

# Development and performance characterisation of new electrocatalysts for PEMFC

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## Abstract

New electrocatalysts based on Pt, Pt-Ru and Pt-Pd have been prepared by the microemulsion method. This method allows the production of a very narrow size distribution of metal particles, with an average size smaller than that of conventional electrocatalysts prepared by impregnation. Eight membrane electrode assemblies (MEAs) with an active surface area of 50 cm<sup>2</sup> were characterised in a single fuel cell. The MEAs consist of Nafion 117 as membrane and a commercial electrocatalyst (40% Pt/C from E-TEK) on the cathode side. Four MEAs have electrocatalysts prepared by the microemulsion technique and the other four have commercial electrocatalysts on the anode side. The performance of the eight MEAs was evaluated by measuring the fuel cell polarisation curves and the internal resistance with H<sub>2</sub>/O<sub>2</sub> and H<sub>2</sub>/air, at 60 °C and pressure in the range from 1 to 3 bar. The MEAs with the electrocatalysts prepared by microemulsion showed a performance comparable to that of the MEAs with commercial electrocatalysts. The satisfactory results obtained show that microemulsion is a promising method for the preparation of electrocatalysts for fuel cells. Further effort will be devoted to the optimisation of the method, mainly, the deposition of the metal particles on the carbon support, which it is expected to enhance the fuel cell performance. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Polymer electrolyte membrane fuel cell (PEMFC); Membrane electrode assembly (MEA); Electrocatalyst; Microemulsion method

## 1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are efficient and environmentally clean electrical generators that are being developed for both stationary and mobile applications [1–5]. A broad commercialisation of PEMFCs requires, however, an important reduction in the cost of components such as electrocatalysts, ionomer membranes, membrane electrode assemblies (MEAs) and bipolar plates [6]. Research is ongoing world-wide to decrease the price of both the materials and manufacture of each of those components.

Platinum and its alloys are used as electrocatalysts for hydrogen oxidation and oxygen reduction in PEMFCs. When H<sub>2</sub> is obtained by reforming of hydrocarbons, the CO content of the hydrogen feed stream has to be lowered to less than 10 ppm before entering the anode because pure Pt electrocatalysts are not resistant to CO poisoning [7]. Several Pt alloys, like Pt–Ru, Pt–Sn and Pt–Mo alloys have been proposed to alleviate this poisoning problem [7,8]. Among these alloys, Pt–Ru is certainly the most studied

electrocatalyst mainly because its CO tolerance is known since more than 30 years [7–10]. Low Pt consumption is necessary without affecting the cell performance.

For structure-sensitive reactions, the formation of smaller particles of supported electrocatalysts is of considerable importance in order to enlarge the catalytic area and, accordingly, enhance the catalytic activity [11]. Thus, the catalytic behaviour of small particles for structure-sensitive reactions has become of much interest. As a consequence, the development of catalyst preparation methods for loading small and uniform metal particles has become necessary. However, methods of controlling the metal particle size of supported catalysts, regardless of metal content are not available to date [12]. We have applied the microemulsion method to the catalyst preparation. Monodisperse nanoparticles can be synthesised in microemulsions and their sizes can be varied with the preparation conditions [13]. However, the preparation method for the catalyst based on microemulsions has been scarcely studied, because it is very difficult to deposit the nanoparticles in microemulsions on carriers without formation of large aggregates [14].

In this study, new electrocatalysts based on Pt, Pt-Ru and Pt-Pd with a low platinum load (0.37–0.50 mg/cm<sup>2</sup>) have

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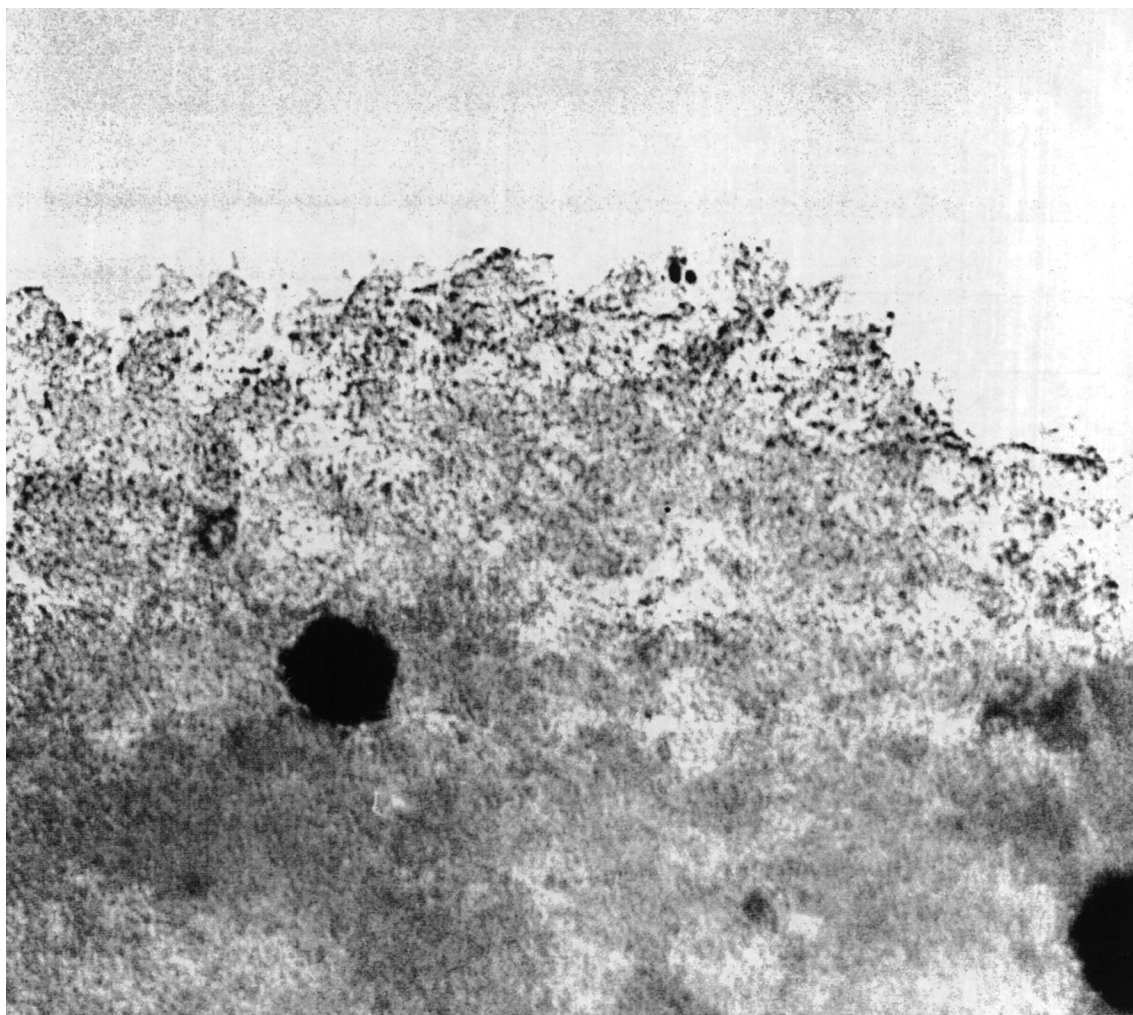


Fig. 1. TEM micrograph of 40% Pt-Ru electrocatalyst prepared from microemulsion.

been prepared by the microemulsion method. This method allows for a very narrow size distribution of metal particles, with an average size smaller than that of conventional electrocatalysts prepared by impregnation [12,14]. The new electrocatalysts were characterised in a single fuel cell and compared to the commercial ones. The fuel cell performance was assessed by measuring the polarisation curves (voltage versus current) and internal resistance under different operation conditions.

## 2. Experimental

### 2.1. Preparation of electrocatalysts

The electrocatalysts used for the preparation of the MEAs were 40% Pt on vulcan XC-72 and 40% Pt:Ru (1:1 ratio) vulcan XC-72 commercial catalysts from E-TEK and 40% Pt:Ru (1:1) charcoal and 40% Pt:Ru (1:2) charcoal prepared by the microemulsion method.

Table 1  
Composition of MEAs including commercial (C) and microemulsion electrocatalyst (M)

MEA	Cathode composition	Pt load (mg/cm <sup>2</sup> )	Anode composition	Metal total load (mg/cm <sup>2</sup> )	Pt load (mg/cm <sup>2</sup> )
C1	40% Pt/vulcan XC-72	0.95	40% Pt-Ru/vulcan XC-72	0.44	0.29
C2	40% Pt/vulcan XC-72	0.46	40% Pt-Ru/vulcan XC-72	0.22	0.15
C3	40% Pt/vulcan XC-72	0.71	40% Pt/vulcan XC-72	0.50	0.50
C4	40% Pt/vulcan XC-72	0.69	40% Pt-Ru/vulcan XC-72	0.50	0.33
M1	40% Pt/vulcan XC-72	0.80	40% Pt-Ru/charcoal	0.56	0.37
M2	40% Pt/vulcan XC-72	0.76	40% Pt-Ru/charcoal	0.64	0.43
M3	40% Pt/vulcan XC-72	0.78	40% Pt/charcoal	0.47	0.47
M4	40% Pt/vulcan XC-72	0.73	40% Pt-Pd/charcoal	0.44	0.22

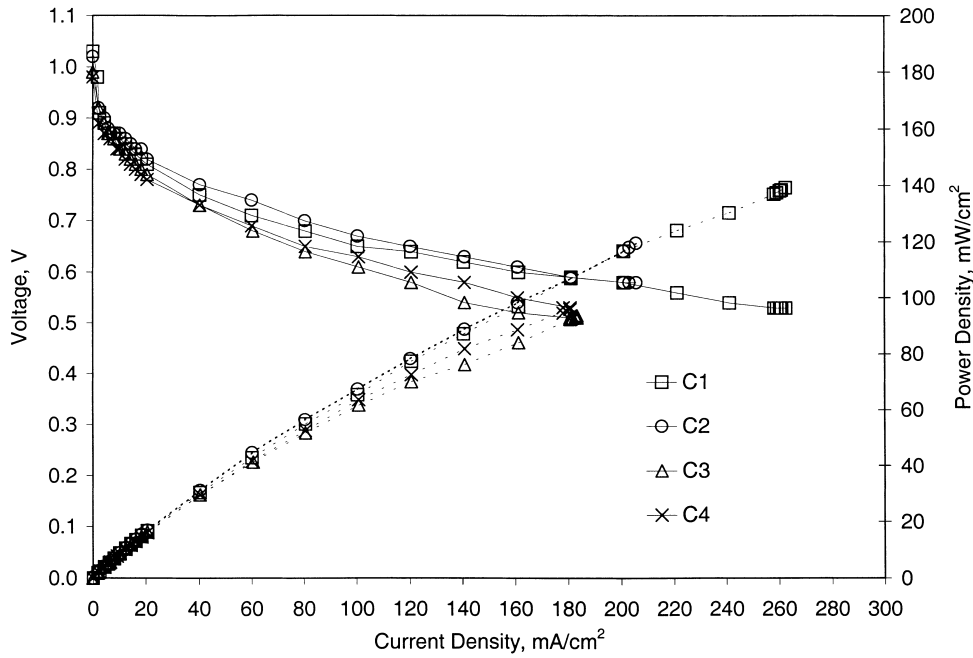


Fig. 2. Polarisation curves of four MEAs with commercial electrocatalysts,  $H_2/O_2$  at  $60^\circ C$  and 1 bar.

This method has been previously described by Boutonnet et al. [15]. It consists of incorporating metal salts in the aqueous core of the small aggregates that are formed by surfactant molecules in a non-polar solvent at certain concentrations. Typically, the mixture consists of 20 wt.% surfactant (Berol 050, Azko Nobel) in *iso*-octane and 5–10 wt.% water. In order to prepare mixed Pt-Ru metal particles and mixed Pt-Pd metal particles, aqueous solutions

of chloroplatinic acid, ruthenium chloride and palladium chloride have been used in the preparation of the micro-emulsion solution. The reduction of the metal salts with hydrazine at room temperature engenders the formation of metal and metaloxide particles. The obtained suspension of metal particles is very stable. Therefore, tetrahydrofuran was added to the suspension and an ultrasonic treatment was used to destabilise the suspension and to get the particles

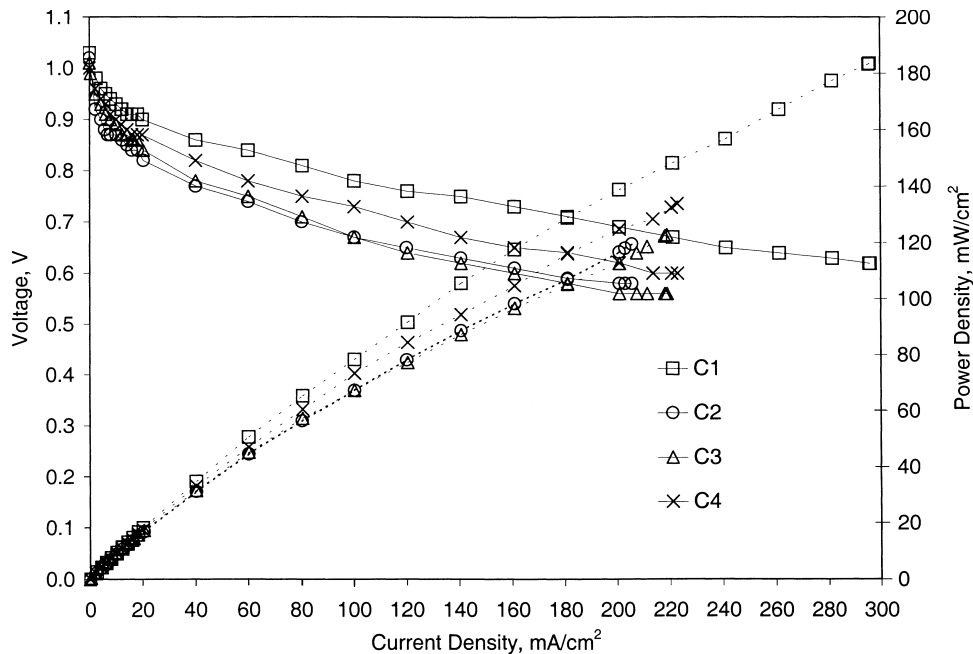


Fig. 3. Polarisation curves of four MEAs with commercial electrocatalysts,  $H_2/O_2$  at  $60^\circ C$  and 3 bar.

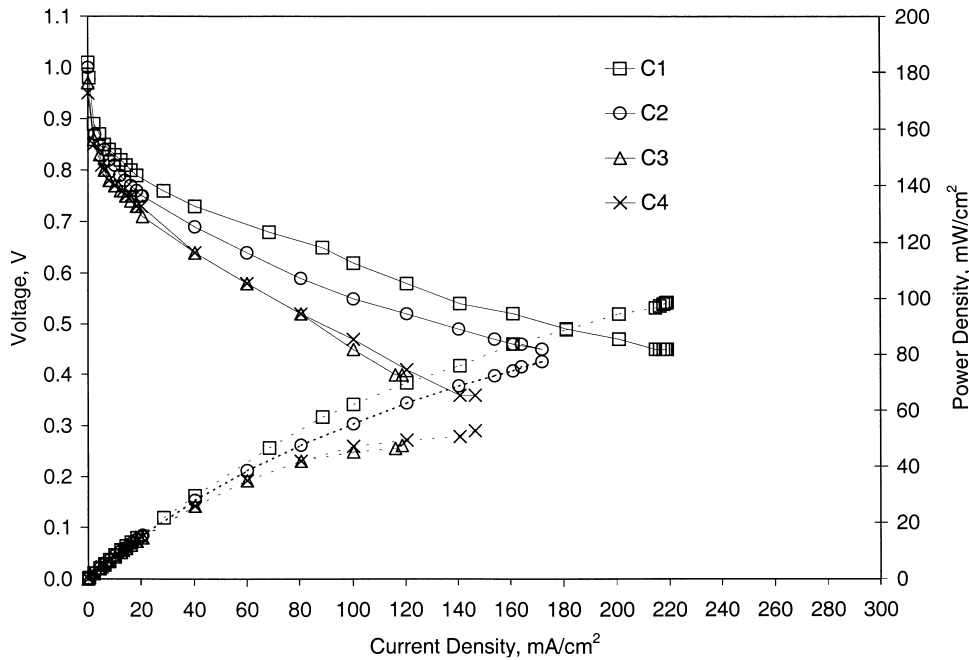


Fig. 4. Polarisation curves of four MEAs with commercial electrocatalysts,  $H_2$ /air at 60 °C and 1 bar.

onto the charcoal support. The obtained electrocatalyst was washed several times with ethanol in order to eliminate the organic residues and, then, heated in a gas mixture of 50%  $N_2$  and 50%  $H_2$  at 300 °C during 2 h.

## 2.2. Characterisation of electrocatalyst

Transmission electron microscopy (TEM) studies of the 40% Pt-Ru electrocatalyst prepared by microemulsion method were carried out using a JEOL 2000FX TEM

working at 200 kV and equipped with an EDX analyser. The powders were ultrasonically suspended in butanol and deposited onto a nickel grid. A TEM micrograph of the 40% Pt-Ru electrocatalyst prepared from microemulsion is displayed in Fig. 1. Both separated particles and particle aggregates can be observed. While the size of the metal particles is in the range from 2 to 5 nm, the size of the particle aggregates is about 20 nm.

As a high concentration of metals is required for the electrocatalysts that contain up to 40 wt.% of metal, the

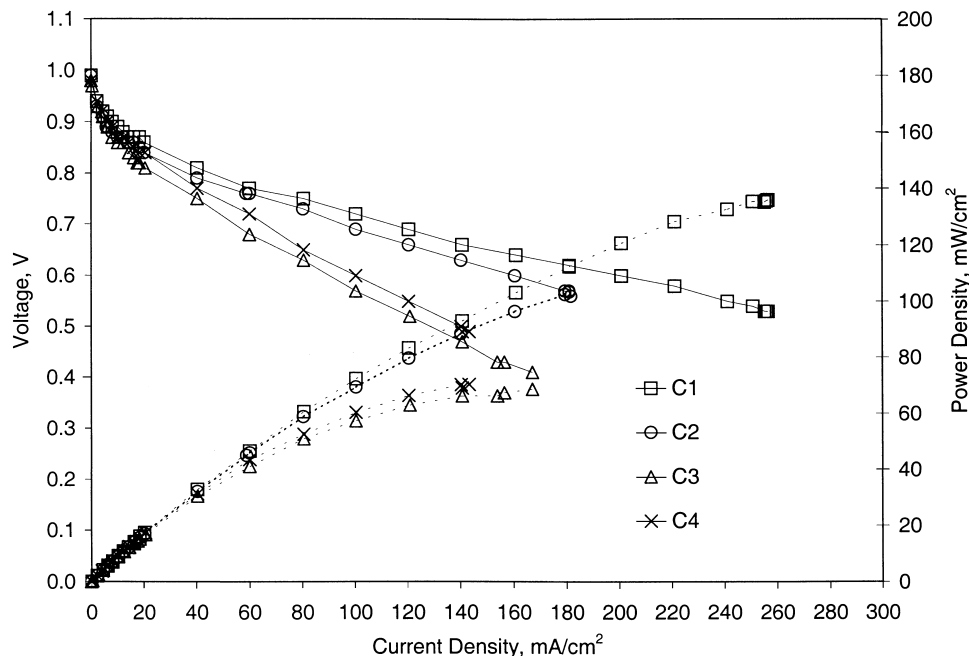


Fig. 5. Polarisation curves of four MEAs with commercial electrocatalysts,  $H_2$ /air at 60 °C and 3 bar.

amount of the microemulsion solution required to obtain such metal concentration is quite large compared to the amount of charcoal powder added to the solution during the deposition process. That makes it difficult to control the deposition of the metal particles onto the support in order to obtain an even distribution of particles without any agglomeration. This observation shows that the method of deposition of the metal particles onto the support needs to be improved.

### 2.3. Preparation of the membrane electrode assembly

Table 1 summarises the main characteristics of the MEAs used in this work. The Nafion 117 membrane was preliminary washed with 3–10%  $\text{H}_2\text{O}_2$ , 0.5 M KOH, and deionised water between each treatment. Finally, its surface was cleaned with heptane. The ink composition for the anode and cathode was 27.3% of Nafion solution, 29.1% of metal and 43.6% charcoal or vulcan (Vulcan). After spraying the ink on the membrane, the membrane was treated with 10% *iso*-propanol, 0.15 M  $\text{H}_2\text{SO}_4$  at 90 °C for 2 h, and deionised water between each treatment until the pH was 7. Then, the membrane was dried at 50 °C for 2 h and hot pressed (3.5 ton, 120 °C, 5 min) except for M1, where the backing carbon cloth was free, in loose contact with the MEA, since hot pressing was not applied.

### 2.4. Electrochemical measurements

The MEAs in Table 1 have an active area of 50 cm<sup>2</sup>. They were tested in a commercial fuel cell purchased from Electrochem. The eight MEAs were divided in two groups. The first group corresponds to the MEAs C1, C2, C3 and C4 that contain commercial electrocatalysts in both cathode and

Table 2

Internal resistance of the MEAs with commercial catalyst

Cell reactants	Pressure (bar)	$R$ ( $\Omega$ cm <sup>2</sup> )			
		C1	C2	C3	C4
$\text{H}_2/\text{O}_2$	1	0.65	0.66	1.10	0.90
	2	0.63	0.62	0.77	0.73
	3	0.61	0.67	1.12	0.74
$\text{H}_2/\text{air}$	1	0.65	0.72	1.13	1.11
	2	0.62	0.69	0.94	0.84
	3	0.60	0.61	0.93	0.72

anode sides. The second group includes the MEAs M1, M2, M3 and M4, which include commercial electrocatalysts in the cathode side and electrocatalysts prepared by microemulsion in the anode side.

The performance of the fuel cells was assessed by measuring the polarisation curves with a varying resistive load (HP 6060B). Besides, the fuel cell internal resistance was measured with a milliohmmeter (HP 4338B). All the experiments were carried out at 60 °C with the temperatures of the anode and cathode humidifiers at 70 and 65 °C, respectively. Both  $\text{H}_2/\text{O}_2$  and  $\text{H}_2/\text{air}$  were used as reactants at pressures of 1, 2 and 3 bar.

## 3. Results and discussion

### 3.1. MEAs with commercial catalysts

The polarisation curves and power density of the MEAs with commercial catalysts in the cathode and the anode

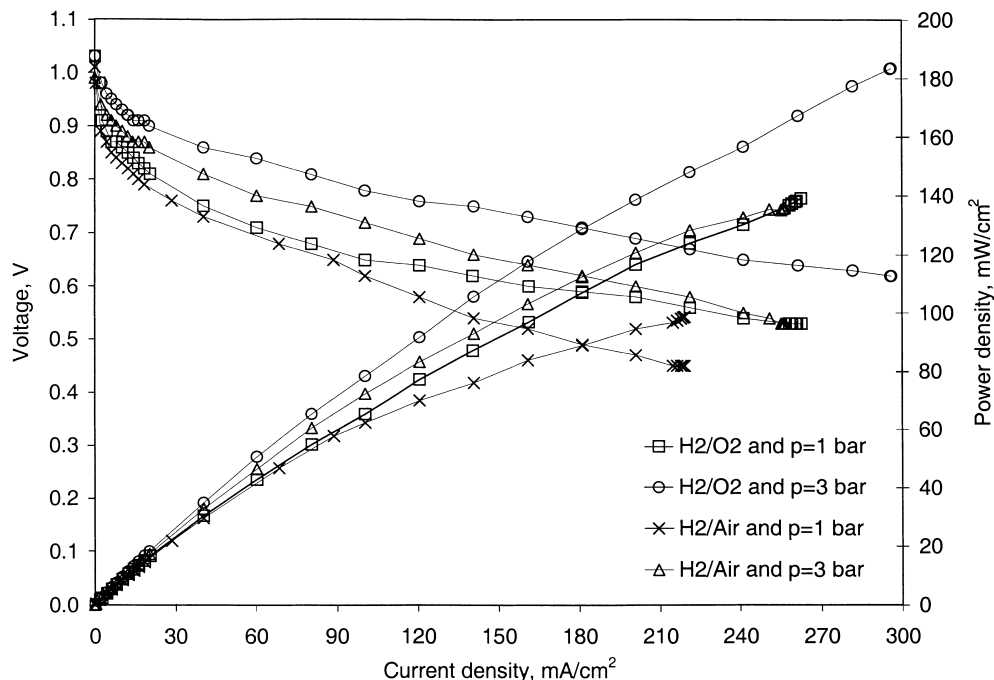


Fig. 6. Polarisation curves of a MEA with commercial electrocatalyst (C2) at 60 °C,  $\text{H}_2/\text{O}_2$  and  $\text{H}_2/\text{air}$ , 1 and 3 bar.

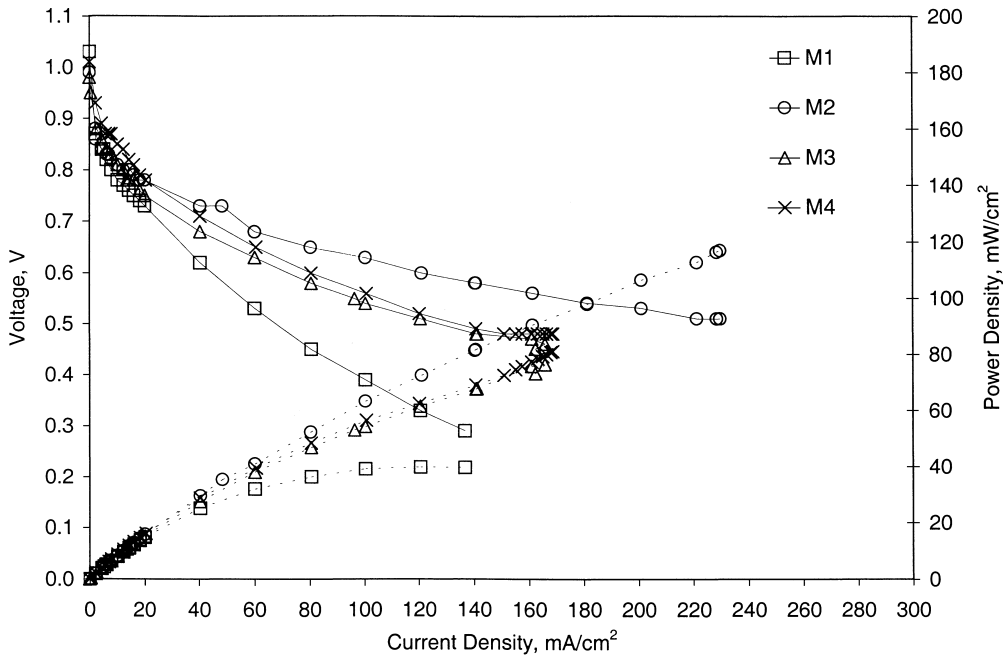


Fig. 7. Polarisation curves of four MEAs with microemulsion electrocatalysts, H<sub>2</sub>/O<sub>2</sub> at 60 °C and 1 bar.

are plotted in Figs. 2–5. MEAs C1 and C2 were similar except for the Pt load; the Pt content of C2 was one-half that of C1 in both cathode and anode sides. Despite that, the two MEAs behaved similarly and they showed the same internal resistance, as can be seen in Figs. 2–5 and Table 2.

On the other hand, MEAs C3 and C4 differ only in the anode catalyst. The two MEAs contain the same amount of

metal, which was pure Pt in C3 and a Pt–Ru alloy in C4. Although C4 exhibited a slightly better performance than C3, the differences between the two MEAs were insignificant in the all cases.

The first two MEAs, C1 and C2, performed better than the last two, C3 and C4. The reason could be the higher internal resistance values of the fuel cell measured with C3 and C4, as shown in Table 2.

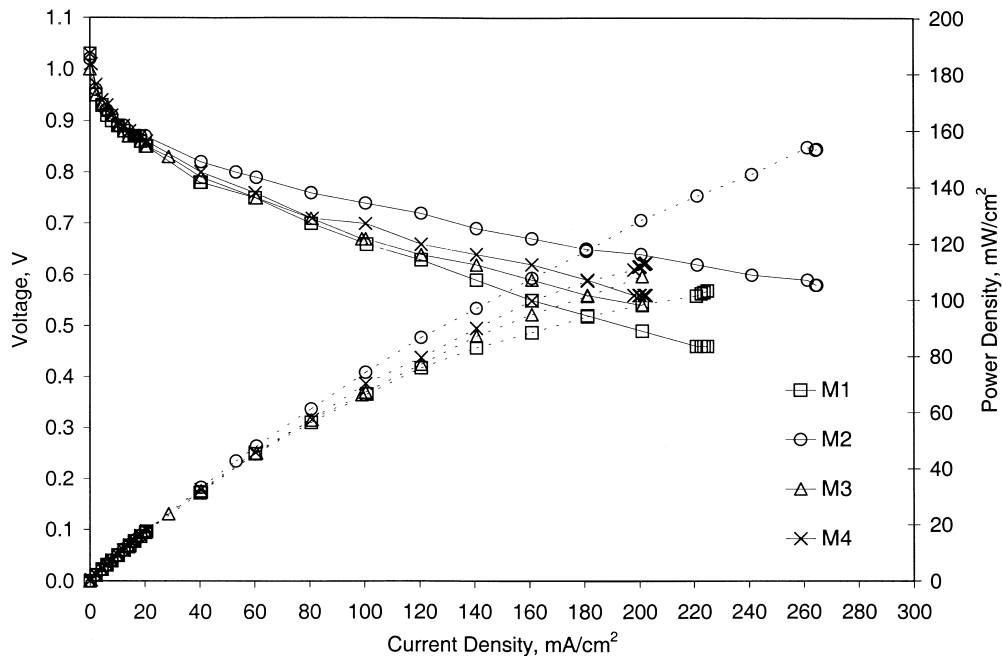


Fig. 8. Polarisation curves of four MEAs with microemulsion electrocatalysts, H<sub>2</sub>/O<sub>2</sub> at 60 °C and 3 bar.

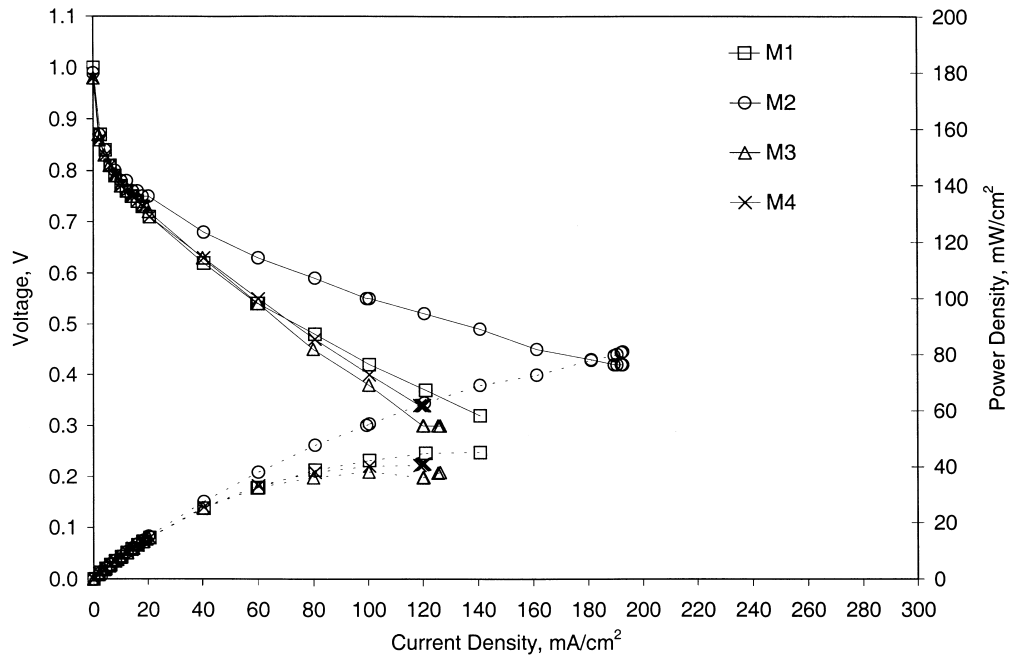


Fig. 9. Polarisation curves of four MEAs with microemulsion electrocatalysts, H<sub>2</sub>/air at 60 °C and 1 bar.

Fig. 6 shows the polarisation curves corresponding to C2. As expected, the fuel cell performance improved with pressure. This can be attributed to both the improvement of the oxygen electrode kinetics and the better supply of reactants to the active sites at high pressure. With oxygen as reactant, the fuel cell performance increased in a factor of about 2, with respect to air. This behaviour is likely due to the more severe mass transport limitations that arise when air is used as oxidant.

### 3.2. MEAs with microemulsion catalysts

The polarisation curves and power density of the MEAs with catalysts prepared by microemulsion in the anode can be seen in Figs. 7–10. The four MEAs used commercial electrocatalysts with nearly the same load of Pt in the cathode. The MEAs differ mainly in the metal composition and amount of Pt in the anode (Table 3).

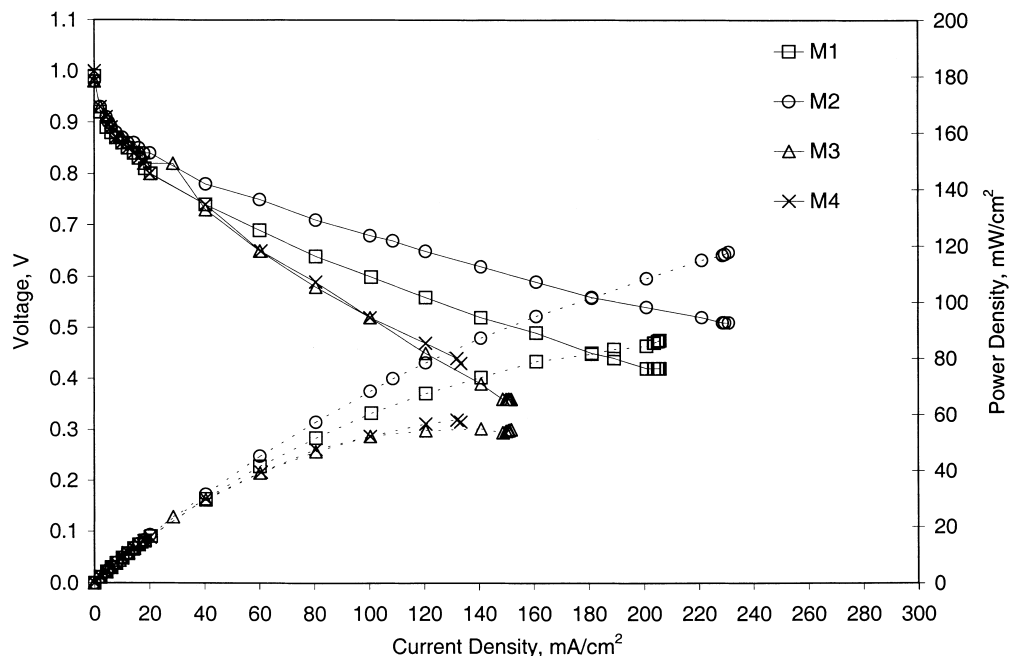


Fig. 10. Polarisation curves of four MEAs with microemulsion electrocatalysts, H<sub>2</sub>/air at 60 °C and 3 bar.

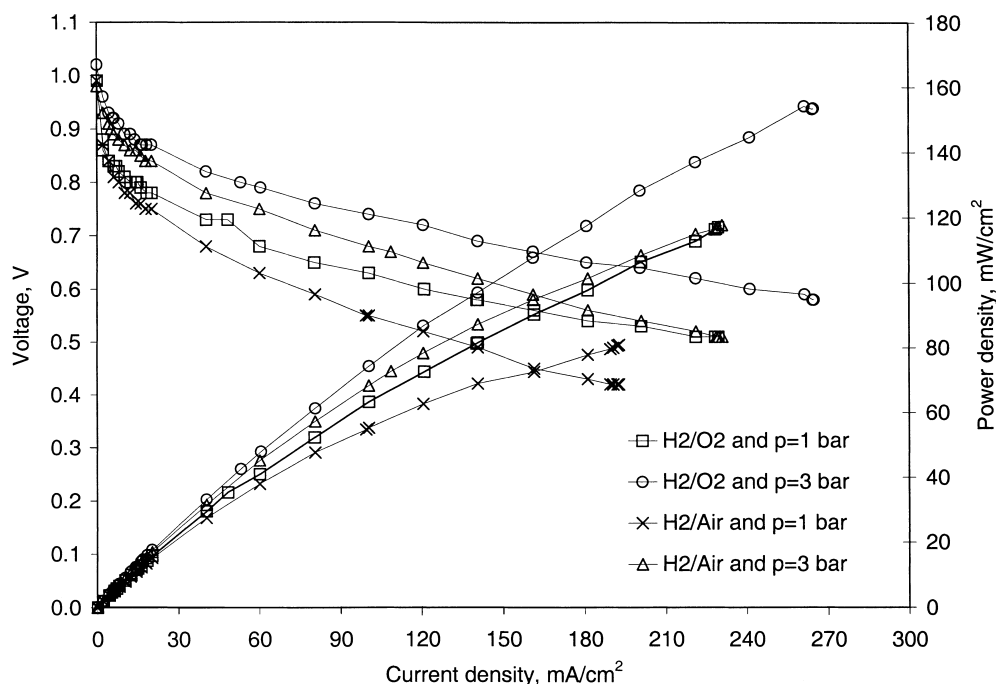


Fig. 11. Polarisation curves of a MEA with microemulsion electrocatalyst (M2) at 60 °C, H<sub>2</sub>/O<sub>2</sub> and H<sub>2</sub>/air, 1 and 3 bar.

Table 3

Internal resistance of the MEAs with microemulsion catalyst

Cell reactants	Pressure (bar)	$R$ ( $\Omega$ cm <sup>2</sup> )			
		M1	M2	M3	M4
H <sub>2</sub> /O <sub>2</sub>	1	1.10	0.71	1.75	1.55
	2	0.98	0.67	1.14	0.84
	3	0.94	0.65	1.11	0.92
H <sub>2</sub> /air	1	1.03	0.65	1.42	1.17
	2	0.91	0.74	1.39	0.96
	3	0.89	0.64	1.10	0.91

The best performance corresponds to M2 (Pt-Ru) in comparison to M3 (Pt) and M4 (Pt-Pd). M1 had a Pt-Ru anode, but it behaved worse than M2. The reason is the high internal resistance values of the fuel cell with M1, due to the poor contact of the loose backing carbon cloth and the MEAs. Moreover, M1 had a lower metal content in the anode than M2. In M4, Pd replaced half of the Pt content in the anode of M3, which did not affect the fuel cell performance, as can be seen in the figures.

The polarisation curves corresponding to M2 are plotted in Fig. 11. The effects of both pressure and oxidant on the fuel cell performance were similar to those observed in Fig. 6 for C2.

In general, the behaviour of the fuel cells with the MEAs containing the microemulsion electrocatalysts was comparable to that of the fuel cells with the MEAs including the commercial electrocatalysts. In particular, the performance of M2 compared rather well with that of C2, whereas M3 and M4 performed similar to C3 and C4.

#### 4. Conclusions

The microemulsion technique has been applied to prepare new electrocatalysts based on Pt, Pt-Ru and Pt-Pd with low platinum (0.37–0.50 mg/cm<sup>2</sup>). These new electrocatalysts showed a small particle size and a good particle distribution.

The new electrocatalysts were characterised in a single fuel cell and compared to the commercial ones. In general, the electrochemical performance of the fuel cells with the MEAs containing the microemulsion electrocatalysts was comparable to that of the fuel cells with the MEAs including the commercial electrocatalysts.

The results obtained show that microemulsion is a promising method for the preparation of electrocatalysts for fuel cells. Although, it would be necessary to optimise the method, the deposition of the metal particles on the carbon support could improve the fuel cell performance.

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