

Polyoxymethylenedimethylether ($\text{CH}_3\text{—O—}(\text{CH}_2\text{—O})_n\text{—CH}_3$) oxidation on Pt and Pt/Ru supported catalysts

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Abstract

Polyoxymethylenedimethylethers $\text{CH}_3\text{—O—}(\text{CH}_2\text{—O})_n\text{—CH}_3$ with n varying from 1 to 4 are studied for a possible application as fuels in PEMFC. Cyclic voltammetry is performed at Pt, Pt/Ru(50/50), Pt/Ru(80/20) electrodes in acidic medium to evaluate their electroactivity. Electrical performance of the fuels are evaluated in a 5 cm^2 direct fuel cell for different temperatures and pressures with Pt and Pt/Ru(50/50) catalysts at the anode and Pt at the cathode. The determination of the reaction products is performed in a 25 cm^2 direct fuel cell under working conditions at constant current for 3 h. Preliminary results are very promising regarding achieved power densities. Results pointed out the important role of hydrolysis of these compounds into methanol and formaldehyde in electroactivity. It is probable that the cell performances are due to the oxidation of the products coming from hydrolysis rather than to direct oxidation of the polyoxymethylenedimethylethers. Polyoxymethylenedimethylethers appear to be attractive candidates as alternative to methanol, which moreover is a toxic (neurotoxin) molecule.

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1. Introduction

Low temperature Fuel Cells are very promising power supplies for different applications such as transportation (propulsion and/or Auxiliary Power Units) [1,2], nomad devices (mobile phones, computer, emergency, etc.) [3,4] or stationary systems [5,6].

Because of the difficulty of handling and storing of hydrogen (which is the most efficient fuel), many research groups tend to develop the direct combustion of liquid fuels: the drastic decrease in overall mass energy density when hydrogen is stored makes the use of liquid fuels, such as alcohols, very attractive. Amongst the most studied fuels, methanol and ethanol can be cited. With methanol, which only contains one carbon atom, power densities in the range of $150\text{--}200\text{ mW cm}^{-2}$ can be achieved at $90\text{ }^\circ\text{C}$ [7–10], which makes methanol a good liquid fuel. But, because of its high toxicity, methanol does not appear as the best candidate, mainly for vehicle and nomad

applications (cellular phone). Other alcohols have been considered and studied for this purpose. Ethanol is of course the most often studied [11,12] because it is the simplest alcohol after methanol; it displays a limited toxicity and can be produced from biomass (whereas methanol is mainly produced from natural gas). Other oxygenated compounds were also considered for their potential use in fuel cell: dimethyl ether [13–18] and other methoxy fuel [15,19,20]. The direct combustion of polyoxymethylenedimethylethers ($\text{R—O—}(\text{CH}_2\text{O})_n\text{—R}$) compounds in a fuel cell can also be an alternative [21]. Some physico-chemical characteristics are given in Table 1. These compounds are liquid at room temperature and thus easy to store. Although their solubility in water decreases with increasing number of oxymethylene groups, these compounds are a good potential “reservoir” of C1-like species. Other possible advantages for their use as fuel in fuel cells are the followings:

1. no C–C bonds to cleave, then a complete oxidation into CO_2 of polyoxymethylenedimethylethers can be foreseen,
2. the crossover of the ionomeric membrane by polyoxymethylenedimethylethers could be limited due to the size of the molecules,

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Table 1
Physicochemical characteristics of methanol, formaldehyde and polyoxymethylenedimethylethers

Molecule	Boiling point (°C)	Density	Flash point (closed cup, °C)	Solubility in water at 20 °C (wt.%)	Molar weight (g mol ⁻¹)
CH ₃ –(OCH ₂)–OCH ₃ , dimethoxymethane	42	0.8558	–18	32.3	76
CH ₃ –(OCH ₂) ₂ –OCH ₃ , POM-M ₂	105	0.9597	14	30	106
CH ₃ –(OCH ₂) ₃ –OCH ₃ , POM-M ₃	156	1.024	n.d.	28	136
CH ₃ –(OCH ₂) ₄ –OCH ₃ , POM-M ₄	202	1.0678	n.d.	n.d.	166
CH ₃ OH methanol	65	0.79	12	∞	32
HCHO formaldehyde	–21	–	–	∞	30

n.d., non determined.

3. polyoxymethylenedimethylethers display lower toxicity than methanol.

For these reasons, it is important to estimate the electroactivity of these compounds under fuel cell operating conditions. The aim of such a study is to compare the behavior of the different compounds of this alternative fuel family in order to determine the optimum value of n (number of oxymethylene units), in terms of electrical performance and reaction product distribution. In the present paper, the activity of platinum-based electrocatalysts towards polyoxymethylenedimethylethers oxidation is considered. Results on the performance of Direct Polyoxymethylenedimethylethers Fuel Cell are reported and discussed according to the catalysts composition. Stability under operating conditions and product distributions in the anode compartment were also evaluated.

2. Experimental

2.1. Electrochemical measurements

The electrochemical set-up consists of a Voltalab PGZ 402 potentiostat controlled by a computer, a Radiometer Speed Control Unit CTV 101 and a rotating disk electrode (RDE) Radiometer BM-EDI 101. The solutions were prepared from H₂SO₄ (Suprapur, Merck), polyoxymethylenedimethylethers (called POM-M_{*n*}, synthesized and provided by ARKEMA) and ultra-pure water (MilliQ, Millipore, 18 MΩ cm). The electrochemical experiments were carried out at 20 °C in N₂-purged (U quality from Air Liquide) 0.1 M H₂SO₄ as support electrolyte and 0.1 POM-M_{*n*}, using a conventional thermostated standard three-electrode electrochemical cell. The counter electrode was a glassy carbon plate (8 cm² geometric surface area) and the reference electrode was a mercury mercurous sulphate electrode (MSE) in contact with a saturated K₂SO₄ solution; the electric circuit being completed by a Luggin capillary for the reference electrode. However, all potentials are related to the reversible hydrogen electrode (RHE). CVs are recorded at a potential scan of 50 mV s⁻¹ in sulphuric acid medium (0.1 M). The working electrode is a glassy carbon (GC) rotating disc and the rotation rate is 2000 rpm. The surface area is 0.07 cm². The reference electrode is a mercury–mercurous sulphate (MSE) electrode. All potentials are referred to the reversible hydrogen electrode (RHE).

Pt/C and PtRu(1:1)/C catalysts from E-TEK and home made PtRu(8:2)/C are used in this study. The home made catalyst is prepared using a method derived from that of Bönneken et al. [22,23]. The synthesis method is described elsewhere [24,25]. The morphology of this kind of dispersed catalyst was described elsewhere [24–26].

The electrode was prepared according to a method developed by Gloaguen et al. [27], which briefly consist to the addition under stirring of 25 mg of the catalytic powder to a mixture of 0.5 cm³ of Nafion[®] solution (5 wt.% from Aldrich) and 2.5 cm³ of ultrapure water (Millipore MilliQ – 18 MΩ cm). After ultrasonic homogenisation, the dispersed catalysts were deposited on a vitreous carbon disc (0.071 cm² geometric surface area) in order to obtain a metal loading close to 0.068 mg cm⁻². Three different electrodes were used: Pt (40 wt.%)/C and Pt_{0.5}Ru_{0.5} (30 wt.%)/C from E-TEK, and homemade Pt_{0.8}Ru_{0.2}/C.

2.2. HPLC analysis

A high performance liquid chromatograph (Dionex CHROMELEON[®]) fitted with an isocratic pump, an auto-sampler, a refractometer detector was used to analyze qualitatively the reaction products at the outlet of the anode side of the fuel cell and quantitatively the permeation of POM-M_{*n*} through a Nafion[®] 117 membrane. An Aminex Ion Exclusion HPX-87H column was used with an eluent (0.01 M H₂SO₄ solution) flow of 0.6 mL min⁻¹.

Formic acid and formaldehyde are trapped in a first flask. Because formaldehyde is a very volatile compound, a second flask is used to trap the gaseous aldehyde in a 2.4 DNPH acidic solution. A last flask containing a NaOH 1 M solution is used to trap CO₂ by generating CO₃²⁻ that could be then analyzed by HPLC. The experimental analysis set-up is described elsewhere [28].

2.3. Fuel cell tests

Fuel cell tests in single 5 or 25 cm² geometric surface area cells are carried out with a Globe Tech test bench. The cell voltage U versus the current density j and the power density P versus the current density 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. The cathodes (Pt/C) and anodes (PtRu/C)

were supplied by ETEK. The gas diffusion electrode layers were loaded 30 wt.%. PTFE. The metal and Nafion® loadings of the electrodes are 2.0 mg cm^{-2} and 0.8 mg cm^{-2} , respectively. The membrane electrode assemblies (MEA) were prepared by hot-pressing (35 kg cm^{-2} at 130°C for 90 s). Two series of tests were performed:

- Evaluation of the activity of each catalyst towards electrooxidation of POM- M_n . These tests are carried out in a 5 cm^2 active area cell.
- Identification of the oxidation products. These tests are carried out at 80°C with constant current density of 80 mA cm^{-2} (2 A) for 3 h in a 25 cm^2 active surface area fuel cell. The value of the applied current has to be high enough to lead to the formation of sufficient amount of products, but low enough to avoid limitation due to the mass transfer. Therefore, the electrical characteristics of the 25 cm^2 MEA (j - U polarisation curves and P - j power curves) are first determined.

3. Results and discussion

3.1. Cyclic voltammetry (CV) experiments at a Pt/C electrode

Three different supported catalysts are used to compare their activity towards the electrooxidation of polyoxymethylenedimethylethers (dimethoxymethane or POM- M_1 , POM- M_2 , POM- M_3 and POM- M_4). The goal of this preliminary work is to check electroreactivity of these compounds in comparison with methanol for a possible use in PEMFC. In acid medium POM- M_n are partially hydrolyzed into methanol and formaldehyde, according to the following equation:

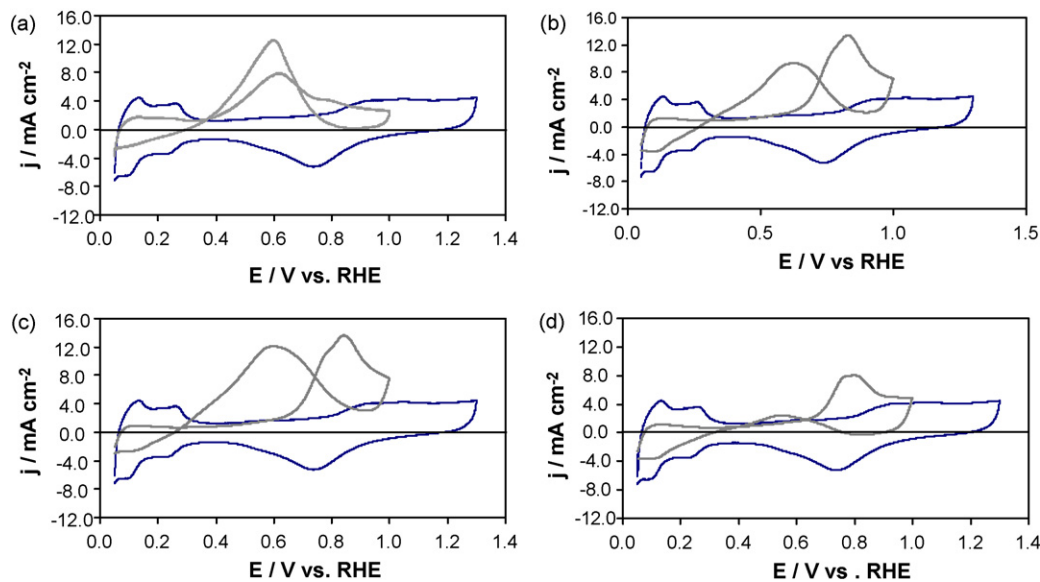
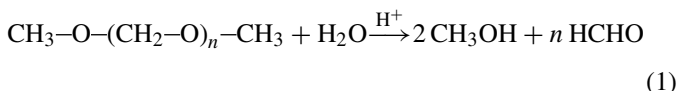


Fig. 1. Cyclic voltammograms recorded on Pt (40 wt.%) / C catalysts from E-TEK in $0.1 \text{ M H}_2\text{SO}_4 + 0.1 \text{ M POM-}M_n$ at $v = 50 \text{ mV s}^{-1}$ and 20°C . (a) Dimethoxymethane; (b) POM- M_2 ; (c) POM- M_3 ; (d) POM- M_4 . In each graph are represented the Pt/C cyclic voltammogram in support electrolyte (black plain line —).

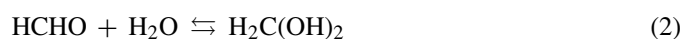
For example, HPLC analysis of a 24 h aged solution of $1 \text{ M POM-}M_2$ in $1 \text{ M H}_2\text{SO}_4$ leads to the detection of methanol and formaldehyde (1.1 mol L^{-1} and 1.03 mol L^{-1} , respectively), i.e. to the hydrolysis of half of the POM- M_2 molecules ($\text{CH}_3\text{O}-(\text{CH}_2\text{O})_2-\text{CH}_3 + \text{H}_2\text{O} \rightarrow 2\text{CH}_3\text{OH} + 2\text{HCHO}$).

Therefore, our first approach consists to investigate the behavior of electrocatalysts known to be active for methanol and formaldehyde electrooxidation.

The $j(E)$ curves (where E is the electrode potential and j the current density) obtained at a Pt/C catalyst in presence of different POM- M_n are given in Fig. 1. The oxidation wave differs according to the nature of POM- M_n . For n from 2 to 4 the same shape of the $j(E)$ curves is obtained, the only difference being the lower achieved current densities with POM- M_4 , which can reveal a lower reactivity of this latter compound. The most reactive fuel is dimethoxymethane. Clearly, the oxidation wave starts at lower potential than for the other POM- M_n and the maximum current density is reached between 0.5 and 0.6 V/RHE against 0.8 V vs. RHE for higher values of n . However, a second oxidation peak appears between 0.7 and 0.8 V vs. RHE . Only one peak at 0.6 V vs. RHE was observed in the negative potential scan direction and the related current density was higher than that of the peak in the positive scan direction (10.8 mA cm^{-2} and 6.2 mA cm^{-2} , respectively). In the positive potential scan the maximum current densities obtained with POM- M_2 , POM- M_3 and POM- M_4 was recorded close to 0.85 V vs. RHE , whereas in the negative potential direction the maximum current densities are located at a potential close to 0.6 V vs. RHE . Such a behavior is clearly the consequence of the poisoning of the electrode at low potential at Pt catalyst.

Unlike a shoulder located close to 0.7 V vs. RHE , the polarization curves for n from 2 to 4 looks like that of methanol electrooxidation at platinum with a decreased hydrogen region, an onset of the oxidation wave close to 0.6 V vs. RHE and a maximum of the oxidation peak located close to 0.85 V vs. RHE . In

contrary, the oxidation curve of dimethoxymethane displays a main peak starting at a potential of 0.3 V vs. RHE, i.e. 0.2–0.3 V lower than that generally obtained with methanol at Pt electrocatalyst. Miki et al. [29] studied the catalytic electrooxidation of formaldehyde. They obtained, at a Pt film electrode formed by electroless plating, two oxidation peaks located close to those obtained in this study. However, these peaks were visible only for the first two potential cycles. The repetition of potential cycles led to a positive shift of the main oxidation peak from 0.7 to 0.85 V vs. RHE and an important increase of its oxidation current densities. At the same time, the current densities of the first oxidation prepeak in the low overpotentials region (from 0.3 to 0.7 V vs. RHE) disappeared. They attributed this behavior to the acid-catalyzed decomposition of dimethoxymethane to methanol [19]. In our case, using dispersed nanoparticles of platinum, the same behavior was recorded in the first and fifth potential cycles. Nevertheless, the shoulder observed close to 0.8 V/RHE fits with the peak observed with methanol and is probably due to the oxidation of the species coming from dimethoxymethane hydrolysis. Therefore, it seems that the kinetics of dimethoxymethane decomposition depends also on the electrode surface and is increased at platinum film compared with nanoparticles. The main question remains the identification of the oxidation products from 0.3 to 0.6 V vs. RHE while no OH species is expected to be adsorbed at the platinum surface in this potential range. Surface-enhanced infrared study performed during the first potential cycle of dimethoxymethane oxidation by Miki et al. [29] only identified characteristic bands of linear and bridged CO at low potentials and of formate at potentials higher than 0.6 V vs. RHE, but no reaction products leading to explain the oxidation current density from 0.3 to 0.6 V vs. RHE. On the basis of Electromodulated Infrared Spectroscopy (EMIRS) studies, Olivi et al. [30,31] proposed that formaldehyde reacts reversibly with water to form methylene glycol according to the following reaction:



Then methylene glycol can be further oxidized into either HCOOH or CO₂ according to the following reactions:

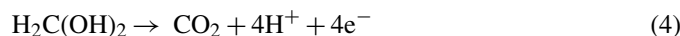


Fig. 2 compares the $j(E)$ curves obtained in the first and fifth voltammetric cycles in the case of POM-M₃. One can see the appearance of a prepeak between 0.4 and 0.65 V vs. RHE which did not exist in the first potential cycle. This prepeak appears for all tested polyoxymethylenedimethylethers with $n > 1$. The shape of this voltammogram looks like a combination of those of methanol and formaldehyde electrooxidation. Such a prepeak was already observed by Olivi et al. [30] during formaldehyde electrooxidation. Also, the onset potential of this prepeak is close to that of the onset potential of dimethoxymethane as it is shown in Fig. 3. This prepeak is likely due to the oxidation formaldehyde coming from hydrolysis of the POM-M_n. Therefore, polyoxymethylenedimethylethers clearly display a significant electroreactivity. They can be then considered, at

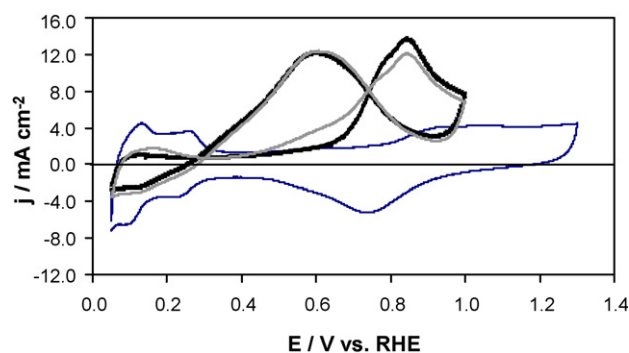


Fig. 2. (—) first and (—) fifth potential cycles recorded on Pt (40 wt.%) / C catalysts from E-TEK in 0.1 M H₂SO₄ + 0.1 M POM-M₃ at $v = 50 \text{ mV s}^{-1}$ and 20 °C. Black plain line (—) is for Pt/C cyclic voltammogram in support electrolyte.

least partially, as C1 compounds storage for fuel cell application, which are produced by hydrolysis.

3.2. Cyclic voltammetry (CV) experiments at PtRu/C electrodes

In their work about electrooxidation of formaldehyde, Olivi et al. [30,31] also showed that CO formation is faster in methanol-containing solutions than in pure formaldehyde solutions. Therefore, the adsorption sites for methylene glycol electrooxidation are directly blocked by CO and the activity of the electrode is decreased. Considering the hypothesis that methanol is produced from the hydrolysis of POM-M_n, it was then interesting to test the electroactivity of PtRu alloys which are known to be the most active catalysts for methanol oxidation [32–36]. Fig. 4 displays the $j(E)$ curves obtained in presence of POM-M_n at PtRu/C catalysts with different atomic ratios.

In the case of dimethoxymethane, addition of ruthenium to platinum does not lead to decrease the onset potential of the oxidation wave decreases the electrocatalytic activity of the catalyst. This behavior was rather unexpected considering fuel cell results (see next Section). However, the higher the ruthenium content the lower the achieved current densities, over the whole studied potential range. In acid medium the hydrolysis of one molecule of dimethoxymethane leads to two molecules

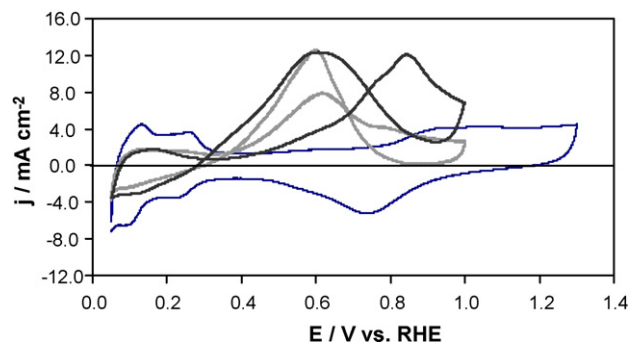


Fig. 3. Cyclic voltammograms recorded on Pt (40 wt.%) / C catalysts from E-TEK in 0.1 M H₂SO₄ + 0.1 M POM-M_n at $v = 50 \text{ mV s}^{-1}$ and 20 °C. (—) Dimethoxymethane; (—) POM-M₃. (—) is for Pt/C cyclic voltammogram in support electrolyte.

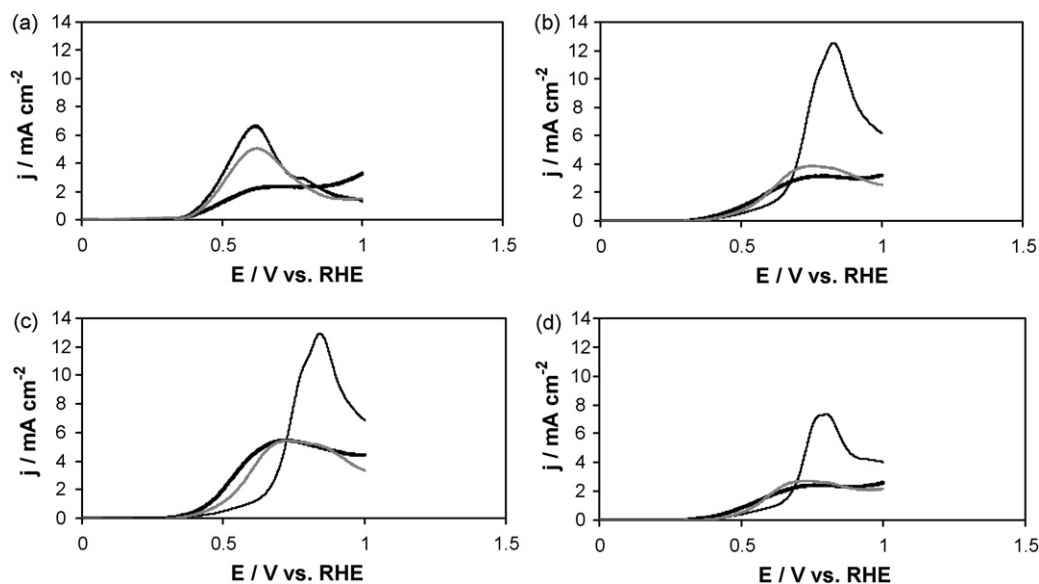


Fig. 4. cyclic voltammograms recorded on different catalysts in 0.1 M H_2SO_4 + 0.1 M POM-M_n at $v = 50 \text{ mV s}^{-1}$ and 20°C . (—)E-TEK Pt (40 wt.%) /C; (——) homemade $\text{Pt}_{0.8}\text{Ru}_{0.2}$ (30 wt.%) /C; (——) E-TEK $\text{Pt}_{0.5}\text{Ru}_{0.5}$ (30 wt.%) /C. (a) Dimethoxymethane; (b) POM-M_2 ; (c) POM-M_3 ; (d) POM-M_4 .

of methanol; it seems then that the presence of ruthenium limits the decomposition of dimethoxymethane into methanol and formaldehyde, at least at low temperature. For $n > 1$, addition of ruthenium to platinum does not decrease the onset potential of the oxidation wave but, conversely to that is observed with dimethoxymethane, it leads to increase the electrocatalytic activity of polyoxymethylenedimethylethers oxidation as higher current densities are achieved from 0.35 V to close to 0.70 V vs. RHE. The maximum of the current density is located at a potential 0.1 V lower than that on pure platinum.

It was expected to obtain a more important positive effect with a $\text{Pt}_{0.8}\text{Ru}_{0.2}/\text{C}$ catalyst than with $\text{Pt}_{0.5}\text{Ru}_{0.5}/\text{C}$, as often observed for methanol oxidation [24,25,37,38]. But, higher current densities are achieved with ruthenium rich catalyst for all polyoxymethylenedimethylethers, conversely to what happens with dimethoxymethane. Moreover, although POM-M_2 and POM-M_3 lead to very close $j(E)$ curves at a Pt/C catalyst, the latter compound is more electroreactive at PtRu catalyst. Hydrolysis of these compounds leads to the formation of methanol and formaldehyde in a ratio of 2:2 and 2:3 with POM-M_2 and POM-M_3 , respectively. The increase of the activity may either be

related to the higher activity of PtRu rich catalyst for the oxidation of formaldehyde or to a concentration effect of reactants. In the case of POM-M_4 (ratio methanol:formaldehyde of 2:4), the electroreactivity is lowered compared with POM-M_3 , which can be due to the increase of the formaldehyde concentration leading to higher surface poisoning. The observed electroactivity in term of maximum achieved current density with $\text{Pt}_{0.5}\text{Ru}_{0.5}/\text{C}$ is relatively low at room temperature, which was already pointed out by Wakabayashi et al. [39] with methoxy fuels. However, the positive effect of ruthenium addition to platinum for POM-M_n with $n > 1$ is demonstrated.

3.3. Fuel cell experiments

The different POM-M_n are tested in a single 5 cm^2 Fuel Cell, with Pt/C and $\text{Pt}_{0.5}\text{Ru}_{0.5}/\text{C}$ electrodes from E-TEK. Experiments are performed either under atmospheric pressure or under 3 bars oxygen and 2 bars POM-M_n . Temperatures are varying from 50 to 90°C . Results are given in Table 2 for all tested compounds. As expected, the increase of the temperature and of the pressure leads to enhance electrical performances of the cell, in terms

Table 2
Maximum power densities obtained at different temperature and fuel pressure in a 5 cm^2 single cell fitted with E-TEK Pt/C and PtRu/C anodes

	Fuel pressure (bar)	Temperature ($^\circ\text{C}$)	P (mW cm^{-2})			
			DMM	POM-M_2	POM-M_3	POM-M_4
Pt/C	1	50	12.4	15.3	20.5	13.0
	1	70	28.2	24.2	21.8	24.3
	1	90	50.0	34.3	23.4	25.6
	2	90	49.8	43.5	35.8	38.8
PtRu/C	1	50	17.9	18.4	22.6	25.9
	1	70	41.0	33.8	38	41.6
	1	90	70.0	39.4	51.3	48.5
	2	90	80.0	53.5	67	73.8

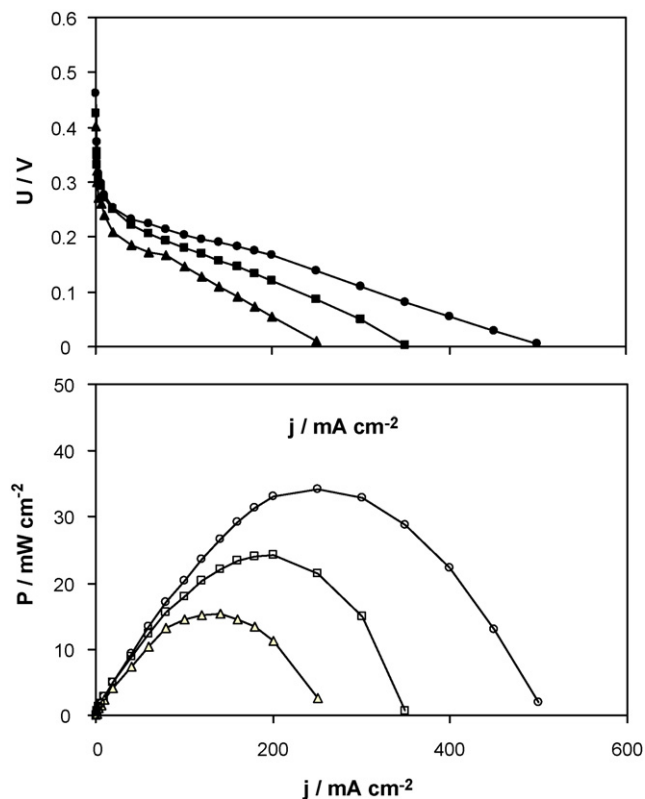


Fig. 5. Cell voltage (plain symbol) and power density (empty symbol) vs. current density curves recorded at different temperatures for 1.0M POM-M₂. (▲, △) 50°C, (■, □) 70°C, (●, ○) 90°C. Anodes and cathodes are E-TEK Pt (40 wt.%)/C, 2.0 mg cm⁻² platinum loading, Nafion® 117 membrane. $P_{O_2} = P_{POM-M_2} = 1$ bar; $d_{O_2} = 120$ mL mn⁻¹, $d_{POM-M_2} = 1$ mL mn⁻¹.

of maximum achieved power density, as it can be seen as an example for POM-M₂ at a Pt/C//Nafion 117//Pt/C assembly in Fig. 5. Such behavior is observed for all studied fuels and with both E-TEK Pt/C and PtRu/C anodes. Fig. 6 shows the electrical performances obtained with an E-TEK Pt/C anode for different pressures of either dimethoxymethane (Fig. 6a) or POM-M₂ (Fig. 6b). For POM-M_n compounds with $n > 1$, the increase of the fuel pressure leads to the increase of the cell electrical performances in terms of open circuit voltage (ocv) and maximum achieved power density. In contrary, the increase of the dimethoxymethane pressure leads to a decrease of the ocv and to the same achieved power density. From 0 to 300 mA cm⁻², the best electrical performances in term of higher achieved power densities (higher cell voltages) are obtained with lower fuel pressure, whereas for higher current density range the increase of the pressure leads to higher power densities. The increase of the fuel pressure can lead to the increase of local fuel concentration and further to higher catalyst poisoning in the low current density range, whereas it can partially avoid the limitation of mass transport in the high current density range. Of course, such explanation should also be given for other POM-M_n. However, this can be explained by considering that dimethoxymethane hydrolysis produces mainly methanol compared to hydrolysis of other POM-M_n and that according to Olivi et al. [30] methanol leads at platinum to higher surface poisoning than formaldehyde in the low anode overpotentials region.

In Fig. 7 are reported the $U(j)$ and $P(j)$ curves obtained in a single cell fitted with a Pt/Ru (50/50) anodes for the different compounds. The positive effect of addition of ruthenium to platinum on electroactivity towards POMM_n oxidation is clearly demonstrated, even for dimethoxymethane, conversely to the obtained results in a three-electrode electrochemical cell. In this

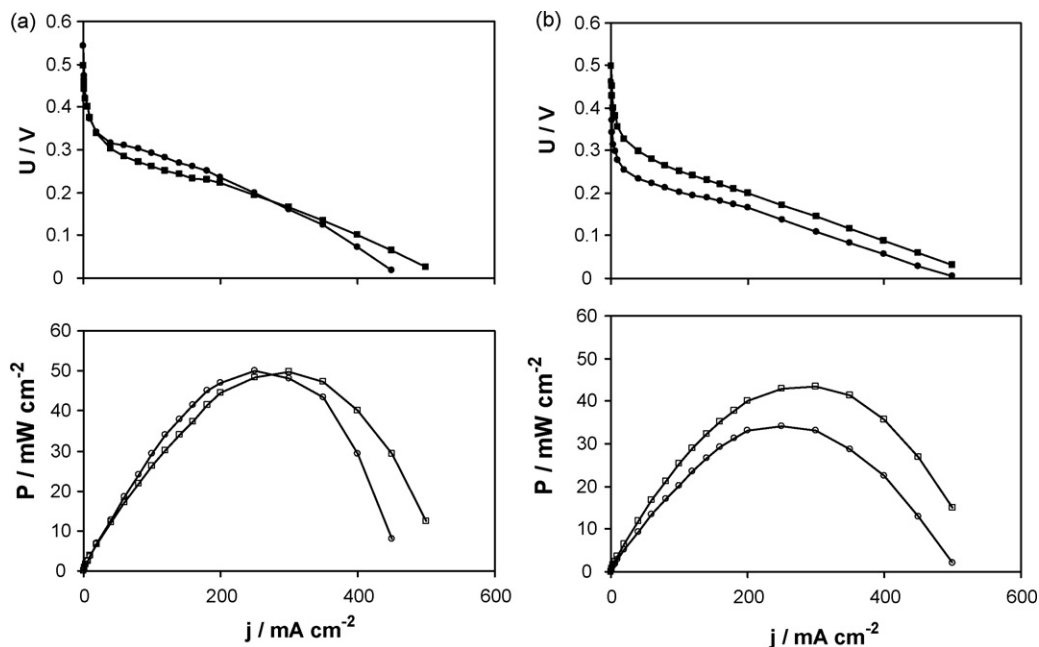


Fig. 6. Direct Oxidation Fuel Cell voltage (plain symbol) and power density (empty symbol) vs. current density curves recorded at 90°C for different pressures for (a) 1.0M dimethoxymethane and (b) 1.0M POM-M₂. (●, ○) $P_{O_2} = P_{POM-M_n} = 1$ bar, (■, □) $P_{O_2} = 3$ bar, $P_{POM-M_n} = 2$ bar. Anodes and cathodes are E-TEK Pt (40 wt.%)/C, 2.0 mg cm⁻² platinum loading, Nafion® 117 membrane; $d_{O_2} = 120$ mL mn⁻¹, $d_{POM-M_2} = 1$ mL mn⁻¹.

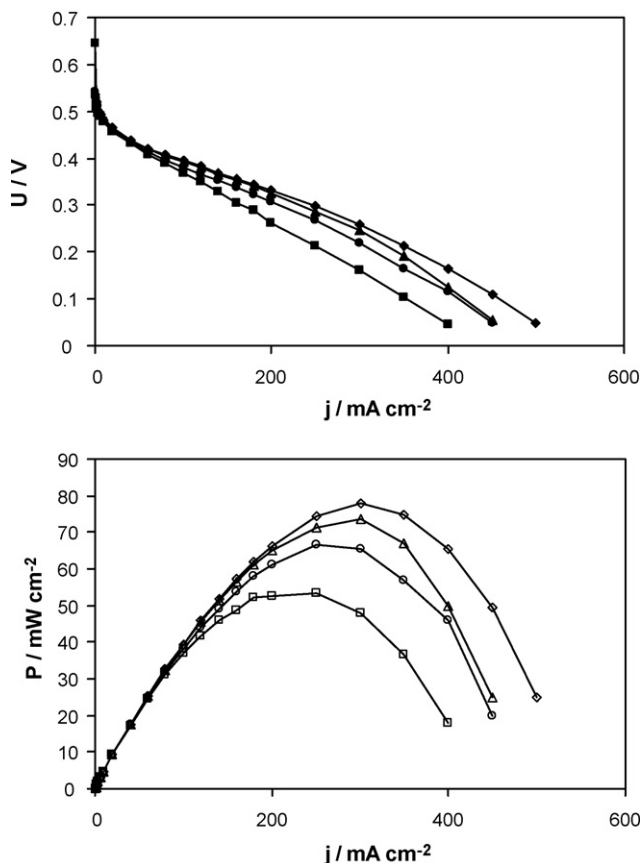


Fig. 7. Direct Oxidation Fuel Cell voltage (plain symbol) and power density (empty symbol) vs. current density curves recorded at 90 °C with different fuels. (◆, ◇) dimethoxymethane 1.0M, (■, □) POM-M₂ 1.0M, (●, ○) POM-M₃ 1.0M, (▲, △) POM-M₄ 1.0M. Cathode E-TEK Pt (40 wt.%)/C, 2.0 mg cm⁻² platinum loading, anode E-TEK Pt_{0.5}Ru_{0.5} (60 wt.%)/C, 2.0 mg cm⁻² metal loading, Nafion[®] 117 membrane. $P_{O_2} = 3$ bar, $P_{POM-M_n} = 2$ bar; $d_{O_2} = 120$ mL mn⁻¹, $d P_{POM-M_n} = 1$ mL mn⁻¹.

case, the maximum achieved power density increases from about 50 to 80 mW cm⁻². But, for all other POM-M_n compounds Pt/Ru is always more active than Pt, the benefic effect of the addition of Ru increasing with increasing n to reach a factor two for POM-M₃ and POM-M₄.

The important increase of the cell performance by addition of ruthenium to platinum in the case of dimethoxymethane was not expected regarding the cyclic voltammetry results. It is likely that at 90 °C, the hydrolysis of dimethoxymethane is higher [39] and is no more a limitation for the reaction, conversely to what is proposed at room temperature in a conventional three-electrode electrochemical cell. For the other POM-M_n the increase of the effect of ruthenium with the increase of n can be related to the increase of the local concentration of C1 hydrolysis compounds, notably of formaldehyde, which conversely to what happens with methanol involves a low poisoning effect of the surface. However, PtRu/C is known to be the most active electrocatalyst for methanol oxidation. But in the present case, methanol is not the only formed product by hydrolysis; it is likely that formaldehyde, POM-M_n with lower values of n can also be formed. Therefore, an optimisation of the anodic catalysts may probably lead to improved performances. It is likely that multi-

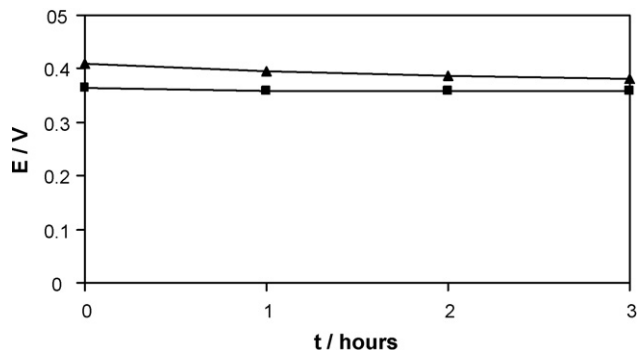


Fig. 8. $E(t)$ curves record at 80 °C in a Direct Oxidation Fuel Cell fed with (▲) 1.0M methoxymethane and (■) 1.0M POM-M₂. Cathode E-TEK Pt (40 wt.%)/C, 2.0 mg cm⁻² platinum loading, anode E-TEK Pt_{0.5}Ru_{0.5} (60 wt.%)/C, 2.0 mg cm⁻² metal loading, Nafion[®] 117 membrane. $P_{O_2} = 3$ bar, $P_{POM-M_n} = 2$ bar; $d_{O_2} = 120$ mL mn⁻¹, $d P_{POM-M_n} = 1$ mL mn⁻¹.

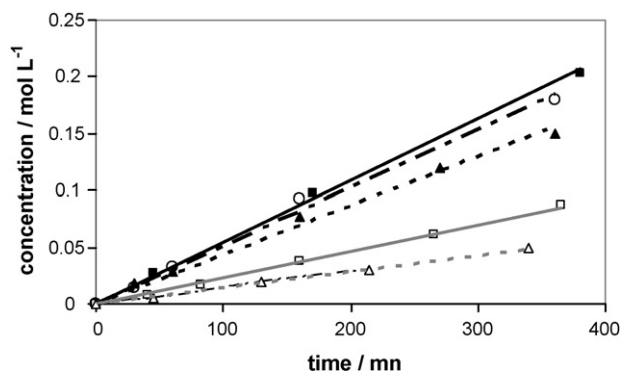
functional catalysts are required to improve the electroreactivity of the POM-M_n compounds and/or their hydrolysis to avoid mass transfer limitation at medium and high current densities.

These preliminary measurements under fuel cell conditions are very promising because without catalysts optimisation acceptable maximum power densities are achieved (Fig. 7) under our experimental conditions. Moreover, a relatively good stability in fuel cell electrical performance is obtained for temperatures close to 90 °C, as it is shown as an example in Fig. 8, with a single 25 cm² fuel cell fitted with a Pt/Ru (50/50) E-TEK electrode and fed with either 1.0 M dimethoxymethane or POM-M₂, at 80 °C under a constant current of 2 A (80 mA cm⁻²). During these experiments, the reaction products collected at the outlet of anode (with 1.0 M dimethoxymethane and 1.0 M POM-M₂ as fuel) were identified by high performance liquid chromatography in order to have a better understanding of the reaction pathway. Under our experimental conditions, a quantity of electricity of 21600 C was consumed for the oxidation reaction. Analytical results are reported in Table 3. The amounts of remaining dimethoxymethane and POM-M₂ after the experiment were 0.32 M and 0.29 M, respectively. The carbon balance is very low, being 60% and 66% for dimethoxymethane and POM-M₂, respectively. This can be explained by the crossover of products through the membrane. The crossover of POM-M_n has not been determined directly under fuel cell working conditions, but the permeability of the Nafion[®] 117 membrane has been determined at room temperature in a two-compartment cell [40]. Fig. 9 displays the variation of concentration in the sample compartment as a function of time for methanol, dimethoxymethane and POM-M_n. The permeation through the membrane diminishes with the increase of the carbon number. The main result is that Nafion[®] 117 membrane displays very close permeability towards dimethoxymethane and POM-M₂ than towards methanol. It is also likely that C₁ products coming from hydrolysis and electrochemical reactions under fuel cell operating conditions cross the membrane, which leads to decrease the carbon balance. Second, the large amount of methanol observed in the anodic outlet, higher than the quantity of POM-M_n after reaction, confirms that the hydrolysis process is important. Considering that the hydrolysis reaction are

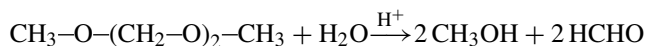
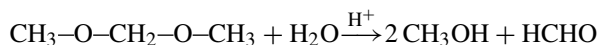
Table 3

Product distribution in the anode outlet of 5 cm² fuel cell obtained at T = 80 °C and j = 80 mA cm⁻²

POM-M ₂					
Products	CO ₃ ²⁻	HCHO	HCOOH	MeOH	POM-M ₂
Concentration (mol L ⁻¹)	0.190	0.460	0.070	0.760	0.320
nb mole	0.015	0.073	0.011	0.120	0.050
POM-M ₁					
Products	CO ₃ ²⁻	HCHO	HCOOH	MeOH	Dimethoxymethane
Concentration (mol L ⁻¹)	0.300	0.100	0.017	0.680	0.290
nb mole	0.024	0.015	0.003	0.100	0.041

Pt/C Cathode and Pt_{0.5}Ru_{0.5}/C anode from E-TEK, Nafion® 117 membrane.Fig. 9. Permeability measurements of methanol and POM-M_n through a Nafion® 117 membrane recorded at 20 °C in a two-compartment cell.

as follows:



The amount of H₂CO should be twice lower than that of CH₃OH for dimethoxymethane and of the same order for POM-M₂. But, in each case, this amount is much more lower, which can be due to either higher electroactivity or higher permeation through the membrane of H₂CO, under these experimental condition. Third, it is not possible to discriminate H₂CO issued from the hydrolysis from that coming from methanol oxidation, and further to propose reliable results between the total experimental charge involved in the oxidation process and the product distribution. However, it can be seen from results in Table 3 that the same amount of remaining fuel and of methanol is detected with both fuels (close to 0.05 and 0.1 M, respectively) whereas the amount of formaldehyde is five times lower with dimethoxymethane than with POM-M₂. This confirms that formaldehyde is more electroactive when present in lower concentration. Then, the increase of the production of CO₂ by a factor 1.5 from POM-M₂ to dimethoxymethane can be explained by the lower concentration of formaldehyde (e.g. lower surface poisoning).

4. Conclusion

In this work polyoxymethylenedimethylethers (POM-M_n) are studied for a possible application as fuels in PEMFC. Results

showed that these compounds undergo hydrolysis into methanol and formaldehyde. It is probable that these hydrolysis products are oxidized in the fuel cell rather than directly POM-M_n and are responsible of the cell performance. The electrical performances of the fuel cell working with a PtRu anode are promising considering that this kind of anode is optimized for methanol electrooxidation. It is likely that the development of multifunctional catalysts is required to improve the electroactivity of the POM-M_n compounds. Notably, the control of their catalyzed hydrolysis process and the enhancement of the hydrolysis products electrooxidation (notably formaldehyde oxidation) is one of the main goals. Nevertheless, despite the lower cell performances compared with methanol, the lower toxicity and higher safety of this family of compounds makes it interesting to replace methanol in fuel cell working with direct combustion of fuel.

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