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Effect of operational parameters of mini-direct methanol fuel cells operating at ambient temperature

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Abstract

There is currently increased interest in small-size direct methanol fuel cells for portable applications. This work presents results of the influence of operational parameters on the performance of a mini-direct methanol fuel cell. The effects of methanol concentration, Pt load, membrane thickness and PTFE content in the cathode diffusion layer on the performance were studied. Two anodic materials were prepared, PtRu 75:25 at.% and PtRu 90:10 at.%, as nanoparticles supported on Vulcan XC-72 carbon, while for the cathodes Pt/C E-TEK catalysts were used. The materials were characterized physically by EDX and DRX and electrochemically in a half-cell. The results with single cells showed better performances with cells operating with 3 mg Pt cm^{-2}, 5 mol l^{-1} methanol solution, Nafion® 112 membrane and with 30 wt.% PTFE in the cathode diffusion layer deposited on only one face of the electrode support.

1. Introduction

Direct methanol fuel cells (DMFC) oxidize methanol at the anode and recent progress indicates that they can operate for long periods of time with high efficiency and low emission of pollutants. An important aspect is that they can work at ambient temperature and pressure. Because of these characteristics, there is much interest in developing DMFC for portable electronic equipment.

Portable electronic equipment is usually powered by batteries, the most common ones being nickel–cadmium, metal hydride and lithium ion. However, increasing demands of energy availability and longer periods between charges can be met only by suitable DMFC's.

Specific energy is one of the main advantages of the DMFC. According to Hockaday et al. [1] the specific energy of methanol (6000 Wh kg^{-1}) is an order of magnitude larger than that of a lithium ion battery (600 Wh kg^{-1}). A DMFC operating at 50% efficiency with pure methanol would have a specific energy of 3000 Wh kg^{-1}, which is about 30 times the energy density of lithium ion batteries (100 Wh kg^{-1}).

Another factor in favor of the DMFC is the volume of the system. For an energy content of 200 Wh the volume required by a DMFC is about 200 ml, while that of a lithium ion battery is about 700 ml [2].

The nickel–metal hydride system (Ni/MH) is presently much used but it has a theoretical energy density of 1000 Wh l^{-1}, while that of a methanol/air system is about 4900 Wh l^{-1} [1, 2].

Considering the cost, it may be estimated that to produce a 100-Wh system the cost of a battery would be USD 145, while that of a DMFC would be USD 55, considering a projected cost of USD 5 W^{-1} for a mini-DMFC [2].

An alternative approach is to consider hybrid systems [3]. For example, a cell phone uses the battery in operation; when not in use, the fuel cell charges the battery. Bostaph et al. [4] and Blum et al. [5] presented an approach by Motorola in which battery chargers are operated with direct methanol fuel cells. Still other approaches have been discussed [6–9].

1.1. *Development of mini-direct methanol fuel cells*

The conventional DMFC requires peripherals to control the temperatures of the cell and the humidifier, the flux of reagents, the pressure and other parameters. A DMFC for portable systems should operate without peripherals to decrease weight and volume [10, 11] and has to run on passive feeding; that is methanol has to reach the catalyst/electrolyte interface just by diffusion. Without temperature controllers the system operates at ambient temperature, or just above, and the efficiency of the cell is reduced because electrode reactions and ionic transport are temperature dependent processes.

The first results for DMFCs of reduced size were published by Kelley et al. [12]. The active area was 0.25 cm^2, the cathode had 2.5 mg of unsupported platinum black and the anode 4 mg of PtRu. The electrolyte was a Nafion® 117 membrane and a 0.5 $mol\ l^{-1}$ methanol solution was fed at 0.2 $l\ min^{-1}$. The cell produced 12 $mW\ cm^{-2}$. Extensive work at Los Alamos National Laboratory [13] shows that methanol solutions should not exceed 1 $mol\ l^{-1}$ to reduce methanol crossover. An auxiliary equipment supplied a 0.5 $mol\ l^{-1}$ methanol solution under 30 psig, to a 100 mW stack that produced 10 $mW\ cm^{-2}$ and was operated for 3000 h. This is a good result except for the fact that the system still uses peripherals.

Obviously, the goal should be to feed the methanol solution just by diffusion. By reducing the internal resistance of the cell, Naranayan et al. [14] worked under this condition and produced 8 $mW\ cm^{-2}$ using a 1 $mol\ l^{-1}$ methanol solution.

The demand that several cells must be connected in series to produce suitable voltages was exemplified by Lee et al. [15], with a configuration called a “flip-flop” where part of the electrode acts as anode and part as cathode.

In spite of the importance of using fuel cells for portable applications, not all of the working conditions for a DMFC operating at ambient temperature and pressure and with passive transport of the reactants have been evaluated. Thus, in this work a detailed study of the operational parameters was carried out under those conditions. On the basis of previous studies PtRu supported on carbon (PtRu/C) was used in the anodes and Pt/C in the cathodes.

2. Experimental

PtRu/C catalysts were prepared using the formic acid reduction method (FAM) developed in this laboratory [16]. The support was Vulcan XC-72 carbon (Cabot) and the precursors $H_2PtCl_6{\cdot}6H_2O$ and $RuCl_3{\cdot}H_2O$. Solutions of $RuCl_3{\cdot}H_2O$ were made in 1 $mol\ l^{-1}$ HCl to minimize the formation of ruthenium complexes [17] which prevent the reduction and anchoring of Ru on the support.

EDX analyses were implemented in a scanning electron microscope LEO, 440 SEM-EDX (Leica-Zeiss, DSM-960) with a microanalyzer (link Analytical QX 2000) and SiLi detector, using a 20 keV electron beam. X-ray diffractograms were obtained using a Carl Zeiss-Jena URD-6 equipment, operated with $K_{\alpha}Cu$ radiation ($\lambda = 1.5406$ Å).

Two-layer gas diffusion electrodes were prepared. A diffusion layer was made by mixing Vulcan XC-72 carbon powder (250 $m^2\ g^{-1}$) with a PTFE dispersion (60 wt.%, DuPont). For the half-cell experiments the diffusion layer of the electrodes (geometric area 1.23 cm^2) was prepared with 3 $mg\ cm^{-2}$ of the mixture, 30 wt.% PTFE and 70 wt.% carbon, and deposited on both faces of a carbon cloth (PWB-3, Stackpole). For the mini-DMFC tests all anodes (geometric area 1.13 cm^2) were prepared with 3 $mg\ cm^{-2}$ of the mixture containing 15 wt.% of PTFE, deposited on both faces of the carbon cloth. For the cathodes 3 $mg\ cm^{-2}$ of the mixture were applied to only one of the faces of the carbon cloth. The catalytic layer was made by preparing an ink with the catalyst and Nafion® solution (5% in alcohols, DuPont), and applied on top of the diffusion layer [18].

The electrochemical behavior of the catalysts was studied in 0.5 $mol\ l^{-1}$ H_2SO_4 and in the same solution with different concentrations of methanol in a three-electrode cell [18]. The techniques were cyclic voltammetry, linear sweep voltammetry and chronoamperometry, using a Solartron 1285 potentiostat and the software Corrware (Scribner).

The membrane and electrode assemblies (MEA) were prepared by hot pressing an anode and a cathode onto a Nafion® membrane (112 or 117 DuPont) at 125 °C and 5 MPa for 2 min.

The mini-DMFC (Figure 1) had a methanol solution reservoir (1.5 ml), made into an acrylic plate, with the opening directly in contact with the anode backing, while the cathode backing was open to the atmosphere. Current collection was by gold-plated printed circuit plates.

3. Results and discussion

3.1. *Physical characterization of the catalysts*

Two PtRu anode catalysts with different composition and metal/carbon ratio were prepared. One was 20 wt.% metal on carbon and had an EDX composition $Pt_{75}Ru_{25}$. The other material was 50 wt.% metal and the atomic composition was $Pt_{90}Ru_{10}$.

Figure 2 shows the X-ray diffractograms for the PtRu catalysts, together with that of a commercial material Pt/C E-TEK, 40 wt.% metal on carbon. The peaks at 2θ values 40, 47, 67 and 82° are associated to the (110), (200), (220) and (311) planes of the fcc structure of platinum (JCPDS card 4-802). No peak was observed

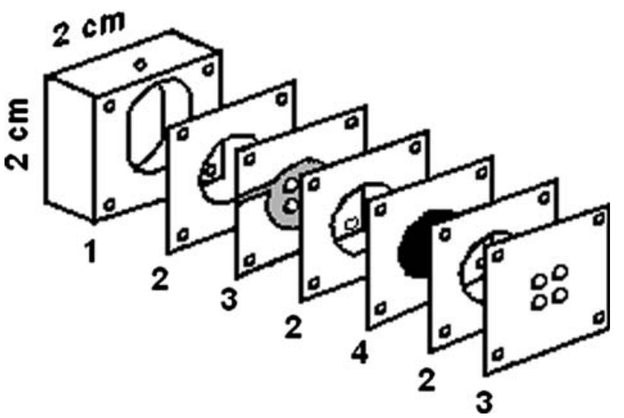

Fig. 1. Scheme of the mini-direct methanol fuel cell. (1) Methanol reservoir, (2) gaskets, (3) current collector, and (4) membrane/electrode assembly.

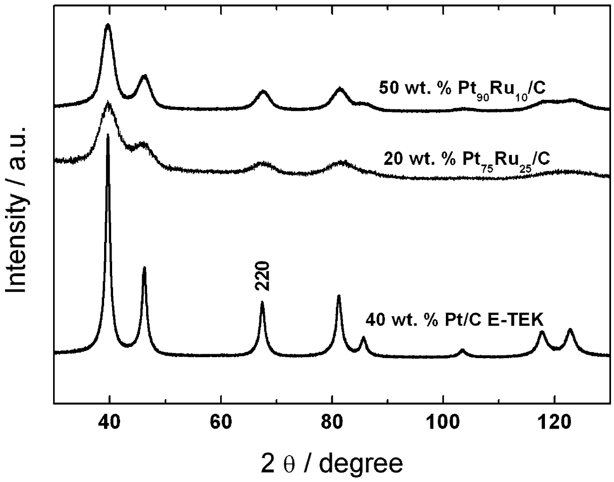

Fig. 2. X-ray diffractograms for the different supported catalysts. $\lambda = 1.5406$ Å (K_αCu), scan rate 3° min^{-1}.

that may correspond to the hexagonal structure of ruthenium (JCPDS card 6-663). But the reflections of platinum are much more intense, and the difference is enhanced because of the larger platinum contents.

The approximate value of the mean particle size of the catalysts was determined from the X-ray diffractograms using Scherrer's equation [19] and assuming a spherical shape for the particles. For this, the peak (220) (recorded at 0.5° min^{-1} for 2θ between 65 and 75°) was used, because it appears in a region of 2θ values with no influence of the broad bands of the carbon substrate, and a Gaussian fitting of the peak was performed. The values of the mean particle size and the corresponding lattice parameters are presented in Table 1. For comparison, the values for commercial 20 wt.% Pt/C E-TEK [20] have also been included. The catalyst with the larger amount of metal on carbon has a larger particle size, which may be due to coalescence of the particles when the amount of metal on the carbon increases.

The values of the lattice parameters (Table 1) are very similar to that for pure platinum (0.3923 nm), so it is very likely that the PtRu materials are not true solid solutions. Unfortunately, the limited physical analyses carried out here are insufficient for a complete characterization of the state of the Pt and Ru elements in the catalysts.

Table 1 also shows the theoretical (calculated from the XRD particle sizes [21]) metal surface areas for the different catalysts.

Table 1. Mean diameter (*d*), lattice parameter (*a*) and active areas (*S*) of the catalyst particles obtained from the X-ray diffractograms

Catalyst	*d* / nm	*a* / nm	*S* / m^2 g^{-1}Pt and (m^2 g^{-1}PtRu)
20 wt.% $Pt_{75}Ru_{25}/C$	2.2	0.3925	127 (137)
50 wt.% $Pt_{90}Ru_{10}/C$	3.2	0.3922	88 (89)
20 wt.% Pt/C E-TEK [20]	2.9	0.3924	97
40 wt.% Pt/C E-TEK	3.3	0.3922	85

3.2. *Electrochemical studies*

Figure 3 presents cyclic voltammograms for PtRu/C electrodes (1 mg Pt cm^{-2}) in 0.5 mol l^{-1} H_2SO_4 in the absence of oxygen. The catalyst with the larger metal contents gives lower currents, indicating that it has a smaller electroactive area, which is consistent with the smaller theoretical metal surface areas. Also, the voltammogram of $Pt_{90}Ru_{10}$ is more similar to that of pure Pt, with the hydrogen upd region (0.075–0.35 V vs. RHE) better defined than that of $Pt_{75}Ru_{25}$. In Ru-rich PtRu catalysts the hydrogen adsorption/desorption peaks are less defined because they are not developed on Ru [18]. The double-layer region of $Pt_{75}Ru_{25}$ is larger than that of $Pt_{90}Ru_{10}$, because of the formation of more oxygenated species, due to the larger Ru content, and to the larger surface area resulting from a smaller particle size.

Figure 4 shows linear sweep voltammetry carried out with different methanol concentrations. The activity for methanol oxidation increases up to 2 mol l^{-1} with little or no increase for more concentrated solutions. Similar

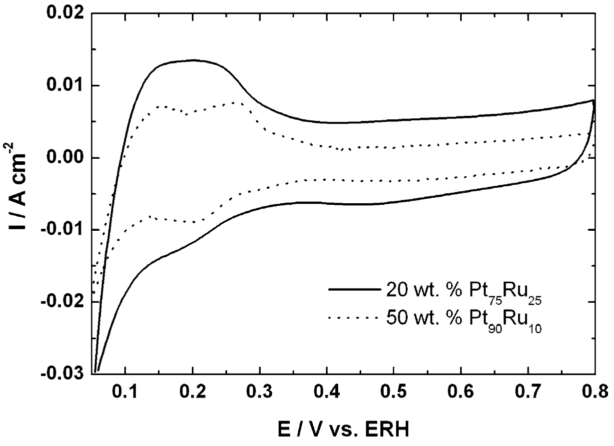

Fig. 3. Cyclic voltammograms for the PtRu/C catalysts. 1 mg Pt cm^{-2}, 0.5 mol l^{-1} H_2SO_4, $v = 20$ mV s^{-1}.

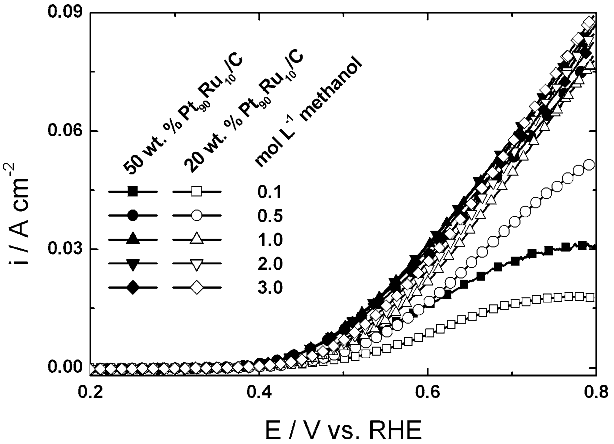

Fig. 4. Linear sweep voltammograms for the two PtRu/C catalysts in different concentrations of methanol. 1 mg Pt cm^{-2}, 0.5 mol l^{-1} H_2SO_4, $v = 10$ mV s^{-1}.

results were found in chronoamperometric experiments, where the electrode was maintained at 500 mV vs. RHE and the current was recorded after 1800 s. Figure 5 shows that current densities increase up to about 1 mol l^{-1}. Electrochemical experiments show that a methanol concentration of 2 mol l^{-1} is adequate for a direct methanol fuel cell operating at ambient temperature [18]. This is because in the half cell there are no mass transport limitations for the methanol but, as will be discussed below, the situation is different in the mini-fuel cells.

3.3. *Studies with direct methanol mini-fuel cell*

The results above, indicate that methanol concentrations near 2 mol l^{-1} give the higher current levels. Also, in conventional DMFCs, the majority of studies were carried out with that concentration [22]. However, other studies recommend the use of lower concentrations to minimize the problem of methanol crossover [23].

Here, the electrodes were prepared containing 1 mg Pt cm^{-2} and used in a mini-cell with a Nafion® 112 membrane. Figure 6 shows the potential–current density and the power–current density curves obtained with different methanol concentrations. It is clear that in the mini-cell a better performance is obtained with a 5 mol l^{-1} solution. The difference with respect to the electrochemical half cell can be explained by considering that in the mini-fuel cell methanol is delivered to the active sites only by diffusion, and for this process the only driving force is the concentration gradient. On the surface of the catalyst the methanol is oxidized [24, 25] and it has to be replenished by diffusion [26]. Other authors have found better performances with higher concentrations of methanol in mini-fuel cells [27, 28]. On the other hand, still others recommend methanol concentrations as low as 0.5 mol l^{-1} to minimize methanol crossover [27, 23], but because of the lower concentration gradient less methanol reaches the catalyst surface, so they were not able to produce acceptable current densities. Because of the operating conditions, in the mini-fuel cell the electrode reaction is faster than the diffusion of the reactant, which requires different operational parameters than in the conventional fuel cell to improve performance.

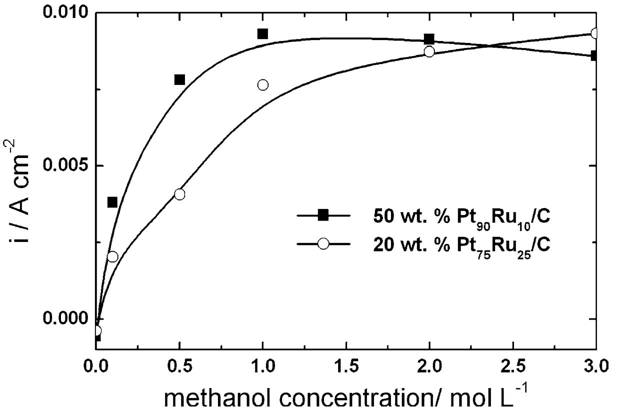

Fig. 5. Current density at the 30th minute in chronoamperometric experiments at 0.5 V vs. RHE. 1 mg Pt cm^{-2}, 0.5 mol l^{-1} H_2SO_4.

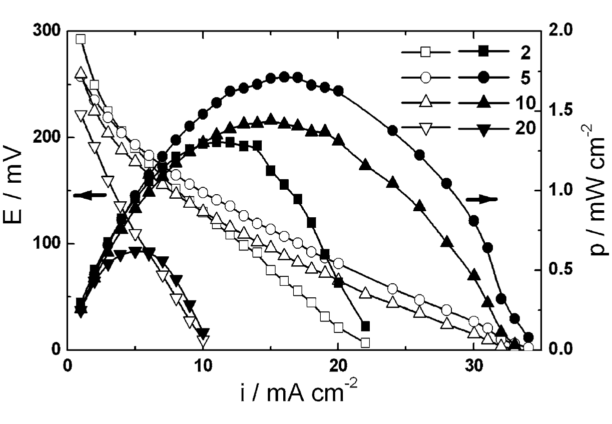

Fig. 6. Cell potential and power density as functions of the current density in mini-DMFCs for different methanol concentrations (mol l^{-1}). Anodes with 20 wt.% $Pt_{75}Ru_{25}/C$ and cathodes with 20 wt.% Pt/C E-TEK. 1 mg Pt cm^{-2} and diffusion layer with 15 wt.% PTFE on both sides of the support (Nafion® 112 membrane).

Using methanol concentrations above 5 mol l^{-1} the performance of the mini-cell drops, probably because the crossover of methanol increases too much [27, 28].

Figure 7 compares the results of mini-cells having the same Pt load in the anode, 1 mg Pt cm^{-2}, but with different metal/carbon ratios. Cell 1 has 20 wt.% $Pt_{75}Ru_{25}/C$ in the anode and 20 wt.% Pt/C in the cathode, while Cell 2 has 50 wt.% $Pt_{90}Ru_{10}/C$ in the anode and 40 wt.% Pt/C in the cathode. The maximum power densities obtained were 1.7 and 2.0 mW cm^{-2}, respectively. The somewhat better performance of the cell with larger metal/carbon ratios may be attributed to a thinner catalytic layer (both have the same Pt load) with a lower internal resistance [29]. An extrapolation of this situation is found with the use of non-supported

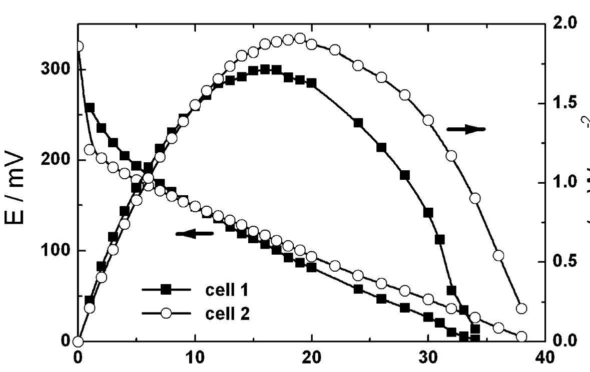

Fig. 7. Cell potential and power density as functions of the current density in mini-DMFCs for the same Pt load (1 mg Pt cm^{-2}) and different metal/carbon ratios on the electrodes. Cell 1:20 wt.% $Pt_{75}Ru_{25}/C$ in the anode and 20 wt.% Pt/C E-TEK in the cathode. Cell 2: 50 wt.% $Pt_{90}Ru_{10}/C$ in the anode and 40 wt.% Pt/C E-TEK in the cathode. Diffusion layers for anodes and cathodes with 15 wt.% PTFE on both sides of the support (Nafion® 112 membrane).

catalysts [27, 28, 30], but it usually requires the use of high Pt loads, between 3 and 8 mg Pt cm^{-2} [27]. These are extreme cases of very thin catalytic layers.

Here, electrodes containing from 1 to 7 mg Pt cm^{-2} were prepared. There is a marked increase in power density when the load is increased from 1 to 3 mg Pt cm^{-2} but for larger loads a very small gain is observed, and there is even a decrease for 7 mg Pt cm^{-2}. Because these are supported catalysts there is a large increase in the thickness of the catalytic layer, which increases the resistance path for the reagent to reach the active sites and for the elimination of reaction products [29].

Considering the membrane thickness there is some controversy with respect to the best membrane for the mini-cell. Some authors propose the use of thicker membranes because they prevent more effectively the crossover of methanol [28]. The loss in performance due to increased resistance would be compensated by the reduced depolarization of the cathode [31]. Other authors invoke the resistance as the main parameter in determining the cell performance and propose thinner membranes [28]. The performance of the mini-cell studied here was evaluated with Nafion® 112 and 117 and the results are presented in Figure 8. Up to current densities of about 10 mA cm^{-2} there is no significant difference in performance, but above that current density the thinner 112 membrane allows larger power densities to be attained. These results are in favor of the use of thinner membranes, because for the conditions used here the reduction of ionic resistance more than compensates the negative effect of methanol crossover.

On the cathode side, oxygen has to reach the active sites by diffusion, that is the cathode “breaths” the ambient air. This may require a different diffusion layer than that used in conventional DMFCs where the air is supplied under forced convection, which increases the transport of oxygen to the active sites and helps to remove the product water. The PTFE of the diffusion layer creates hydrophobic channels through which both the transport of air and the removal of product water are more effective. The removal of water is of fundamental importance because its presence forces the oxygen to a two-phase flow, and the diffusion of oxygen through water is a much slower process than diffusion in the gas phase. In the mini-cell this effect is enhanced by the low operational temperature. This situation may be improved by increasing the amount of PTFE in the diffusion layer, but this will necessarily increase the electrical resistance. So, again, a compromise has to be reached concerning the amount of PTFE in the diffusion layer.

Diffusion layers for the cathode were made with 15, 30 and 50 wt.% PTFE and deposited on both faces of the carbon cloth (see Experimental Section). The results are presented in Figure 9. Obviously, an amount of 15 wt.% is not enough to produce the hydrophobic channels necessary to transport the oxygen gas and the product water formed [32]. The results for 30 and 50 wt.% are similar, but depending on the current density region one composition predominates over the other. In order to test alternative configurations of the diffusion layer, these were also made by depositing the PTFE/carbon mixture on only one face of the carbon cloth. In this case, the catalytic layer was applied onto the face covered with the diffusion layer. The results are shown in Figure 10. In comparison with the results obtained by depositing the diffusion layer on both faces of the carbon cloth it is clear that when the amount of PTFE in the diffusion layer is adequate, the performance of the cell improves when depositing the diffusion layer on only one face. Except at low current densities, the results with 30 wt.% PTFE are better and at the maximum power density the gain with respect to the electrode with 50 wt.% PTFE is about 0.5 mW cm^{-2}.

The composition of the diffusion layer determines its porosity, which seems to be a key issue in the

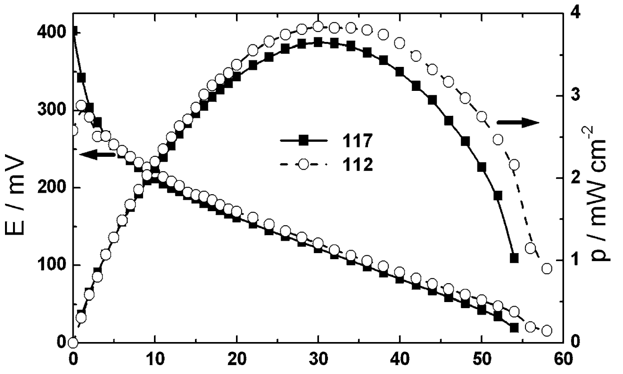

Fig. 8. Cell potential and power density as functions of the current density in mini-DMFCs for the same Pt load (3 mg Pt cm^{-2}) and membranes with different thicknesses. Anodes with 50 wt.% $Pt_{90}Ru_{10}/C$ and cathodes with 40 wt.% Pt/C (3 mg Pt cm^{-2}). Diffusion layers for anodes and cathodes with 15 wt.% PTFE on both faces of the support.

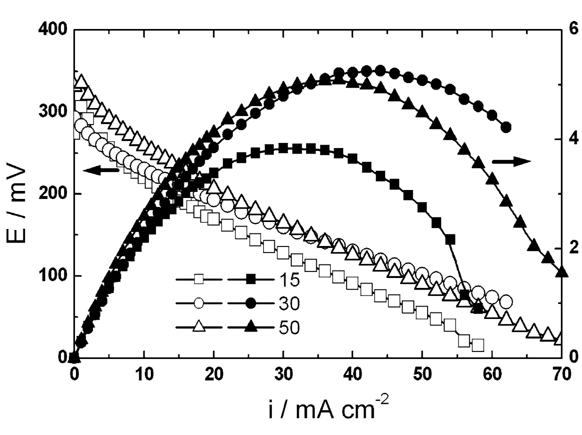

Fig. 9. Cell potential and power density as functions of the current density in mini-DMFCs for the same Pt load (3 mg Pt cm^{-2}) and different amounts (wt.%) of PTFE in the diffusion layer deposited on both faces of the carbon cloth. 50 wt.% $Pt_{90}Ru_{10}/C$ in the anode and 40 wt.% Pt/C E-TEK in the cathode (Nafion® 112 membrane).

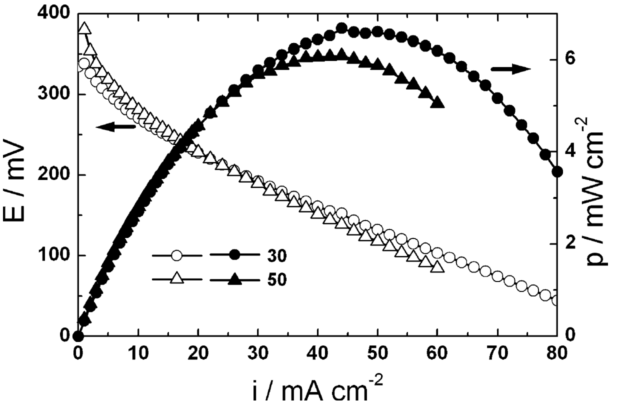

Fig. 10. Cell potential and power density as functions of the current density in mini-DMFCs for the same Pt load (3 mg Pt cm^{-2}) and different amounts (wt.%) of PTFE in the diffusion layer of the cathode deposited on only one face of the carbon cloth. 50 wt.% $Pt_{90}Ru_{10}/C$ in the anode and 40 wt.% Pt/C E-TEK in the cathode (Nafion® 112 membrane).

performance of the mini-cell. The ideal porosity seems to be around 50–60% [29], and it was suggested that the pore size should be 60–80 μm [32, 33]. With increased porosity there is an increase in electrical resistance [29]. However, Oedegaard et al. [34] substituted the carbon paper backing by a metal screen without PTFE, which resulted in an increase in pore size from 20–50 μm to 200–500 μm which nevertheless led to better performance and stability. Passos et al. [35] studied a PEMFC under low humidification at 80–90 °C with diffusion layers containing from 15 to 45 wt.% PTFE. A higher PTFE content in the diffusion layer should help to maintain the hydration of the catalytic layer, but the increase in resistance resulted in a poorer performance.

Overall, it may be said that the major problem in the mini-direct methanol fuel cell lies in the cathode. Gottesfeld et al. [13] operated a mini-cell with a breathing cathode and pressurized the methanol to 30 psi, without observing an increase in performance. On the anode side, a critical aspect seems to be the thickness of the catalytic layer which favors the use of non-supported catalysts, as proposed by Chang et al. [26] and Kho et al. [28], to produce thinner layers.

4. Conclusions

Operational parameters of a mini-direct methanol fuel cell operating at room temperature and with the reactants fed by diffusion should be markedly different than those normally used for a conventional DMFC. In particular, it was found that the concentration of methanol should be increased to 5 mol l^{-1} and the Pt load increased to 3 mg Pt cm^{-2}. With respect to the diffusion layer for the cathode it should contain 30 wt.% PTFE and be deposited only on the catalytic layer side of the electrode.

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