Influence of operational parameters and of catalytic materials on electrical performance of Direct Glycerol Solid Alkaline Membrane Fuel Cells

A. Ilie[a], M. Simoes[b], S. Baranton[b], C. Coutanceau[b], S. Martemianov[a,*]

[a] Institut Pprime UPR CNRS n° 3346 CNRS-Université de Poitiers, ENSMA; ESIP, 40 avenue du Recteur Pineau, 86022 Poitiers Cedex, France
[b] e-Lyse, LACCO UMR 6503 CNRS-Université de Poitiers, 40 avenue du Recteur Pineau, 86022 Poitiers Cedex, France

ARTICLE INFO

ABSTRACT

The present study focused on the improvement of some aspects of the membrane electrode assembly (MEA) fabrication and on some working conditions of the SAMFC (Solid Anionic Membrane Fuel Cells) fed with glycerol. The fuel solution composition has a great importance. Higher performances were achieved with 1 M glycerol +6 M NaOH solution composition. Further increase of the glycerol concentration led to transport limitations due to the increasing of the mixture viscosity. The electrical performance of a SAMFC reached the maximum value with a glycerol flow of $10\,mL\,min^{-1}$; the oxygen flow rate displayed no significant influence on the electrical performance. The temperature has a great effect on the fuel cell performance. The anion exchange membrane available in the present study led to higher performance in the temperature range between 60 and 70 °C. The fuel cell measurements performed with monometallic Pt/C, Pd/C materials, and bimetallic PtPd/C, PtBi/C and PdBi/C compounds as anode catalysts showed encouraging results with respect to the decrease of platinum loading and elaboration of Pt-free catalysts. Low platinum loaded Pt_5Pd_5/C and non-platinum based Pd_9Bi_1/C catalysts allowed reaching fuel cell performances very close or even higher than those obtained with a Pt/C catalyst at 25 °C and 60 °C.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Fuel cells have a great potential as power supply for portable electronic devices [1]. While hydrogen as a fuel allows reaching higher electric efficiency, its production, purification and storage are still problematic issues [2–4] which can limit the large scale development of fuel cells. The use of liquid fuels such as alcohols and polyols can then be advantageous considering their relatively high specific energy [5–7]. New fuel cell technologies are under development which could be convenient for using such compounds as fuel: Solid Anionic Membrane Fuel Cells (SAMFC).

The SAMFC is a hybridization of a solid polymer electrolyte fuel cell (SPEFC) with an alkaline fuel cell (AFC); it looks like an AFC with a solid membrane. Such technology has many advantages compared with PEMFC. In alkaline medium, the electrode reaction kinetics are expected to be higher than those in acid medium [8,9]. Moreover, in such medium non noble metal catalysts display better stability [10]. These properties imply that (i) other fuels than hydrogen can be considered in alkaline medium and (ii) non-platinum based materials can be used as anode catalysts [11–14]. It is known since very long time that non-platinum based materials,
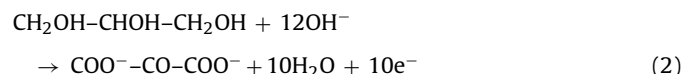
such as silver-based compounds [15–17], iron or cobalt macrocycles [13,18,19], manganese oxides [20–22], can be used as cathode catalysts. In addition, cheap liquid fuels coming from biomass or agro-resources can be used in a SAMFC.

Methanol (MeOH) displays generally a relatively good reactivity as its complete oxidation into CO_2, producing 6 moles of electrons per mole of methanol, can be easily performed at PtRu catalysts [23]. But it is a toxic compound with high solubility in water, which can lead to environment hazards. Moreover, methanol is mainly produced from partial oxidation of natural gas in industrial processes. Ethanol is less toxic and is attractive because it can be produced from the fermentation of sugar issued from cereals or beets. But, because the breaking of the C–C bond is very difficult to realize at low temperature, the main reaction products are acetaldehyde and acetic acid or acetate [24], which leads to a low faradic efficiency (17–33% of the theoretical energy) and to non-value added compounds. Moreover, the first reaction product is toxic and the second one has relatively low added value. The use of polyols as fuels can be an interesting alternative. Polyols such as ethylene glycol and glycerol are less toxic than methanol and display relatively high theoretical energy density (5.2 and $5.0\,kWh\,kg^{-1}$ for ethylene glycol and glycerol, respectively, versus 6.1 and $8.0\,kWh\,kg^{-1}$, for MeOH and EtOH, respectively [5,6]). Moreover, in these compounds each carbon carries an alcohol group and as a consequence their partial oxidation to oxalate and

* Corresponding author.
E-mail address: serguei.martemianov@univ-poitiers.fr (S. Martemianov).

mesoxalate (according to reactions (1) and (2)), without C–C bond breaking and CO_2 production, leads to 8 and 10 electrons exchanged for ethylene glycol and glycerol, respectively, against 10 and 14, respectively, for the complete oxidation in CO_3^{2-}:

$$CH_2OH-CH_2OH + 10OH^- \rightarrow COO^--COO^- + 8H_2O + 8e^- \qquad (1)$$

$$CH_2OH-CHOH-CH_2OH + 12OH^-$$
$$\rightarrow COO^--CO-COO^- + 10H_2O + 10e^- \qquad (2)$$

Therefore, the possibility to oxidize the alcohol groups without breaking the C–C bonds could allow achieving 80% and 71.5% of the whole energy available. However, only glycerol is a product from biomass as ethylene glycol is mainly produced by oxidation of ethylene.

Glycerol is generated during the production of both bioethanol and biodiesel [25]. In bioethanol production process, about 4 wt% of the sugar fermentation leads to the formation of glycerol as by-product. However, glycerol is mainly a natural product issued from the methanolysis of vegetable oils, with 10 wt% of crude glycerol produced by the transesterification reactions used for the production of methyl esters from vegetable oil [26,27]. The increasing demand of methyl esters as fuel additives leads to an increase of glycerol production, which becomes a cheaper raw material from chemistry [27]. Moreover, the objectives for biofuel utilization are very ambitious: in 2007, the European Commission proposed an "integrated energy and climate change" package, where 10% binding minimum for biofuels is targeted in 2020.[1] The USA has the same objectives. Today, the global biofuels market consists of approximately 85% bioethanol and 15% biodiesel. Bioethanol is produced and consumed mainly in Brazil and North America. On the other hand, Europe is the world leader in biodiesel production and this fuel represents about 3/4 of the European biofuel market.[1] The increase of biodiesel production in Europe will lead to the increase of crude glycerol stock. An effective usage or conversion of crude glycerol to specific products will then cut down the bio-diesel production costs. The direct oxidation of glycerol in a fuel cell may not only lead to the production of electrical energy but also to the formation of oxygenated products that usually are difficult and expensive to produce from catalytic or biological process [28,29]. The oxygenated derivatives of glycerol (glycerate, tartronate, hydroxypyruvate and mesoxalate ions) have a very limited market because they are produced by costly processes at present [28]: many oxidations are carried out using stoichiometric proportion of oxidants (e.g. permanganate, nitric acid or chromic acid) and these routes entail the production of significant amounts of undesired by-products [30].

The nature, structure and composition of multi-metallic catalysts have then an important effect on the electrooxidation of glycerol in terms of activity (energy production) and of selectivity with regard to the reaction products (cogeneration of chemicals) [7]. Because all the carbon atoms of this polyol bear an alcohol group, it is assumed that their oxidation at the anode of a SAMFC could be easily performed, allowing the production of electrical energy for devices requiring small power supply (portable applications) and value added chemicals.

However, to make such system interesting for the considered application, the overall fuel cell electrical performance has to be enhanced. This will lead not only to the production of higher electric power, but also to a higher chemical yield in a given product with added value. Such performance not only depends on the catalytic activity of the catalysts, but also on the fuel cell working parameters such as composition and concentration of the fuel solution, fluidic

Table 1
Physicochemical characterization of the different catalysts prepared using the "water in oil" microemulsion method.

	Loading by TGA (wt%)	Atomic composition by ICP-OES (at%)	Particle size by TEM (nm)
Pt	37	100	~5.0
Pd	41	100	~4.0
Pt_9Bi_1	36	90/10	~5.0
Pd_9Bi_1	38	92/8	~5.0

limitations (viscosity of the solution and mass transport), working temperature of the cell and kind of anion exchange membrane (AEM). Therefore, in order to reach acceptable cell performance, the influence of several fuel cell working parameters (glycerol and hydroxyl anions concentrations in fuel solution, reactant flow rates, cell working temperature, AEM), different Membrane Electrode Assembly (MEA) fabrication methods, i. e. Catalyst Coated Backing (CCB) and Catalyst Coated Membrane (CCM), and the utilization of different mono and bimetallic materials as anode catalysts were studied in the present work. A comparison between platinum based and palladium based anode catalysts in terms of achieved maximum power density will be presented. Also, because of the difficulty of membrane providing, two different AEMs were used and compared under Direct Glycerol SAMFC working conditions (ADP-® from Solvay and Fumapem FAA from Fumatech). The main goal of this paper is to provide to readers some indications allowing optimizing the electrical performance of a cell working with glycerol as fuel.

2. Experimental

Catalysts were prepared according to the water in oil microemulsion method as described elsewhere [7,11,31,32]. Pt/C, Pd/C, Pt_9Bi_1/C, Pd_9Bi_1/C and Pt_5Pd_5/C were characterized by TGA for their loading, ICP-OES for their compositions and TEM for their structure and particle size. Results are given in Table 1.

Diffusion layers (DLs) of the fuel cell electrodes were prepared from an Electrochem Inc carbon cloth (CC-060). Four cross layers of hydrophobic ink composed of carbon powder Vulcan XC72 and 20 wt% PTFE in suspension in isopropanol (PA. from Aldrich) have been painted on the carbon cloth leading to 3.5–4 mg cm^{-2} (C + PTFE). After drying, a catalyst ink (catalyst (40 wt%)/C with 15 wt% PTFE/C in isopropanol) was deposited on the GDL (or on the anionic membrane) in order to obtain the anode and the cathode electrodes. All anodes contained 2 mg cm^{-2} of metal. The cathodes were identical for all measurements: Pt (40 wt%)/C, 2 mg$_{Pt}$ cm^{-2}.

The MEAs have been manufactured by mechanical pressing of the two electrodes (anode and cathode) against an anionic membrane at ambient temperature. The commercial membranes were provided from Solvay and Fumatech. The membranes have been activated by immersion in a freshly prepared solution of 1 M NaOH for 24 h at room temperature. Then, the membranes were rinsed with ultrapure water and hydrated during an hour.

A single cell with an active surface of 5 cm^2 was used for the measurements of fuel cell performance. The MEA was placed between two mono-polar plates and assembled in a single fuel cell under 8 Nm torque wrench [33,34]. The experiments were performed using a test bench from Fuel Cell Technologies, Inc. The bench allows controlling the fuel cell operating parameters (flow rates, pressures, humidification of the reactants and cell temperature) and performing automatic data acquisition of polarization curves and power density curves in real time. The liquid fuel alimentation is made using a BVP Ismatec peristaltic pump with manual adjustable speed. The fuel cell is fed with pure oxygen at the cathode and solution of glycerol + NaOH at the anode.

Table 2
Configuration of parameter levels for the DOE; values of the cell open circuit voltage (OCV) and of the maximum power density achieved in each experiment at 25 °C, at a fuel flow of 0.8 mL min^{-1}, an oxygen flow of 40 mL min^{-1}, both at atmospheric pressure.

No.	[Glycerol] (mol L^{-1})	[OH$^-$] (mol L^{-1})	OCV (V)	P_{max} (mW cm^{-2})
1	1	2	0.765	8
2	1	4	0.774	10.6
3	1	6	0.787	11.3
4	2	2	0.698	9.4
5	2	4	0.780	4.0
6	2	6	0.863	6.5
7	3	2	0.784	3.8
8	3	4	0.776	6.4
9	3	6	0.825	0.0

3. Results and discussion

3.1. Influence of the fuel composition

The breaking of the C–C bond in course of alcohol or polyol oxidation is very difficult to perform at low temperature. Rousseau et al. [24] showed that at 80 °C in acid medium the main oxidation products of ethanol were acetaldehyde and acetic acid, whatever the catalyst (Pt/C, Pt$_9$Sn$_1$/C and PtSnRu/C) and the working voltage of the Direct Alcohol Fuel Cell (DAFC). Assuming that the same is true in alkaline medium, the chemical equation for the complete oxidation reaction of glycerol into mesoxalate ion without breaking the C–C bond can be written as follow:

$$CH_2OH-CHOH-CH_2OH + 5/2O_2 + 2OH^- \rightarrow COO^--CO-COO^- + 5H_2O$$
(3)
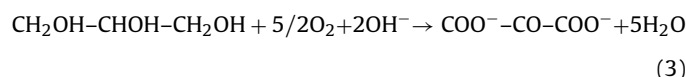
The main information is that hydroxyl anions are consumed for the oxidation of glycerol in alkaline medium. The fuel solution should contain hydroxyl ions not only to respect the reaction stoichiometry, but also in order to ensure the ionic continuity within the active layer of the anode (three phase boundary); both improvements are expected to increase the SAMFC electrical performance. Such aspect was already verified in the case of the electrooxidation of methanol and ethylene glycol in a SAMFC [35].

Therefore, the first step for optimizing the SAMFC operational parameters was the study of the optimum fuel solution composition. A simple Design Of Experiments (DOE) based on the Tagushi method has been implemented for this purpose. Two factors were considered: the glycerol concentration (three levels: 1 M, 2 M and 3 M) and the hydroxyl anions concentration (three levels: 2 M, 4 M, 6 M). A L$_9$ (3^3) Tagushi DOE was used; the 9 experiments were carried out according to Table 2, which indicates the level of each factor for each experiment. Fuel cell measurements were carried out with a 150 μm thick ADP® Solvay membrane sandwiched between two identical Pt(40 wt%)/C electrodes (2.0 mg$_{Pt}$ cm^{-2}). The operating parameters are specified in Table 2. The considered response in the DOE for the optimization of the fuel solution composition was the maximum power density delivered by the fuel cell as determined after recording the polarization curves at 25 °C, at a fuel flow of 0.8 mL min^{-1}, an oxygen flow of 40 mL min^{-1}, both at atmospheric pressure (Fig. 1). It can be seen that the fuel solution composition has an important effect on the electrical performance of the cell. Best results in terms of higher power density are obtained with the lower glycerol concentration (1 M) and with relatively high hydroxyl anion concentrations (4 M and 6 M), with ca. 11 mW cm^{-2}. A further increase of the glycerol concentration leads to the decrease of the cell performance; moreover, no trend can be drawn from the results of fuel cell electric performance measurements for higher glycerol concentration. This is likely related to the increase of the solution viscosity (pure glycerol has a high
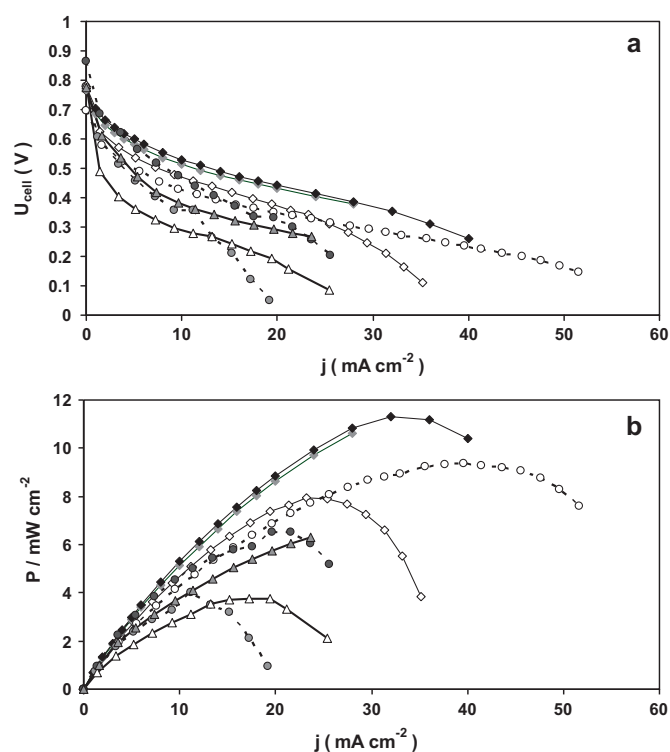

Fig. 1. (a) Polarization curves and (b) power density curves recorded in SAMFCs fed with a fuel solution of different concentrations in glycerol and hydroxyl anions; anode and cathode: Pt (40 wt%)/C, 2.0 mg$_{Pt}$ cm^{-2}; ADP® membrane. (◆) 1 M glycerol, 6 M NaOH, (◆) 1 M glycerol, 4 M NaOH, (◇) 1 M glycerol, 2 M NaOH; (●) 2 M glycerol, 6 M NaOH, (●) 2 M glycerol, 4 M NaOH, (○) 2 M glycerol, 2 M NaOH; (▲) 2 M glycerol, 2 M NaOH, (△) 3 M glycerol, 4 M NaOH, T = 25 °C, P$_{fuel}$ = P$_{O_2}$ = 1 atm, fuel flow rate = 0.8 mL min^{-1}, oxygen flow rate = 40 mL min^{-1}).

kinematic viscosity of 1490 cp at 20 °C), which can limit the transport of the fuel through the diffusion layer toward the active layer. It appears then that it is preferable to work with low glycerol concentration (1 M).

3.2. Influence of the reactant flow rates

The viscosity of the fuel can then limit its transport through the diffusion layer toward the active sites; so supplementary studies regarding possible mass transport limitations have been carried out using the same MEA as that described above. First, the electrical behavior of a 5 cm^2 SAMFC fed with a glycerol 1 M/NaOH 6 M fuel solution and delivering a constant current density j = 40 mA cm^{-2} has been studied for low fuel flow rates ranging from 0.8 mL min^{-1} to 7.5 mL min^{-1}. A notable dependence of the electrical performance on fuel flow rate is evidenced; the electrical power delivered by the cell increases by the factor 4 over such flow rate range (Fig. 2a).

Supplementary measurements have been done using more powerful pump and a new MEA. For the same fuel concentration and for a constant load j = 8.4 mA cm^{-2} the cell delivered a voltage almost independent on the flow rate, with a very small increase (Fig. 2a and b) when the fuel flow rate is increased from 10 mL min^{-1} to 100 mL min^{-1}. These measurements were performed several times with different MEAs in order to check the repeatability: similar results were obtained. It can be concluded that at some critical flow rate (Q_A = 10 mL min^{-1} under our experimental conditions) the mass transport limitation can be decreased at the anode of the SAMFC.

We then focused on the influence of the oxygen flow rate on the fuel cell performances. It has been observed that for a constant
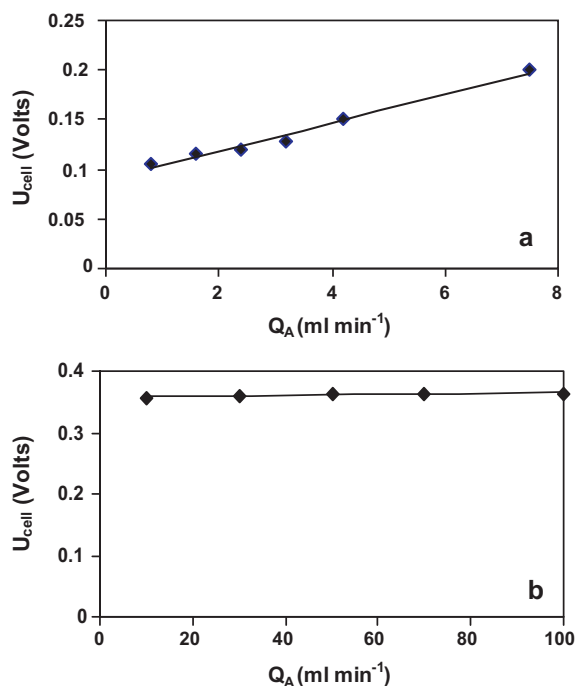
Fig. 2. Dependence of the cell voltage on the fuel flow rate Q_A of the same SAMFC as in Fig. 1, (a) working with a constant current $j = 40$ mA cm^{-2} and Q_A in the range from 0.8 to 7.5 mL min^{-1} and (b) working with a constant current $j = 8.4$ mA cm^{-2} and Q_A in the range from 10 to 100 m/min^{-1}.

electric load ($j = 28$ mA cm^{-2}) the cell potential remained approximately constant while the oxygen flow rate was increased from 100 mL min^{-1} to 500 mL min^{-1}, as shown in Fig. 3. Such tests were also repeated with different MEAs (fitted with a Fumapem® FAA Fumatech commercial membrane); same results were obtained. It was then concluded that the oxygen flow rate did not affect directly the electrical performance of the cell. An oxygen flow rate $Q_C = 100$ mL min^{-1} was used for further fuel cell measurements.

3.3. Influence of the catalytic layer deposition method: Catalyst Coated Backing (CCB) vs Catalyst Coated Membrane (CCM)

CCM methods for the preparation of MEAs have already shown important potentialities for the improvement of fuel cell performance. In the present case, because it was shown that mass transport of glycerol and hydroxyl anions from the fuel solution toward the anode active sites was an important limitation for
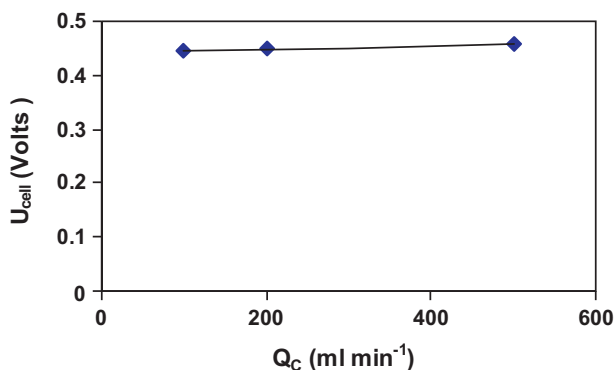

Fig. 3. Dependence of the cell voltage on the oxygen flow rate Q_C of the same SAMFC as in Fig. 1, working with a constant current $j = 28$ mA cm^{-2}.
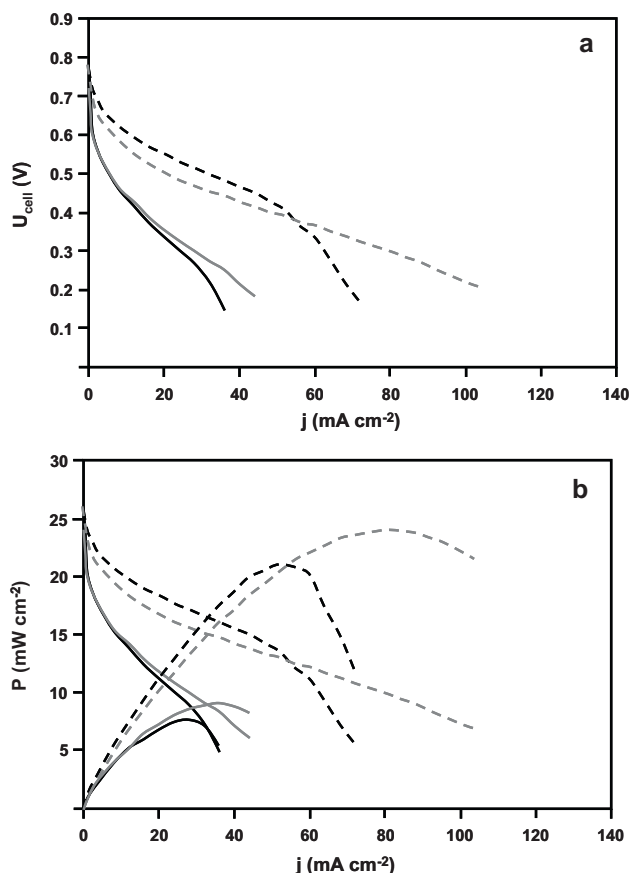

Fig. 4. (a) Polarization curves and (b) power density curves recorded at 25 °C (plain lines) and at 60 °C (dashed lines) in SAMFCs fed with a fuel solution of 1 M glycerol and 4 M hydroxyl anions and fitted with MEAs realized by CCB method (black line) and CCM method (grey line). anode = Pt(40 wt%)/C, 1.0 mg$_{Pt}$ cm^{-2} and cathode = Pt(40 wt%)/C, 2.0 mg$_{Pt}$ cm^{-2}; ADP® membrane ($P_{fuel} = P_{O_2} = 1$ atm, fuel flow rate = 4 mL min^{-1}, oxygen flow rate = 40 mL min^{-1}).

achieving high cell performance, the use of such a method could be interesting. The use of a hydrophobic diffusion layer (which contains PTFE) could be avoided and the mass transport limitation decreased. Fig. 4 compares the SAMFC performance obtained at 25 °C and 60 °C with CCB (Fig. 4a) and CCM (Fig. 4b) configurations. Clearly, the MEA prepared by CCM at the anode side allows achieving higher maximum power densities than the MEA prepared by CCB. Under such experimental conditions, a power density of ca. 25 mW cm^{-2} is achieved at 60 °C with the CCM MEA against ca. 20 mW cm^{-2} with the CCB MEA. It has to be noted that at 25 °C, both MEAs led to superimposed polarization curves in the low current density range ($j < 20$ mA cm^{-2}); the CCM MEA led to higher power densities for higher current densities than the CCB one likely due to the lower mass transfer limitation. For higher temperature (60 °C), the CCB MEA led to higher cell performance than the CCM one in the low current density region ($j < 50$ mA cm^{-2}). This indicates that even in the anode potential region, were activation process of the oxidation reaction is expected to prevail, the presence of a diffusion layer has a beneficial effect on the electrode performance. This could be due to a better repartition of the reactive species over the whole catalytic layer surface, or to a better removal of reaction products from the active surface layer or also to a better reactant concentration ratio (glycerol and hydroxyl anions) in the active layer leading to a lower poisoning of the catalyst surface. Both polarization curves from 10 to 40 mA cm^{-2} are parallel, which seems to indicate that the cell resistance is the same for both MEAs. For current densities higher than 50 mA cm^{-2}, the absence of a diffusion layer allows achieving higher power densities.

3.4. Influence of the Anionic Exchange Membrane (AEM)

However, the main problems related with the development of SAMFC is the availability of commercial AEMs, their low conductivity (ADP® Solvay membrane used for the optimization of the SAMFC operating parameters has a rather high specific resistance of ca. 0.5 $\Omega\,cm^2$) and their lower thermo-stability in comparison with solid acid electrolytes such as Nafion membranes [36]. Authors have attempted to develop or to use different kinds of alkaline membranes for developing SAMFC technology. For example, Matsuoka et al. [37] studied the electrooxidation of different alcohols and polyols for Direct Alkaline Fuel Cell applications using an anion exchange membrane (from Tokumaya Co., Japan) functionalized by tetraalkyl ammonium as cation groups (thickness = 240 μm). Ethylene glycol led to achieve the best cell performance with a maximum power density close to $10\,mW\,cm^{-2}$ with PtRu catalyst at the anode. Varcoe and Slade [38] developed an ETFE alkaline anion-exchange membrane. Power densities close to $1.5\,mW\,cm^{-2}$ at 50 °C and $8.5\,mW\,cm^{-2}$ at 80 °C were achieved with reactants (methanol and oxygen) pressurization and $4.0\,mg\,cm^{-2}$ PtRu and Pt at the anode and cathode, respectively.

In order to find a better candidate for SAMFC, a commercial anionic membrane Fumapem® FAA from Fumatech (35–40 μm thickness, 0.59 $\Omega\,cm^2$ at 20 °C) was compared with the ADP® membrane from Solvay (150 μm thickness, 0.5 $\Omega\,cm^2$ at 20 °C). The tests were performed in a $5\,cm^2$ cell with identical anode and cathode (Pt(40 wt%)/C, $2\,mg_{Pt}\,cm^{-2}$ deposited on a diffusion layer PTFE(15 wt%)/C). The fuel composition was glycerol 1 M/NaOH 4 M, and oxygen was used as oxidant. Before use, both membranes were immersed in a 1 M NaOH solution for 24 h for their activation and rinsed 1 h in ultra pure water. Fig. 5a and b compares the polarization curves and the power density curves obtained at different temperatures with a SAMFC fitted with a ADP membrane (Fig. 5a) and with a SAMFC fitted with a Fumatech membrane (Fig. 5b). First, it can be seen that the open circuit voltages are always lower with the Fumatech membrane than with the Solvay membrane, which is certainly related to higher fuel crossover due to lower membrane thickness.

Higher maximum power densities were achieved with the Fumatech membrane with $13.5\,mW\,cm^{-2}$ at 60 °C and $7.8\,mW\,cm^{-2}$ at 25 °C, against $6.4\,mW\,cm^{-2}$ at 60 °C and $3\,mW\,cm^{-2}$ at 25 °C for the Solvay membrane. On the other hand, the Solvay membrane displayed higher stability for higher temperatures with improved maximum power density (e.g. $7.8\,mW\,cm^{-2}$ at 70 °C), whereas the Fumatech membrane performance decreased rapidly at 80 °C (e.g. $3.8\,mW\,cm^{-2}$).

It is important to note that the increase of the temperature from 25 °C to 60 °C led in both cases to the increase of the power density by almost a factor two, which indicate that the reaction kinetics at the electrode are improved. The increase of the SAMFC working temperature is one of the main issues for the development of such technology. Although the Fumatech membrane appears less stable with temperature than the ADP one, the former was chosen for further investigations because it led to higher fuel cell electrical performance in terms of achieved maximum power densities. However, although higher electrical performance is achieved with the Fumatech membrane in comparison with the Solvay one, the maximum achieved power density (ca. $8\,mW\,cm^{-2}$ at room temperature) is lower that those obtained under close experimental conditions for a SAMFC fitted with a Pt/C anode and a Solvay membrane and fuelled with MeOH 2 M + NaOH 4 M or Ethylène Glycol 2 M + NaOH 4 M solutions, with $18\,mW\,cm^{-2}$ and $20\,mW\,cm^{-2}$, respectively [35]. This indicates that the activation of the glycerol oxidation reaction is much more difficult to perform, and that more active catalysts have to be developed.
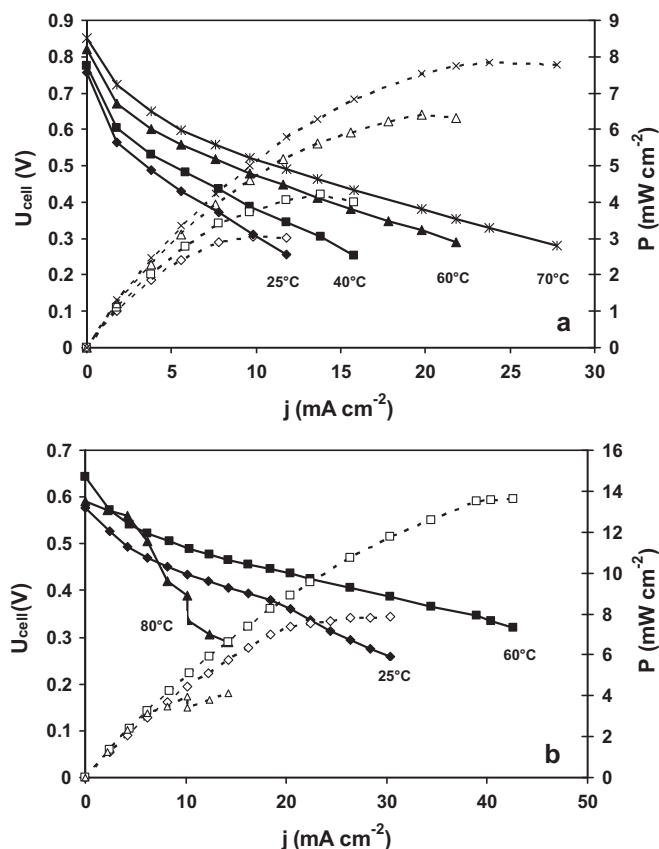

Fig. 5. Polarization curves and power density curves recorded at different temperatures in SAMFCs fed with a fuel solution of 1 M glycerol and 4 M hydroxyl anions and fitted with MEAs realized with (a) ADP-® membrane and (b) Fumatech membrane; anode and cathode: Pt(40 wt%)/C, $2.0\,mg_{Pt}\,cm^{-2}$; ($P_{fuel} = P_{O_2} = 1$ atm, fuel flow rate = 0.8 mL min⁻¹, O_2 flow rate = 40 mL min⁻¹).

3.5. Catalysts for increasing the Direct Glycerol SAMFC performance

The reactions involved in a SAMFC working with a glycerol-NaOH fuel occur with higher kinetics than those in acid fuel cell. Thus, the possibility of either decreasing the Pt loading or even of using non-platinum-based catalysts can be considered. It was already shown that some Pt-based and Pd-based catalysts displayed high catalytic activity for alcohols or polyols electrooxidation in alkaline medium [39–43]. Moreover Pd-based bimetallic catalysts seem to be more stable with respect to degradation than pure Pd on carbon black [44–47].

Monometallic Pt and Pd, and bimetallic PtPd, PtBi and PdBi materials have already shown interesting performance as anode catalysts for the oxidation for ethylene glycols [11,35]. Pt/C, Pd/C, Pd_5Pt_5/C, Pd_9Bi_1/C and Pt_9Bi_1/C catalysts were synthesized by the so called "water in oil" microemulsion method [7,11,31,32].

The catalytic activity of these catalysts was estimated in a single $5\,cm^2$ Direct Glycerol SAMFC. Fig. 6a and b compares the power density curves obtained at different temperatures (25 °C and 60 °C) with Pt/C and Pd/C monometallic materials, and Pd_5Pt_5/C, Pt_9Bi_1/C and Pd_9Bi_1/C bimetallic compounds as anode catalysts. First, the MEA fitted with a Pd/C anode led to the lower cell performance with ca. $6\,mW\,cm^{-2}$ and ca. $10\,mW\,cm^{-2}$ at 25 °C and 60 °C, respectively. The power density achieved at 25 °C matches well with that reported by Bianchini and Shen [42] for a Direct Glycerol Fuel Cell with a 2 mol L⁻¹ KOH solution of glycerol (5 wt%), containing a Tokuyama A006 membrane, an anode coated with Pd/MWCNT ($1\,mg_{Pd}\,cm^{-2}$) and a Hypermec K-14 Fe-Co cathode. However, at
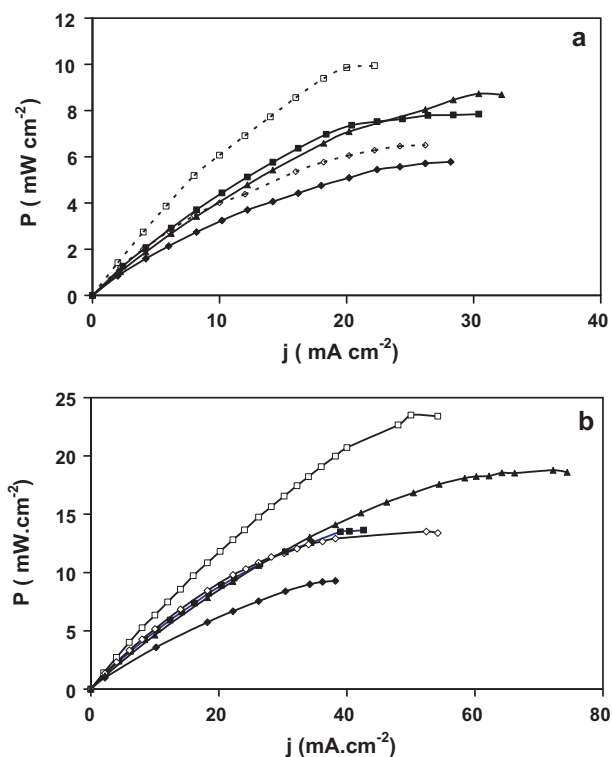
Fig. 6. Power density curves recorded with SAMFCs fed with a fuel solution of 1 M glycerol and 4 M NaOH at (a) 25 °C and (b) 60 °C. The MEA is fitted with a Fumapem® FAA Fumatech membrane, a cathode with 2 mg$_{Pt}$ cm^2 Pt(40 wt%)/C and different anode catalysts with 2.0 mg$_{metal}$ cm^{-2}, loaded at 40 wt% in metals. (■) Pt/C, (□) Pt$_9$B$_1$/C, (♦) Pd/C, (◇) Pd$_9$Bi$_1$/C, (▲) Pt$_5$Pd$_5$/C ($P_{fuel} = P_{O_2} = 1$ atm, fuel flow rate = 0.8 mL min^{-1}, O$_2$ flow rate = 40 mL min^{-1}).

60 °C, Bianchini et al. report much higher performance with ca. 70 mW cm^{-2}. Second, it is interesting to note that the Pt$_5$Pd$_5$/C anode catalyst allowed achieving equivalent cell performance than the Pt/C catalysts at 25 °C (both at ca. 8–9 mW cm^{-2}), higher cell performance was even achieved at 60 °C with the bimetallic catalyst (ca. 19 mW cm^{-2}) compared with the Pt/C catalyst (ca. 14 mW cm^{-2}). Replacing half of the platinum atoms by palladium in the catalyst did not lead to decrease its catalytic activity, but in contrary it led to the enhancement of the cell electrical performance. Such synergetic effect between platinum and palladium was already observed in the case of the electrooxidation of ethylene glycol [35]. It was explained by a reduced poisoning of the platinum catalytic sites by diluting them with palladium atoms. The addition of bismuth to platinum or palladium led to increase the anode activity and the cell performance in comparison with those obtained when pure Pt/C and Pd/C materials are used as anode catalysts. It is worth to note that at 60 °C, the Pd$_9$Bi$_1$ catalyst allowed achieving the same cell performance as the Pt/C catalyst (ca. 14 mW cm^{-2}). In this case, it is demonstrated that non platinum based materials could be used as anode catalysts alternative to platinum in solid alkaline fuel cell. On the other hand, the higher anode activity was achieved when Pt$_9$Bi$_1$/C material is used as anode catalyst, with 10 mW cm^{-2} and 25 mW cm^{-2}, at 25 °C and 60 °C respectively.

Such performances are higher than those obtained with a pure Pt/C catalyst; however, they remain lower than those achieved with ethylene glycol under very close experimental conditions [32] and than those reported by Bianchini and Shen [42] using Pd–(Ni–Zn)/C anodes, Hypermec K-14 Fe–Co cathode and a Tokuyama membrane (close to 20 mW cm^{-2} and 80 mW cm^{-2} at 25 °C and 60 °C, respectively). The roles of the cathode catalyst and of the membrane properties (conductivity, thermal stability, etc.) are certainly

involved in such difference of electric performances. It has to be noted that, according to these authors, ethanol allows achieving higher power densities with ca. 50 mW cm^{-2} and ca. 120 mW cm^{-2}, at 25 °C and 60 °c respectively; whereas methanol displays very close performances than glycerol.

4. Conclusion

The present study was mainly focused on the optimization of some operational parameters for the improvement of the electrical performance of a SAMFC fed with glycerol. The chemical reaction of glycerol electrooxidation indicated that hydroxyl anions were consumed. It was then important to determine the best glycerol/OH$^-$ ratio in the fuel solution. This study pointed out the problem of mass transfer limitation for achieving higher electrical cell performance. Best performances were achieved with low glycerol concentration (1 M) and high NaOH concentration (6 M). The fuel flow rate has also an influence on the cell performance; under the present experimental conditions a fuel solution flow rate of 10 mL min^{-1} was found as an optimum; no significant influence of the oxygen flow rate was observed. In order to decrease the problem of mass transfer limitation, MEAs prepared using CCM method were compared with MEAs prepared using CCB method. Improvement of the cell performance by a factor 2 was achieved with CCM method.

Two different AEMs were used for MEA fabrication. It was shown that the Fumapem® FAA Fumatech membrane allowed reaching higher performance than the ADP® membrane from Solvay, although the former war less stable at high temperature than the latter one.

At last, Pt and Pd based catalysts were compared in terms of activity in a Direct Glycerol SAMFC. The bimetallic Pd$_5$Pt$_5$/C catalyst presented better SAMFC performances than the P/C reference catalyst. It was also shown that Bi addition to Pt or Pd catalysts improved significantly the SAMFC electrical performance. Although the Pd/C catalyst led to the lower cell electrical performance, the Pd$_9$Bi$_1$/C catalyst allowed achieving the same electrical performance than the Pt/C reference catalyst. The best electrical performance was obtained with Pt$_9$Bi$_1$ anode catalysts with a power density value of 25 mW cm^{-2}, ca. twice higher than that obtained with a pure Pt/C catalyst.

References

[1] G. Hoogers, Fuel Cell Technology Handbook, CRC Press, 2002.
[2] J.W. Gosselink, Int. J. Hydrogen Energy 27 (2002) 1125.
[3] N. Takeichi, H. Senoh, T. Yokota, H. Tsuruta, K. Hamada, H.T. Takeshita, H. Tanaka, T. Kiyobayashi, T. Takano, N. Kuriyama, Int. J. Hydrogen Energy 28 (2003) 1121.
[4] R. Ströbel, M. Oszcipok, M. Fasil, B. Rohland, L. Jorissen, J. Garche, J. Power Sources 105 (2002) 208.
[5] C. Lamy, J.-M. Léger, J. Phys. IV 4 (1994) C1.
[6] F. Vigier, C. Coutanceau, A. Perrard, E.M. Belgsir, C. Lamy, J. Appl. Electrochem. 34 (2004) 439.
[7] M. Simoes, S. Baranton, C. Coutanceau, Appl. Catal. B: Environ. 93 (2010) 354–362.
[8] C.-C. Yang, Int. J. Hydrogen Energy 29 (2004) 135.
[9] Y. Wang, L. Li, L. Hu, L. Zhuang, J. Lu, B. Xu, Electrochem. Commun. 5 (2003) 662.
[10] J. Van Muylder, M. Pourbaix, Atlas d'équilibres électrochimiques à 25 °C, Gauthier-Villars & Cie, Paris, 1963.
[11] L. Demarconnay, S. Brimaud, C. Coutanceau, J.-M. Leger, J. Electroanal. Chem. 601 (2007) 169.
[12] L. Demarconnay, C. Coutanceau, J.-M. Léger, Electrochim. Acta 53 (2008) 3232.
[13] R. Jamard, J. Salomon, A. Martinent-Beaumont, C. Coutanceau, J. Power Sources 193 (2009) 779.
[14] A. Serov, C. Kwak, Appl. Catal. B: Environ. 97 (2010) 1.

[15] K. Strasser, in: W. Vielstisch, H.A. Gasteiger, A. Lamm (Eds.), Handbook of Fuel Cells-Fundamentals, Technology and Applications, vol. 4, Wiley, 2003, p. 775.
[16] H.-K. Lee, J.-P. Shim, M.-J. Shim, S.-W. Kim, J.-S. Lee, Mater. Chem. Phys. 45 (1996) 238.
[17] L. Demarconnay, C. Coutanceau, J.-M. Léger, Electrochim. Acta 49 (2004) 4513.
[18] S.L. Gojkovic, S. Gupta, R.F. Savinell, J. Electroanal. Chem. 462 (1999) 63.
[19] S.L. Gojkovic, S. Gupta, R.F. Savinell, Electrochim. Acta 45 (2000) 889.
[20] B. Klapste, J. Vondrak, J. Velicka, Electrochim. Acta 47 (2002) 2365.
[21] L. Mao, D. Zhang, T. Sotomura, K. Nakatsu, N. Koshiba, T. Ohsaka, Electrochim. Acta 48 (2003) 1015.
[22] M. Chatenet, F. Micoud, I.E. Roche, Chainet Electrochim. Acta 51 (2006) 5452.
[23] C. Lamy, J.-M. Léger, S. Srinivasan, Modern Aspects of Electrochemistry, vol. 34, Kluwer Academic/Plenum Publishers, New York, 2001.
[24] S. Rousseau, C. Coutanceau, C. Lamy, J.-M. Léger, J. Power Sources 158 (2006) 18.
[25] S.S. Yazadani, R. Gonzalez, Curr. Opin. Biotechnol. 18 (2007) 213.
[26] M.A. Dasari, P.P. Kiatsimkul, W.R. Sutterlin, G.J. Suppes, Appl. Catal. A: Gen. 281 (2005) 225.
[27] J.-M. Clacens, Y. Pouilloux, J. Barrault, J. Appl. Catal. A: Gen. 227 (2002) 181.
[28] P. Gallezot, Catal. Today 37 (1997) 405.
[29] A. Behr, J. Eilting, K. Irawadi, J. Leschinski, F. Lindner, Green Chem. 10 (2008) 13.
[30] S. Carrettin, P. McMorn, P. Johnston, K. Griffin, C.J. Kiely, G.A. Attard, G. Hutchings, Top. Catal. 27 (2004) 131.
[31] M. Simões, S. Baranton, C. Coutanceau, J. Phys. Chem. C 113 (2009) 13369.
[32] M. Simões, S. Baranton, C. Coutanceau, Electrochim. Acta 56 (2010) 920.
[33] J.-J. Kadjo, J.-P. Garnier, J.-P. Maye, F. Relot, S. Martemianov, Russian J. Electrochem. 42 (2006) 467.
[34] A.J.J. Kadjo, P. Brault, A. Caillard, C. Coutanceau, J.-P. Garnier, S. Martemianov, J. Power Sources 172 (2007) 613.
[35] C. Coutanceau, L. Demarconnay, C. Lamy, J.-M. Léger, J. Power Sources 156 (2006) 14.
[36] H. Yanagi, K. Fukuta, Anion Exchange Membrane and Ionomer for Alkaline Membrane Fuel Cells (AMFCs), www.electrochem.org/meetings/scheduler/abstracts/214/0783.pdf.
[37] K. Matsuoka, Y. Iriyama, T. Abe, M. Matsuoka, Z. Ogumi, J. Power Sources 150 (2005) 27.
[38] J.R. Varcoe, R.C.T. Slade, Electrochem. Comm. 8 (2006) 839.
[39] N. Dalbay, F. Kadirgan, J. Electroanal. Chem. 296 (1990) 559.
[40] R. Pattabiraman, Appl. Catal. A: Gen. 153 (1997) 9.
[41] P.K. Shen, C. Xu, Electrochem. Comm. 8 (2006) 184.
[42] C. Bianchini, P.K. Shen, Chem. Rev. 109 (2009) 4183.
[43] V. Bambagioni, C. Bianchini, A. Marchionni, J. Filippi, F. Vizza, J. Teddy, P. Serp, M. Zhiani, J. Power Sources 190 (2009) 241.
[44] S.A. Grigoriev, E.K. Lyutikova, S. Martemianov, V.N. Fateev, Int. J. Hydrogen Energy 32 (2007) 4438.
[45] M.R. Tarasevich, V.A. Bogdanovskaya, L.N. Kuznetsova, A.D. Modestov, B.N. Efremov, A.E. Chalykh, Y.G. Chirkov, N.A. Kapustina, M.R. Ehrenburg, J. Appl. Electrochem. 37 (2007) 1503.
[46] M.R. Tarasevich, G.V. Zhutaeva, V.A. Bogdanovskaya, M.V. Radina, M.R. Ehrenburg, A.E. Chalykh, Electrochim. Acta 52 (2007) 5108.
[47] M.R. Tarasevich, A.E. Chalykh, V.A. Bogdanovskaya, L.N. Kuznetsova, N.A. Kapustina, B.N. Efremov, M.R. Ehrenburg, L.A. Reznikova, Electrochim. Acta 51 (2006) 4455.