Short communication

Optimization of properties and operating parameters of a passive DMFC mini-stack at ambient temperature

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ABSTRACT

An investigation of properties and operating parameters of a passive DMFC monopolar mini-stack, such as catalyst loading and methanol concentration, was carried out. From this analysis, it was derived that a proper Pt loading is necessary to achieve the best compromise between electrode thickness and number of catalytic sites for the anode and cathode reactions to occur at suitable rates. Methanol concentrations ranging from 1 M up to 10 M and an air-breathing operation mode were investigated. A maximum power of 225 mW was obtained at ambient conditions for a three-cell stack, with an active single cell area of $4 \, cm^2$, corresponding to a power density of about $20 \, mW \, cm^{-2}$.

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1. Introduction

Direct methanol fuel cells (DMFCs) are promising candidates for portable electric power sources because of their high energy density, lightweight, compactness, simplicity as well as easy and fast recharging [1–4]. In the last decades, a large number of publications were focused on the development of DMFC components, such as catalysts, membranes, electrodes, etc. [5–13]. Initially, DMFC stacks have been developed for assisted power units (APUs) purpose or for electrotraction [14]. These stacks used a classical configuration where single cells are stacked in series through bipolar plates. More recently, the attention has been focused on portable applications and various stack configurations have been proposed [15–20]. Thanks to integrated-circuit (IC) fabrication technology, micro-channel patterns can be featured on the silicon wafer with high resolution and good repeatability [19–21]. Moreover, in order to be commercially viable, it is necessary to eliminate power losses from auxiliaries, i.e. the pump and the fan that are usually used to feed methanol and air into the stack [22,23]. To this scope, the concept of passive-feed DMFCs has been proposed [16,24–29]. Under this configuration, DMFCs operate without any external devices for feeding methanol and blowing air into the cells. Oxygen can diffuse into the cathode from the ambient due to an air-breathing action of the cell (partial pressure gradient), whereas methanol can reach the catalytic layer from a reservoir driven by a concentration gradient between the electrode and the reservoir and through capillary force action of electrode pores. The use of low cost miniaturised "step-up" DC/DC converters, recently commercialised [30], allows to suitably increase the stack potential with a very small dissipation of power (∼90% efficiency). This approach does not require extensive miniaturisation of the DMFC stack favouring the development of low cost DMFC stack architectures with practical electrode area. In the present paper, an optimization of properties and operating parameters, such as methanol concentration and catalyst loading, of a passive direct methanol fuel cell monopolar stack is presented. The influence of Pt loading, already investigated in a conventional forced-flow DMFC [31], was analysed taking into account the mass transfer constrains caused by high catalyst loading under passive operation.

2. Experimental

The electrodes for a three-cell stack were composed of commercial gas-diffusion layer-coated carbon cloth for high temperature (HT-ELAT, E-TEK) and low temperature operation (LT-ELAT, E-TEK) at the anode and cathode, respectively. Unsupported Pt–Ru (Johnson-Matthey) and Pt (Johnson-Matthey) catalysts were mixed with 15 wt.% Nafion ionomer (Ion Power, 5 wt.% solution) and deposited onto the backing layer for the anode and cathode, respectively. Nafion 117 (Ion Power) was used as electrolyte. The MEA for a monopolar mini-stack (three cells) was made by assembling simultaneously three sets of anode and cathode pairs on each side of the membrane and then sandwiched between two plastic plates cov-

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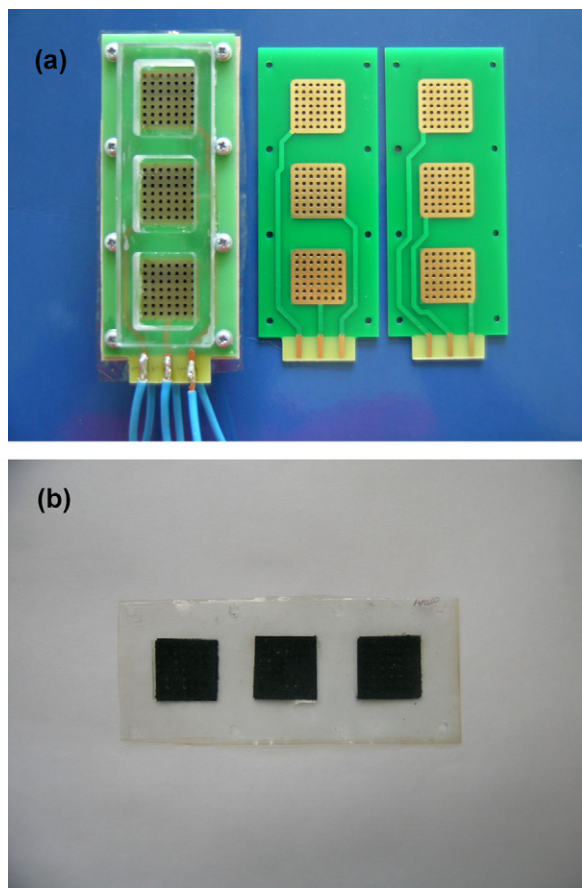*E-mail address:* arico@itae.cnr.it (A.S. Aricò).

Fig. 1. Pictures of the DMFC three-cell stack with the monopolar plates (a) and MEA formed by a single membrane and three couples of electrodes (b).

ered by thin gold film current collectors in the area of electrodes with a distribution of holes through which methanol (from a reservoir) and air (from ambient) could diffuse into the electrodes. Active area of each electrode was $4\,cm^2$ and the total active area of the stack was $12\,cm^2$. Series connections between the cells were made externally through the electric circuit. A picture of the device is reported in Fig. 1a. Fig. 1b shows the complete membrane-electrode assembly for the mini-stack formed by a single membrane and three couples of electrodes.

A Pt loading ranging from 1.5 to $6\,mg\,cm^{-2}$ for both anodes and cathodes was investigated. Different methanol concentrations from 1 M up to 10 M were evaluated. The stack was operating under passive mode at room temperature ($21 \pm 2\,^\circ C$). No auxiliaries such as pumps, heaters, humidifiers or blowers were used. In this passive mode, oxygen molecules spontaneously diffuse into the cathode (air-breathing effect). Such a phenomenon is induced by the concentration gradient at the electrode–electrolyte interface where oxygen is consumed by the electrochemical reaction. Similarly, methanol diffuses from the tank, attached to the anode compartment (see Fig. 1a), to the electrode by effect of the concentration gradient caused by the electrochemical consumption of fuel. Performances were investigated by steady-state galvanostatic polarizations and chrono-potentiometric measurements using an AUTOLAB PGSTAT 302 Potentiostat/Galvanostat (Metrohm).

3. Results and discussion

Different Pt loadings were evaluated in order to investigate the effect of catalytic layer thickness on the electrochemical behaviour
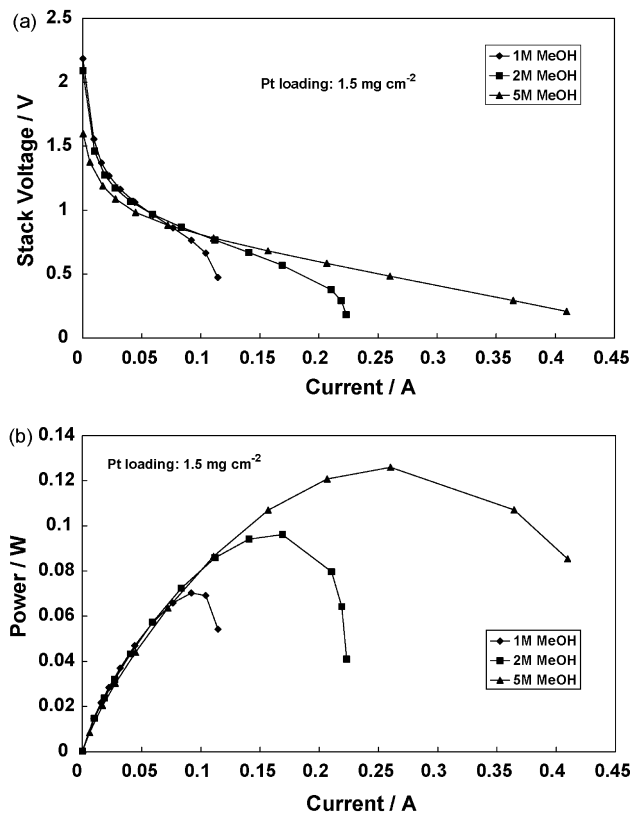

Fig. 2. Polarization (a) and power (b) curves for the three-cell stack with a Pt loading of $1.5\,mg\,cm^{-2}$ on each electrode at different methanol concentrations.

of the air breathing monopolar stack. A small catalyst loading is associated to a small electrode thickness. This favours an easy access of the reactants to the reaction region (electrode–electrolyte interface) and thus lower mass transfer constrains but there is also a small number of catalytic sites. Fig. 2 shows the polarization and power density curves for the three-cell stack equipped with electrodes containing $1.5\,mg\,cm^{-2}$ Pt loading on both sides and different methanol concentrations placed in the reservoir (1 M, 2 M and 5 M). The thickness of the total anode electrode (catalytic, diffusion and backing layers), calculated by SEM (not shown), was $370\,\mu m$; whereas, it was $300\,\mu m$ for the cathode. An open circuit voltage (OCV) higher than 2 V was recorded with 1 M and 2 M methanol solutions; whereas, it decreased to 1.6 V with the concentrated solution (5 M). In particular, the OCV obtained with 1 M was higher than that with 2 M, indicating, as expected, a larger methanol cross-over through the membrane as the fuel concentration was increased. It is pointed out that a single membrane is used; thus, the membrane is not interrupted at the border between each cell. Accordingly, the methanol permeation is not substantially different from that of a single cell of similar membrane area. The same trend of the OCV was observed for the voltage as a function of methanol concentration at low current; whereas, increasing the current, the stack voltage decreased rapidly with 1 M methanol (diffusion limiting current of about 120 mA), less significantly with 2 M (diffusion limiting current of about 225 mA), reaching more than 400 mA with 5 M methanol solution. It is derived that at low fuel concentrations the process is controlled at high currents by the methanol mass transport process, i.e. the limiting current increases twice as the methanol concentration in the reservoir passes from 1 M to 2 M at potential as high as 0.5 V. Whereas, such a linear increase of limiting current is not so strictly observed for 5 M methanol solution since at potentials as low as 0.2 V the recorded value is 4 times less
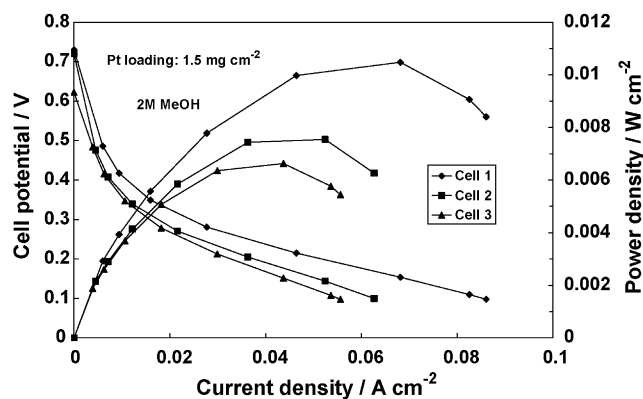
Fig. 3. Polarization and power density curves for each cell of the stack with a Pt loading of 1.5 mg cm^{-2} using 2 M methanol solution.

than that measured with 1 M concentration. Obviously, in the latter case, there is the effect of cross-over that is reflected in the overall range of current density. Furthermore, it is not excluded that increasing methanol concentration, some kinetics constrains may arise from a reduced rate for the water discharging [8]. Thus, the mass transfer control, corresponding to the methanol concentration of 5 M, is not achieved in the practical range of stack voltage. Yet, an important fact is that under conditions where mass transport plays an important role (passive mode), a significant increase of methanol concentration causes an increase of output power. This effect, combined to the better energy density, makes operation at high concentration quite interesting even in the absence of specific tools that favour water back diffusion to the anode from cathode [32]. Under practical operation the "step-up" DC/DC converter should allow the stack potential to remain in a suitable range with a small power dissipation.

A maximum power of 120 mW was reached with the most concentrated solution. Using a diluted solution at the anode, as afore discussed, the maximum power was smaller than that obtained with a concentrated solution due to mass transfer limitations.

An investigation of the electrochemical performance of each cell in the stack was carried out for the electrodes with 1.5 mg cm^{-2} Pt loading, using 2 M methanol solution at the anode (Fig. 3). The three cells showed a slightly different behaviour; in particular, cell 1 (which was closer to the end current collector) appeared to be more performing than the other cells. This is due to the lower cell resistance for this cell (0.64 Ω cm^2) compared to the other ones that are farer from the end current collector (0.7 Ω cm^2 for cell 2 and 0.8 Ω cm^2 for cell 3). The obtained maximum power density and short circuit current density are affected by these values of cell resistance; in fact, higher current and power densities were reached with cell 1 (a maximum power density of 10 mW cm^{-2}); whereas, cells 2 and 3 showed lower performance (7 and 6.5 mW cm^{-2}, respectively).

The performance of the three cells in such a monopolar configuration thus reflects the location of each cell with respect to the external electronic circuit that allows series connection between them.

A stability test of 1 h of continuous operation was carried out on the three-cell stack equipped with electrodes containing 1.5 mg cm^{-2} Pt loading at a voltage of 0.9 V using 20 vol.% methanol solution (Fig. 4). A slight decrease of current was observed with a concentrated solution of methanol, probably due to the large swelling of the membrane causing an increase of methanol cross-over, which results in a decrease of performance with time. Furthermore, due to an excess of methanol/water coming from the anode also promoted by the electro-osmotic drag, a flooding of the
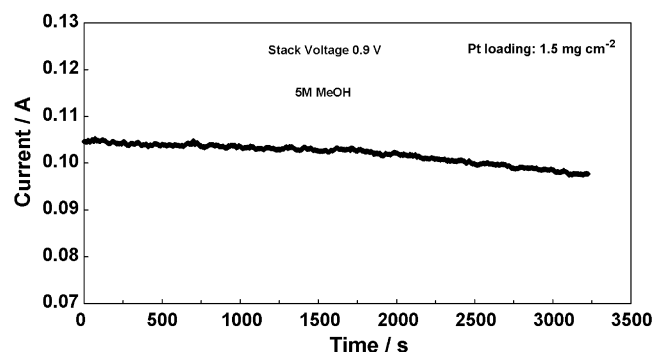

Fig. 4. Chrono-amperometric experiment carried out on the stack with a Pt loading of 1.5 mg cm^{-2} on each electrode at 0.9 V using 5 M methanol solution.

cathode catalytic layer could be responsible of such a decrease of current.

Increasing the Pt loading (4 mg cm^{-2} on both sides), the performance increased significantly at all conditions and it was almost twice in terms of maximum power (225 mW) with a methanol concentration of 5 M compared to the stack based on 1.5 mg cm^{-2} Pt loading (120 mW); whereas, the OCV remained the same. The largest gain appeared to be achieved with 2 M methanol concentration. The performance with 2 M was approaching that of 5 M methanol solution. The limiting current density was practically the same for 1 M methanol, whereas it slightly increased for 2 M and 5 M methanol solutions (Fig. 5). At high methanol concentration no mass transfer control was observed in the practical stack voltage range. The gain in performance was not strictly proportional to the increase of catalyst loading. This is possibly due to the fact
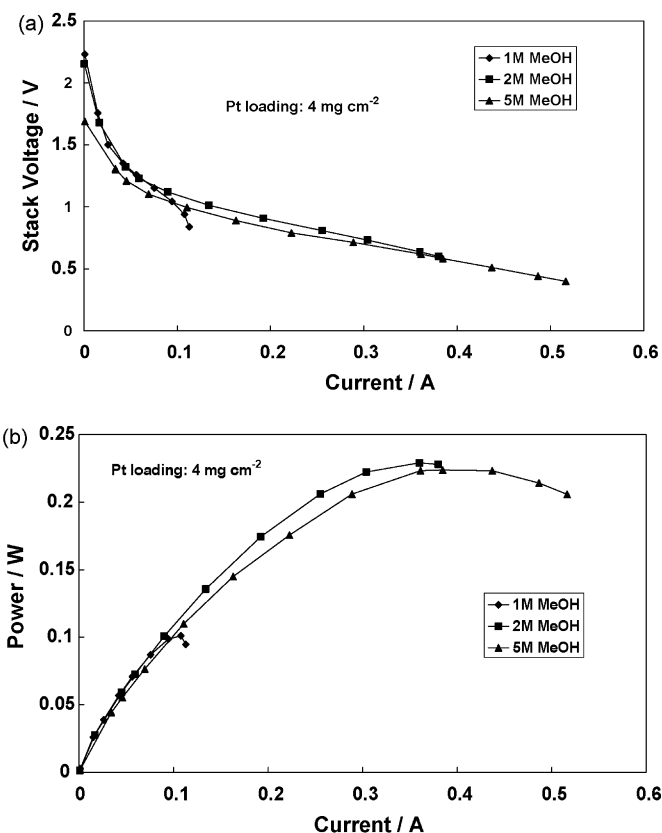

Fig. 5. Polarization (a) and power (b) curves for the three-cell stack with a Pt loading of 4 mg cm^{-2} on each electrode at different methanol concentrations.
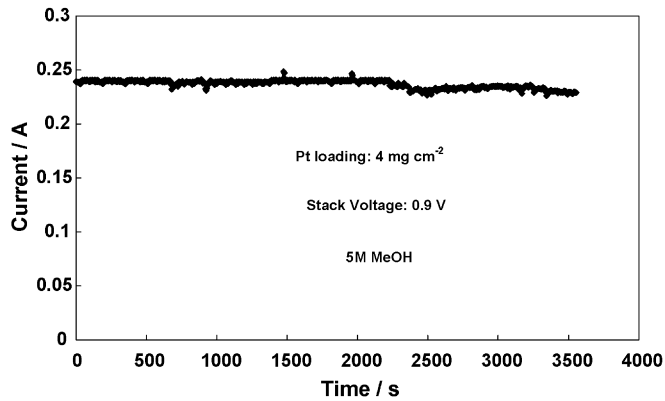
Fig. 6. Chrono-amperometric experiment carried out on the stack with a Pt loading of 4 mg cm^{-2} on each electrode at 0.9 V using 5 M methanol solution.

Fig. 8. Comparison of the polarization and power curves for different stacks varying by the Pt loading on each electrode and using 5 M methanol solution at the anode.

that the extension of the three-phase reaction zone is not proportional to the increase of the electrode thickness (400 μm for the anode, 325 μm for the cathode). Mass transfer constrains influence the behaviour in particular when a diluted methanol solution (1 M) is used. The trend of the OCV and voltage at low current (in the activation region) is the following: 1 M ≥ 2 M > 5 M. At intermediate current, under 2 M and 5 M methanol feed at the anode (passive mode), the behaviour was similar, even if slightly higher performances were recorded with the diluted solution (2 M) probably due to the lower methanol cross-over. At high current, the situation was the opposite, and the concentrated solution gave rise to lower voltage losses. In the latter case, although no limiting current was reached, the mass transfer plays a significant role.

A time stability test of 1 h was carried out also under these conditions (Fig. 6) at a voltage of 0.9 V using 5 M methanol solution. Also in this case, a slight decrease of performance was observed as a function of time, but lower than that recorded with a lower amount of Pt in the electrodes. This may be ascribed to two effects, i.e. anode thickness, which reduces the methanol cross-over rate by increasing the tortuosity factor for permeation, and the increased amount of catalyst (thickness) at the cathode counteracts the effects of poisoning by methanol. A further increase of Pt loadings (6 mg cm^{-2}) produced a significant increase of mass transport constrains (the thickness in this case was 420 μm for the anode and 340 μm for the cathode), in particular with low methanol concentrations (1 and 2 M). Well defined limiting current densities were measured at stack voltages above 0.6 V. The increased thickness of the reaction layer hinders the reactants to reach the active zone at the electrode-membrane interface where most of the reaction process
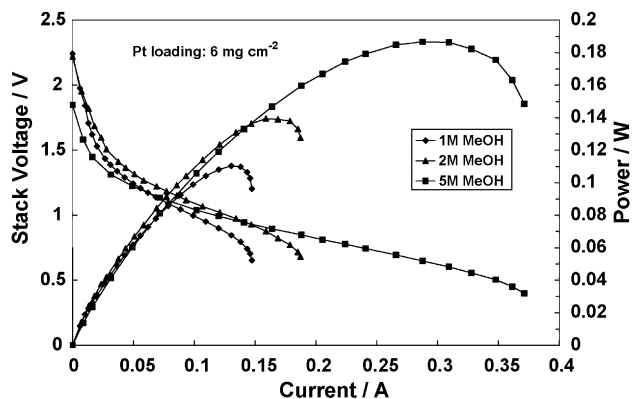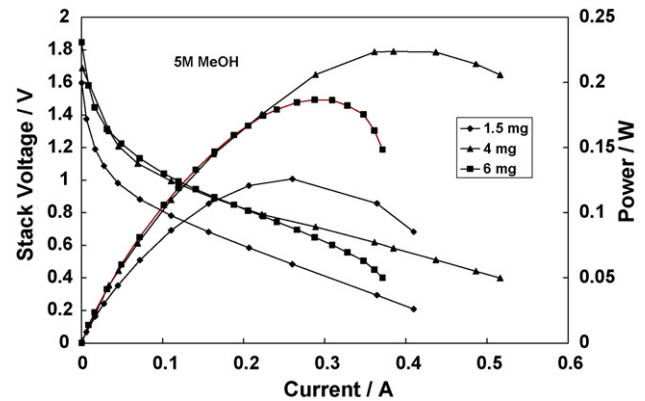
occurs. This effect agrees with the fact that the extension of the three-phase reaction zone is not proportional to the thickness of the catalytic layer. The behaviour of the stack equipped with electrodes containing 6 mg cm^{-2} Pt loading on both compartments (Fig. 7) in the activation and ohmic controlled regions was similar to that recorded with lower amount of catalyst; whereas, the maximum current reached in these conditions was lower than that obtained in the previous experiment carried out using 4 mg cm^{-2} Pt content. By comparing the polarization and power density curves recorded with different Pt loadings (Fig. 8), it is derived that the best performance in terms of power and current output is achieved with 4 mg cm^{-2} Pt loading on both compartments that represents the best compromise between amount of catalytic sites and thickness. Yet, the OCV and voltage at low currents (activation region) was slightly higher using a larger catalyst content as a consequence of reduced cross-over and large number of active sites. Indeed, diffusion constrains occur at high currents during passive mode operation due to the thickness of the electrodes. By increasing the methanol concentration up to 10 M, the performance decreased (Fig. 9) due to the large swelling of the membrane that produces a higher methanol cross-over. A comparison of the polarization profile of the stack fed with 5 M and 10 M concentrations shows that there is a significantly different OCV due to the increased cross-over with 10 M concentration (in the absence of electro-osmotic drag); this voltage loss is reflected on the overall polarization curve. Whereas, the extent of activation losses up to 0.1 A is quite similar. This suggests that the development of alternative membranes
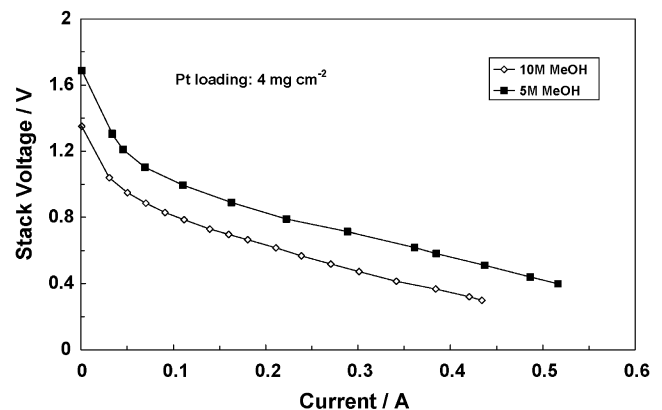

Fig. 7. Polarization and power curves for the three-cell stack with a Pt loading of 6 mg cm^{-2} on each electrode at different methanol concentrations.

Fig. 9. Comparison of the polarization curves for the three-cell stack with a Pt loading of 4 mg cm^{-2} on each electrode at high methanol concentrations (5 M and 10 M).
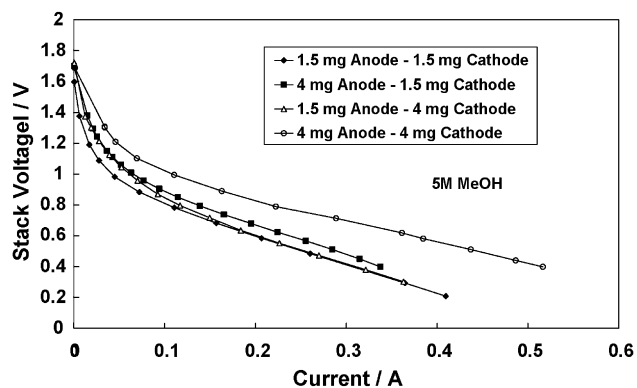
Fig. 10. Comparison of the polarization curves for the stacks varying the Pt loading at the anodes and cathodes, using 5 M methanol solution.

with similar conductivity but significantly smaller cross-over than Nafion may allow to achieve in the presence of highly concentrated methanol solutions the same power density obtained for diluted methanol concentrations (5 M). The water necessary for anode reaction to occur can reach the anode/electrolyte interface by back diffusion from the cathode as demonstrated in the literature [32].

Further experiments were carried out in order to evaluate the effect of variation of Pt loading at the anode and cathode, separately. For this purpose, in a new MEA, a Pt loading of $4\,mg\,cm^{-2}$ at the anode and $1.5\,mg\,cm^{-2}$ at the cathode was used; in another MEA the loading was $1.5\,mg\,cm^{-2}$ at the anode and $4\,mg\,cm^{-2}$ at the cathode. Fig. 10 shows a comparison of the polarization curves obtained with these new MEAs together with those of the MEAs equipped with $1.5\,mg\,cm^{-2}$ or $4\,mg\,cm^{-2}$ Pt loading on both electrodes. Such a comparison is presented for a methanol concentration of 5 M. An increase of performance in the activation region was observed for the two new MEAs with respect to the cell based on $1.5\,mg\,cm^{-2}$ Pt loading on both electrodes. This is due to the increased amount of catalytic sites for methanol oxidation and oxygen reduction when a higher loading at the anode or at the cathode ($4\,mg\,cm^{-2}$) is used. Thus, both electrochemical processes appear to limit the stack performance. The increase in potential is reflected in the whole polarization curve only for the anode with high loading. Obviously, the performance of this cell is inferior to that of the cell equipped with $4\,mg\,cm^{-2}$ Pt loading on both compartments. This is due to the cross-over effect that causes a poisoning of the reaction sites for the ORR on the cathode (taking into account the low Pt loading, $1.5\,mg\,cm^{-2}$). The higher performance in the activation region of the MEA equipped with $1.5\,mg\,cm^{-2}$ at the anode and $4\,mg\,cm^{-2}$ at the cathode compared to the MEA based on $1.5\,mg\,cm^{-2}$ Pt loading on both electrodes could be attributed to the large availability of catalytic sites at the cathode ($4\,mg\,cm^{-2}$ Pt loading) that counteracts the detrimental effect of methanol cross-over. Yet, in this case, an increase of Pt loading at the cathode causes an increase of electrode thickness. This, in turn, produces an increase of mass transport constrains at high currents. Thus, for the air breathing process, a compromise between the number of catalytic sites and the electrode thickness is necessary.

For what concerns the methanol cross-over, due to the fact that no air flow at the cathode is used, the well-established CO_2 sensor method is not applicable. Alternatively, electrochemical determination of methanol passed at the cathode by measuring the methanol oxidation current at the cathode in the presence of an inert gas does not appear appropriate. This method discards the effects of operating current density (concentration gradient at the anode–electrolyte interface) and electro-osmotic drag. Thus,

we have evaluated the cross-over rate on the basis of the faradaic efficiency determination (fuel efficiency) when all methanol in the tank was consumed (before re-fuelling). This approach is based on the assumption that the reduction of faradaic efficiency from the ideal 100% is only due to the methanol loss by the cross-over through the membrane. Our chromatographic analysis of the methanol solution in the tank showed no organic compounds other than methanol and CO_2 at the anode compartment during operation. Particular care was addressed to reduce any methanol loss from the tank by evaporation. From this analysis, a total methanol cross-over rate in the stack of $1.5 \pm 0.2 \times 10^{-6}\,mol\,min^{-1}\,cm^{-2}$ (total geometric electrode area) at $21\,°C$ was determined under passive mode operation with 5 M MeOH, 4 mg Pt loading on both electrodes and $60\,mA\,cm^{-2}$ operating current density.

4. Conclusions

In this study, a characterization of a passive DMFC monopolar stack was carried out, varying the catalyst loading and methanol concentration. From this analysis, it is derived that $4\,mg\,cm^{-2}$ Pt loading in the presence of unsupported catalysts appears to be the best compromise between electrode thickness and amount of catalytic sites for suitable mass transport and kinetics of anode and cathode reactions, in particular using a methanol concentration ranging from 2 M up to 5 M. A maximum power of 225 mW was obtained at ambient temperature for the three-cell stack with $4\,mg\,cm^{-2}$ Pt loading on each electrode using both 2 M and 5 M methanol concentration at the anode, corresponding to a power density of about $20\,mW\,cm^{-2}$. The use of highly concentrated methanol solutions causes a significant decrease of OCV that reflects on the overall polarization curve; however, the activation losses are similar. This strongly suggests the development of proper methanol impermeable membranes.

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