sun, Q. Xin, K. Poulantitis, S. Kontou, P. Tsiakaras, *J. Power Sources* 131 (2004) 217.
- [15] F. Vigier, C. Coutanceau, F. Hahn, E.M. Belgsir, C. Lamy, *J. Electroanal. Chem.* 563 (2004) 81.
- [16] M.M. Mensh, H.M. Chance, C.Y. Wang, *J. Electrochem. Soc.* 151 (2004) 1.
- [17] Y. Tsutsumi, T. Moriyama, S. Kajitani, in: V.W. Wong (MIT) (Ed.), *Proceeding of the 2000 Spring Technical Conference of the ASME Internal Combustion Engine Division, ICE vol. 34-3, 2000*, pp. 58–63.
- [18] H. Bönemann, W. Brijoux, R. Brinkmann, E. Dinjus, T. Jousen, B. Korall, *Angew. Chem. Int. Engl.* 30 (1991) 1312.
- [19] L. Dubau, C. Coutanceau, E. Garnier, J.-M. Léger, C. Lamy, *J. Appl. Electrochem.* 33 (2003) 419.
- [20] L. Dubau, F. Hahn, C. Coutanceau, J.-M. Léger, C. Lamy, *J. Electroanal. Chem.* 554–555 (2003) 407.
- [21] J.-M. Léger, S. Rousseau, C. Coutanceau, F. Hahn, C. Lamy, *Electrochim. Acta* 50 (2005) 5118.
- [22] F. Gloaguen, F. Andolfatto, R. Durand, P. Ozil, *J. Appl. Electrochem.* 24 (1994) 863.
- [23] J.T. Müller, P.M. Urban, W.F. Hölderich, K.M. Colbow, J. Zhang, D.P. Wilkinson, *J. Electrochem. Soc.* 147 (2000) 4058.
- [24] F.N. Büchi, S. Srinivasan, *J. Electrochem. Soc.* 144 (1997) 2767.
- [25] G. Kéranguéven, C. Coutanceau, E. Sibert, F. Hahn, J.-M. Léger, C. Lamy, *J. Appl. Electrochem.*, in press.
- [26] T.J. Schmidt, H.A. Gasteiger, R.J. Behm, *Electrochem. Com.* 1 (1999) 1.
- [27] A. HPPamnett, *Mechanism of methanol oxidation*, in: A. Wieckowski (Ed.), *Interfacial Electrochemistry, Theory, Experiments and Applications*, vol. 47, Marcel Dekker, New York, 1999, pp. 843–883.
- [28] Y. Morimoto, E.B. Yeager, *J. Electroanal. Chem.* 441 (1998) 77.
- [29] Y. Morimoto, E.B. Yeager, *J. Electroanal. Chem.* 444 (1998) 95.
- [30] A.C. Boucher, PhD Thesis, University of Poitiers, 2002.
- [31] F. Delime, J.-M. Léger, C. Lamy, *J. Appl. Electrochem.* 29 (1999) 1249.
- [32] C. Lamy, E.M. Belgsir, J.-M. Léger, *J. Appl. Electrochem.* 31 (2001) 799.
- [33] W.J. Zhou, S.Q. Song, W.Z. Li, Z.H. Zhou, G.Q. Sun, Q. Xin, S. Douvartzides, P. Tsiakaras, *J. Power Sources* 140 (2005) 50.
- [34] H.A. Gasteiger, N. Markovic, P.N. Ross, E.J. Cairns, *J. Electrochem. Soc.* 141 (1994) 1795.
- [35] R. Ianello, V.M. Schmidt, U. Stimming, J. Stumper, A. Wallau, *Electrochim. Acta* 39 (1994) 1863.
- [36] Y. Tsutsumi, Y. Nakano, S. Kajitani, S. Yamasita, *Electrochemistry* (2002) 984.
- [37] A. Kabbabi, R. Faure, R. Durand, B. Beden, F. Hahn, J.-M. Leger, C. Lamy, *J. Electroanal. Chem.* 444 (1998) 41.
- [38] C. Lamy, A. Lima, V. LeRhun, F. Delime, C. Coutanceau, J.-M. Léger, *J. Power Sources* 105 (2002) 283.
- [39] P. Waszczuk, A. Wieckowski, P. Zelenay, S. Gottesfeld, C. Coutanceau, J.-M. Léger, C. Lamy, *J. Electroanal. Chem.* 511 (2001) 55.
- [40] J. Kim, S.M. Lee, S. Srinivasan, C.E. Chamberlin, *J. Electrochem. Soc.* 142 (1995) 2670.
- [41] D.R. Sena, E.A. Ticianelli, V.A. Paganin, E.R. Gonzalez, *J. Electroanal. Chem.* 477 (1999) 164.
- [42] M.P. Hogarth, T. Ralph, *Platinum Metals Rev.* 46 (2002) 146.
- [43] S. Rousseau, PhD Thesis, University of Poitiers, France, 2004.