Experimental investigation on DMFC temporary degradation

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Introduction

The Direct Methanol Fuel Cell (DMFC) power source technology is considered very promising for portable and automotive applications, mainly for the direct use of a liquid fuel. However, the commercialization of this technology is still hindered by some technological issues among which a severe performance degradation, that has a permanent and a temporary contribution [1]. The latter can be partially recovered with an interruption of the operation or by applying appositely developed procedures. The literature generally focuses on the permanent contribution, which is mainly due to irreversible degradation mechanisms such as platinum dissolution and agglomeration or ruthenium dissolution, while the temporary contribution is not yet fully understood and remains less investigated. The experimental investigations of DMFC degradation are continuously increasing but, generally, they only focus on catalyst characterization before and after the degradation tests [2—9], without a separation between the two contributions. A systematic characterization of temporary degradation is thus necessary to be able to effectively distinguish its effects from the permanent ones, permitting then a real dedicated study of the latter.

In a previous work [10], the authors focused on the anode degradation, setting the cathode as a dynamic hydrogen electrode and measuring the overpotential in electrolytic operation, being able to conclude that anode degradation is

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characterized by a relevant temporary contribution, never highlighted before in the literature. The authors identified as the possible origin of such temporary effects the progressive reduction of water and methanol concentrations in both the GDL and the electrode, promoted by the accumulation of gas-phase CO_2 during continuous operation, that determines variation in the anode mass transport phenomena. Cycling operation, with periodic OCV interruption, permits to drastically decrease anode temporary degradation compared to continuous operation. However, in order to further clarify the DMFC temporary degradation mechanisms, an investigation of the phenomena occurring during DMFC operation has to be performed, since the anode contribution does not explain the overall temporary degradation magnitude.

In the literature, several studies discuss on phenomena that could be relevant in the temporary degradation investigation: at the cathode electrode, several mechanisms could occur during the operation, temporarily penalizing the cell performance. In Ref. [11] the progressive surface oxidation of the platinum, promoted at high potentials, is identified as a mechanism determining the reduction of cathode catalyst effectiveness; promoting the reduction of the previously formed oxides, the initial catalyst condition can be restored. Another probably main issues involve the cathode water management; cathode electrode dehydration [12] when the DMFC is dry air fed can penalize the ohmic conductivity of the electrode itself resulting in an equivalent temporary surface area loss.

This work aims to provide an insight into the DMFC temporary degradation through an experimental investigation, based on:

- a sensitivity analysis of the effects of operating conditions on DMFC performance, mass balances and Electrochemical Impedance Spectra (EIS);
- a 600 h degradation test performed in real operation representative conditions;
- appositely developed experimental tests to point out the main temporary degradation mechanisms.

Experimental methodology

Experimental setup

The experimental setup for single cell DMFC characterization is described in Ref. [13], where the set of equations governing mass transport and the recent improvements to the experimental setup are explained in details.

The DMFC MEAs used in this work are commercial 25 cm^2 manufactured by IRD Fuel Cell A/S: membrane is Nafion115, anode catalyst loading is 1.8 mg cm^{-2} (PtRu), cathode catalyst loading is 1.2−1.4 mg cm^{-2} (Pt). Both anode and cathode diffusion layer are Sigracet® SGL35DC (thickness 325 μm, 20% PTFE content, with micro-porous layer). During testing, unless differently indicated, anode and cathode are fed through a triple serpentine graphite flow field respectively with 1.0 M methanol solution with stoichiometry equal to 6 and air, saturated by water at ambient temperature, with stoichiometry equal to 3. Nominal current density is 0.25 A cm^{-2} while the fuel cell temperature is kept at 75 °C.

Data acquisition system continuously acquires at 0.5 Hz frequency. The voltage of the fuel cell is simultaneously measured by the electronic load and by a high precision acquisition board (NI 6210, estimated uncertainty: 1 mV) directly connected to the fuel cell, in order to have multiple readings. An AC milliohmeter (TSURUGA 3566, estimated uncertainty: 1 mΩ cm^2) continuously measures the impedance of the fuel cell at 1 kHz single frequency, a reliable approximation of the membrane Ohmic resistance. As a proxy for methanol crossover, CO_2 measurements are performed at the cathode exhaust with a Vaisala sensor GMP70 (uncertainty 50 + 2% ppm) in a vessel of 0.5 dm^3 volume provided with a liquid−gas gravity separator and a thermocouple (in order to evaluate the vessel saturation temperature). The obtained data are corrected by subtracting the measured ambient CO_2 concentration, thus the uncertainty of the final measurements is evaluated to be 70 + 2.8% ppm [13]. An heat exchanger to warm up the cathode exhaust to evaporate eventual liquid water and a thermo-hygrometer for humidity (uncertainty 2%) and temperature (uncertainty 0.2 °C) measurements, located in a thermo-stated housing to avoid water condensation, permit to measure the water content in the cathode exhaust as explained in Ref. [14]. Moreover, anode exhaust composition has been measured by mean of a SRA R-3000 μGC analyzer equipped by mean of three columns and preceded by a liquid−gas gravity separator. The first column is a nitrogen fed Molsieve for the hydrogen identification, the second one is a helium fed Molsieve for the nitrogen, oxygen, CO and methane identification while the third one is a helium fed PlotU for the CO_2 and light hydrocarbons identification such as methanol.

Performance characterization

To evaluate the influence of the operating conditions on DMFC operation, an initial performance characterization is performed, based on polarization curves, mass transport measurements and EIS. The tested operating conditions for the performance characterization are reported in Table 1; measurement repeatability has been verified by performing the test three times in three different days.

The polarization curve acquisition is composed of 9 single measurement points referred to different current densities, collected following one-way curves increasing current. Each single acquisition point is performed at constant current, measuring voltage, relative humidity and CO_2 cathode exhaust content for 600 s. The data obtained from each single acquisition point are elaborated as explained in Ref. [15]. Each polarization curve is performed with reactants constant flow rates in order to ensure the steady state operation, determining high reliability of methanol crossover, water content in cathode outlet and EIS measurements. For this reason, the stoichiometries λ reported in the polarization curves are equivalent stoichiometries, meaning that the mass flows have been kept constant at the equivalent stoichiometry in the reference current (0.25 A cm^{-2}).

EIS is the most common *in situ* measurement technique that could be performed as a diagnostic tool to quantify fuel

Table 1 – Investigated operating conditions.			
	Unit	Reference condition	Other tested conditions
Temperature	°C	75	65
Methanol concentration	M	1	2
Anode massflow	g min^{-1}	3.86 ($\lambda = 6$ @ 0.25 A cm^{-2}, 1 M)	1.93 ($\lambda = 3$ @ 0.25 A cm^{-2}, 1 M)
Cathode massflow	Nl min^{-1}	0.336 ($\lambda = 3$ @ 0.25 A cm^{-2})	0.672 ($\lambda = 6$ @ 0.25 A cm^{-2})
Current density	A cm^{-2}	0.25	0.01/0.05/0.1/0.15/0.2/0.3/0.35/0.4

cell internal losses during a degradation tests; for this reason, it is adopted also in the present work. EIS are performed during the diagnostic polarization curves at 0.1 and 0.25 A cm^{-2} and periodically during the degradation tests, using a Potentiostat/Galvanostat (Autolab PGSTAT 30) provided with a frequency response analysis (FRA) module. The amplitude of the sinusoidal signal increases by increasing current density in order to provide a trade-off between the linear response in voltage and an adequate measurement quality [16,17]. However the amplitude of the sinusoidal current signal is adjusted so that the potential amplitude does not exceed 10 mV. The impedance is measured at frequencies included between 10 kHz and 50 mHz with a logarithmic distribution.

DMFC degradation test

As explained in Refs. [18,19], a DMFC cannot work in continuous operation due to an excessive degradation rate and, for this reason, it is usually operated by means of operating strategies. In this work, the DMFC reference operating strategy consists in cycles of 20 min of effective operation, followed by 1 min of *Refresh* procedure. The Refresh is an IRD Fuel Cell confidential procedure similar to what reported in Ref. [18], consisting in a sequence of periods of OCV (about 0.8 V) and cathode air interruption. During the air-break the cathode potential drops to less than 0.3 V; when the operation restarts, a significant positive effect on performances is noticeable. A preliminary interpretation of the positive effect of refresh cycles on DMFC performance has been already presented in Ref. [19]. Different operating strategies, when used, will be described in the experimental investigation paragraph. Besides, between two consecutives degradation tests, a one-day interruption for diagnostic is performed.

The method for the degradation rate calculation during a cycling operating strategy has been presented in Ref. [19] and it is based on a robust linear regression on the experimental data; the obtained results can be expressed in μVh^{-1} and the quantification is based on the assumption of linearity of a part of the voltage–time curve. Despite the DMFC degradation presents a bi-exponential behavior, this linear regression method permits the comparison of different tests, performed under different operating strategies, providing a reliable quantification of the slope of the voltage-time decay curve of a DMFC.

During the diagnostic operation interruptions, the DMFC degradation is evaluated performing polarization curves, EIS and cathode cyclic voltammetry (CV) to estimate the catalyst active area of the electrode. During CV measurement, dry hydrogen (3.5 Nml min^{-1}) and fully humidified nitrogen (0.6 Nl min^{-1} saturated at 80 °C) are fed to the anode and cathode compartments respectively and the cell is kept at 75 °C. The anode is taken as reference and counter electrode, while the cathode is taken as the working one. Its potential is then continuously scanned back and forth between 0.05 V and 0.6 V with a scan rate of 25 mV s^{-1}. The cathode catalyst active area is estimated considering the positive current density peak related to the hydrogen desorption [20]. The estimation is done assuming that the cathode catalyst is covered by a monolayer of hydrogen with a charge density of 210 μC cm^{-2}.

Performance characterization

Fig. 1 reports the DMFC polarization curves performed at 75 °C by changing anode (flow rate and methanol concentration) and cathode feeding; the polarization curve performed at low methanol flow and concentration has the highest performances at low current densities due to the low methanol crossover, but the lowest at high current densities. This is due to mass transport limitations at the anode [10]; hence, the reduction of the anode flow rate involves anode limited DMFC polarization. As reported in Ref. [10], a higher methanol concentration is expected to promote the anode performances, but, according to Fig. 1, it determines a worsening in the DMFC polarization curve.

Fig. 2 shows the methanol crossover and cathode water flux measurements acquired during the different polarization curves reported in Fig. 1, performed during the performance characterization.
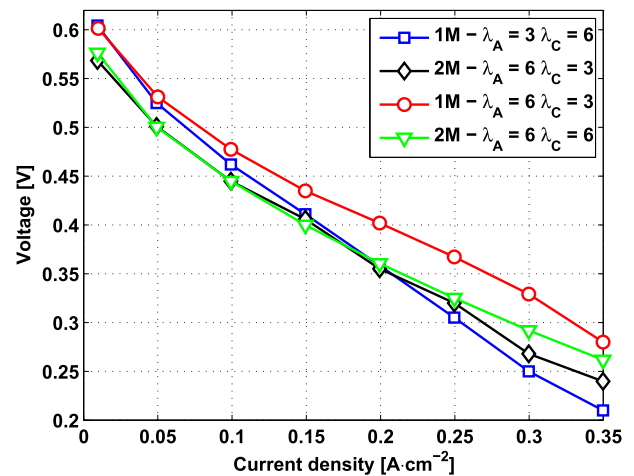
Fig. 1 – Polarization curves during the MEA characterization changing anode and cathode feeding at 75 °C.
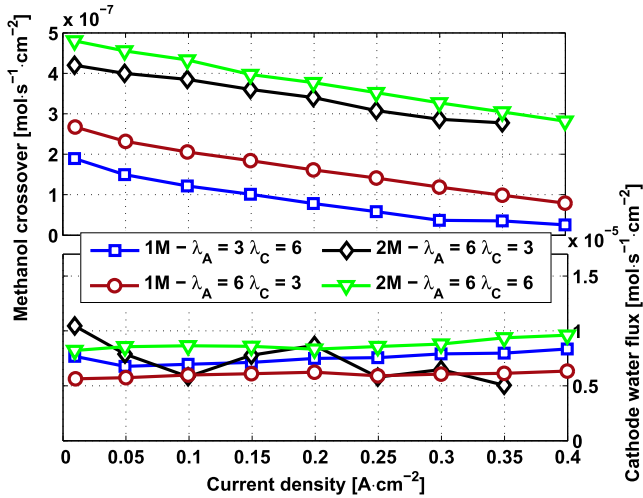
Fig. 2 — Methanol crossover and water content in cathode exhaust measured during the polarization curves reported in Fig. 1.

Fig. 3 — DMFC EIS performed at reference current (0.25 A cm^{-2}) at 75 °C changing anode and cathode feedings.

From the methanol crossover behavior it is possible to notice that the higher the methanol concentration, the higher the methanol crossover. This confirms that the phenomenon is mainly governed by a diffusive mass transport mechanism and, hence, dependent on concentration gradient across the membrane. Instead, both the anode and cathode flows have a slight effect on methanol crossover: a higher cathode airflow results in an increased methanol crossover due to a reduction of the average methanol concentration at the cathode side [13].

From the cathode water flux diagram shown in Fig. 2, the water content in the cathode outlet is reported as a function of the different operating parameters:

- the higher the airflow, the higher the water content, due to the lower average water concentration in the cathode channel [14];
- the water content in cathode outlet does not significantly change by increasing the current density implying a nearly constant water concentration in the cathode electrode.

These results confirm that, in presence of both anode and cathode Micro-Porous Layer (MPL), the water transport through the cathode GDL occurs mainly by diffusion, depending on the concentration gradient across the GDL as investigated in Ref. [14]. In such condition no liquid convection occurs [14], confirming that the adopted GDL configuration permits to avoid severe cathode flooding.

The qualitative interpretation of the EIS, performed at reference current (0.25 A cm^{-2}) and reported in Fig. 3, leads to a further comprehension of the effect of operating conditions on DMFC performances. Considering the reference spectrum (red circles) (in web version), when the methanol flow is reduced and cathode air flow is increased (blue squares) (in web version), anode mass transport limitation appears in the low frequencies region, close to the real axis hindering the anode semicircle appearance [10]. On the other hand, when the methanol concentration is doubled to 2 M with reference
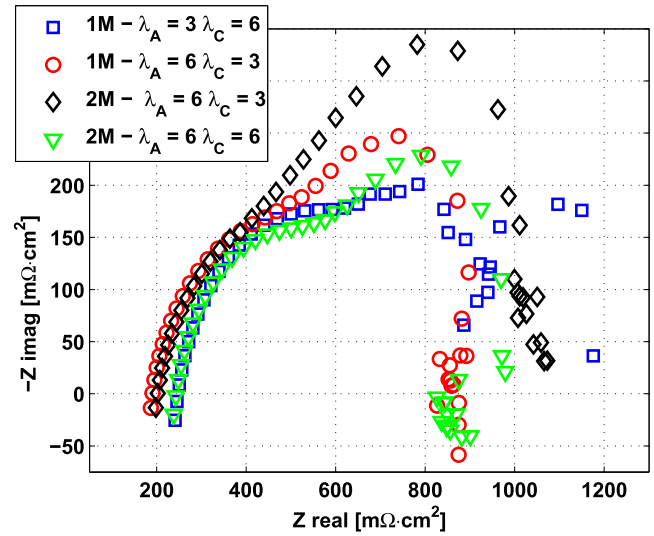
cathode airflow (black rhombuses), important mass transport limitations occur at the cathode. This is probably due to the effect of the increased methanol crossover on the cathode oxygen concentration. These disturbances appear in the medium frequencies region, quite far from the real axis, contrarily to the anode mass transport limitations previously explained. As a confirmation of the cathode mass transport limitation, doubling the cathode flow and maintaining the high methanol concentration (green triangles) (in web version), the disturbances completely disappear and a small inductive behavior is evident at low frequencies due to the anode increased methanol concentration [10]. Methanol crossover effect at the cathode of a DMFC determines the lowest performances of the 2 M polarization curves ($\lambda_c = 3$) reported in Fig. 1. Hence, from the qualitative interpretation of the EIS performed at reference current, it is possible to clearly distinguish anode and cathode mass transport limited DMFC operating conditions. The significant difference in the membrane ohmic resistance between the two used cathode flow rates, measurable from the first intersection with the real axis at very high frequency, shows the effect of the electrolytic membrane dehydration caused by the increased cathode air flow saturated at room temperature.
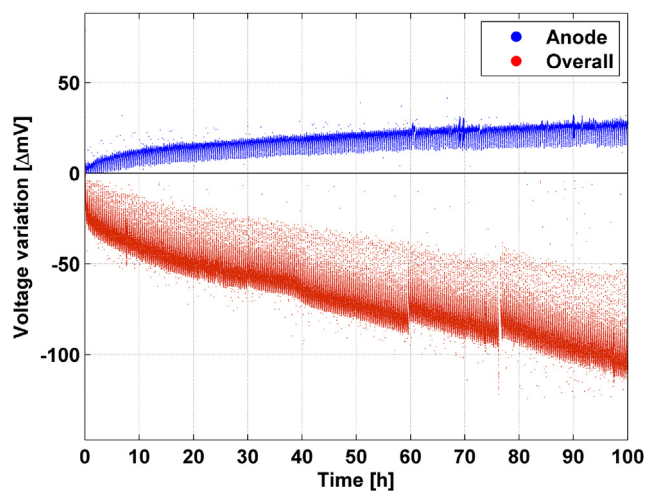
DMFC degradation test

Fig. 4 reports the DMFC MEA voltage behavior during the degradation test performed at constant current and stoichiometries in reference condition (Table 1). The DMFC degradation test has been performed by means of cycles of about 120 h of reference operating strategy, described in paragraph DMFC degradation test, followed by diagnostic measurements that are preceded and followed by a long operation interruption (nearly 12 h) with a very low methanol circulation at the anode, as in Ref. [21], in order to recovery the DMFC performances. During each interruption the previously described
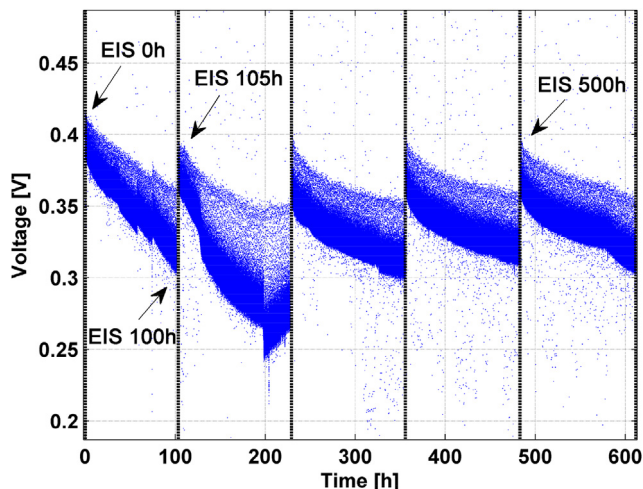
Fig. 4 − DMFC Voltage decay during 600 h degradation test performed at reference current by means of refresh cycle based operating strategy.

polarization curve and cathode CV techniques are performed and, at the operation restarting, a performance recovery has been systematically observed. The performance recovery obtained during each diagnostic interruption further confirms that the adopted operating strategy, based on refresh cycles, does not completely avoid the temporary degradation effects. The second part of the degradation test presents an unusual behavior: a failure of the control system led to not properly performance of the refresh cycle from hour 130 to hour 200 and a very strong voltage decay is observed in this period; this is related to the lack of the cathode air break period during each refresh cycle. When the control system has been restored, the refresh cycles have been again correctly performed and a progressive performance recovery has been observed until the interruption for diagnostic.

Fig. 5 shows in details the comparison between the voltage decay during the first 100 h of DMFC degradation test (voltage

Fig. 5 − Comparison between electrolytic and galvanic performance loss during a reference degradation test based on operating strategy.
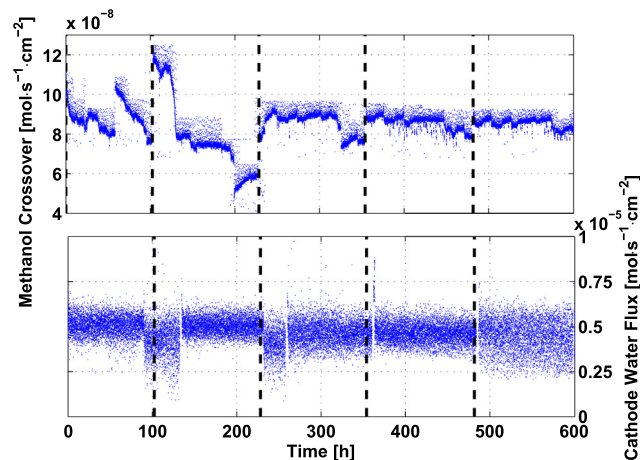

Fig. 6 − Methanol crossover and water content in cathode outlet measured during the DMFC degradation test reported in Fig. 4.

decay rate: 330 μV h^{-1}) and the overpotential increase during the anode degradation test in reference conditions described in Ref. [10] (overpotential increase rate: 147 μV h^{-1}). The significant difference in the slopes confirms that the anode temporary degradation is only a part of the overall DMFC temporary degradation; further mechanisms should be taken into account, probably located at the DMFC cathode. The larger width of the voltage decay curve shows that the performance loss occurring during each 20 min operation cycle in galvanic operation is higher than in the electrolytic operation, confirming that the anode temporary degradation mechanism reported in Ref. [10] is not sufficient to explain the overall DMFC temporary degradation. Moreover, each interruption for refresh determines a higher performance recovery in galvanic operation than in the electrolytic operation,[1] confirming that the refresh cycle acts also on the cathode recoverable performance loss.

Fig. 6 reports the methanol crossover and the water cathode fluxes acquired during the DMFC degradation test of Fig. 4: the crossover value occurring during the test confirms the one obtained from the reference polarization curve. Except for the second period of the test, that present a very unstable profile due to the experimental setup failure above described, the methanol crossover presents a behavior coherent with what described in Ref. [21]; a slight permanent reduction can be noted and each diagnostic interruption corresponds to a weak crossover increase. However, in Ref. [21], the anode has been evaluated as responsible for the temporary variations of the methanol crossover and no unburned methanol crossover has been identified in the cathode exhaust; hence, the methanol crossover evolution during the test should not held responsible for the observed temporary degradation. The water content in cathode outlet presents a widespread, but quite constant, behavior, coherently with the regular trend of the methanol crossover.

The CVs performed during the operation interruption for diagnostic are reported in Fig. 7, together with the detail of the

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[1] The OCV in electrolytic operation corresponds to about 0 V versus RHE.
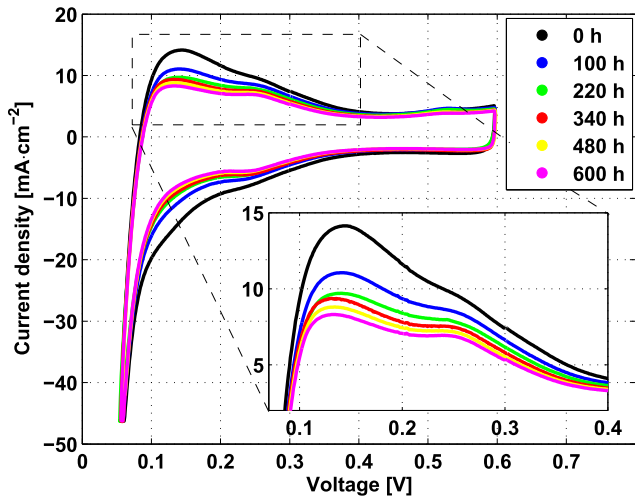
Fig. 7 – CV plots evolution across the diagnostic breaks of the degradation test, with detail of the H₂ desorption peaks.

Fig. 8 – Comparison between cathode ECSA obtained through the CV and Voltage at nominal current density during the Polarization curves.

progressively decreasing hydrogen desorption peaks. From these analyses it is possible to estimate the Electro-Chemical Surface Area (ECSA)[2] progress during the degradation test shown in Fig. 4; the ECSA measured from the begin-of-life to the end-of-life and the voltage values, obtained at reference current (0.25 A cm^{-2}) during the polarization curves, are presented together in Fig. 8. A significant ECSA loss occurs, mainly during the first 100 h, while the decay progressively reduces as the test duration increases, leading to a strong decrease from the BoL value.
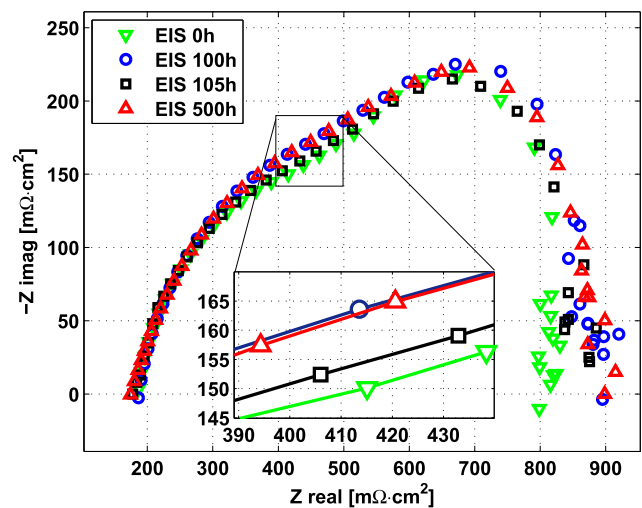
The EIS, performed both during the degradation test and during the diagnostic polarization curves, permit a deeper insight into the performance loss observed. Fig. 8 shows the comparison between four EIS acquired in very different conditions of degradation, and respectively: at the begin-of-life (0 h), just before the end of the first operation period (100 h), just after the first interruption for diagnostic (105 h) and just after the last one (500 h), as marked into Fig. 4. The BoL EIS and the 105 h one allow to clearly distinguish the anode and the cathode semicircles, while the EIS at 100 h and 500 h tend to show cathode limited impedances: the enlargement in Fig. 9 of the medium frequencies region permits to point out a worsening in the cathode operation (according to the characterization reported in Fig. 3, the cathode limitations occur in the mid-frequencies region, contrarily to the anode limitations). The cathode worsening effect, due in the 100 h EIS to the strong temporary degradation of the first period of operation, shows itself as almost fully recoverable as pointed out by the 105 h EIS, performed just after the first diagnostic break of operation. With this interruption, the cathode impedance is recovered and the spectra returns similar to the BoL one, allowing to clearly distinguish the anode and the cathode semicircles again. Instead, the EIS performed at the beginning of the last test
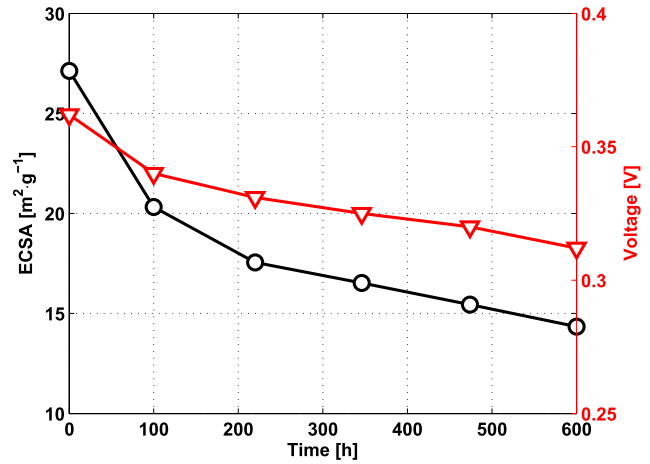
period (500 h), despite performed in conditions of negligible temporary degradation (being just after a diagnostic break, and so recovered of the temporary contribution), appears very similar to the spectra performed at the end of the first test period (100 h), highly affected by high temporary degradation. The limitations at the cathode performance noticed in the 500 h EIS are probably related in this case to the strong ECSA loss, highlighted in the CV of Fig. 8, occurred during the test, and appears very similar to the ones highlighted in the 100 h EIS, where they are due to temporary degradation. Thus, the temporary degradation occurring during the DMFC operation seems to manifest itself as an apparent recoverable cathode ECSA loss.

In the literature two possible temporary mechanisms, that could be responsible for the apparent ECSA loss, have been identified: Platinum oxides formation and reduction [11] and dehydration of the cathode electrode [12]. Both of them could result in a progressive but recoverable loss of ECSA, hindering

Fig. 9 – EIS performed at 0.25 A cm^{-2} during the DMFC degradation test.

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[2] A small amount of Ru at the cathode, due to crossover, could probably alter the cathode CV measurement in a minor way.

the ORR and leading to the relevant DMFC temporary degradation.

Investigation on DMFC cathode temporary degradation mechanisms

Platinum oxides/hydroxides formation

Since the DMFC anode overpotential is usually important, a high cathode potential is required in order to obtain high DMFC performance. The literature does not propose reliable and feasible *in-situ* hydrogen reference electrodes [22] for DMFC and it results in an unknown cathode potential during the operation. Thus, according to the anode overpotential measurements obtained in Ref. [10] and to the DMFC galvanic performances, it is possible to estimate the cathode potential, which, in reference conditions (i.e. 0.25 A cm^{-2}), results over 0.8 V vs RHE.

In Ref. [11] the oxidation of the platinum catalyst is discussed. This mechanism strongly depends on the electrode potential: the oxidation reaction, involving the catalyst surface, is enhanced over values of 0.75–0.85 V, while at low potentials (under 0.5 V vs RHE) the reduced form become more stable and the Pt oxides (and/or hydroxides) tend to reduce. In the work, the platinum oxidation coverage is stated as a main mechanism of performance loss, leading to the inhibition of ORR at the cathode because of the decrease in the number of free Pt sites, covered by the oxidized surface. However, this performance loss seems to be recoverable at low cathode potentials, because of the reversible nature of the platinum oxidation/reduction.

Two main aspects could be fundamental to explain the stronger importance of platinum oxides formation and reduction mechanism in DMFC than in PEMFC: methanol crossover from anode to cathode and ruthenium crossover. It is well known that ruthenium can be easily oxidized and it could favor the platinum oxidation while the effect of methanol crossover on temporary degradation is still unknown.

Coming back to the operating strategy already described and taking into account the theoretical explanation found in Ref. [11], it is possible to conclude that the DMFC operation determines a progressive surface oxidation of the cathode catalyst, resulting in a drop of the performances, while the refresh cycle during the air-break phase tends to reduce the platinum oxides. Indeed, interrupting the air feeding the oxygen in the cathode channel is quickly consumed by the methanol crossover oxidation; this leads to a drop of the cathode potential below the value required to reduce the oxides layer.

Electrode dehydration

In order to take into account all the possible temporary degradation mechanisms, the effects of water management need to be investigated, because of their related issues such as flooding and dehydration of membrane and cathode electrode. They have a fundamental importance for low temperature hydrogen fuel cells (PEFC), while in DMFC water management has been less investigated due to the liquid nature of the anode feeding.

The tested DMFC presents MPL at both anode and cathode permitting to reduce cathode flooding, as explained in the performance characterization. However this kind of diffusion layer configuration could results in membrane and cathode dehydration. Indeed, in Fig. 10 a test performed at a reduced current of 0.1 A cm^{-2} with two different cathode airflows (saturated at ambient temperature) is presented. The methanol solution feeding at the anode has been kept constant and equal to the reference conditions, leading to a very high anode stoichiometry (equal to 15) and temperature equal to 75 °C, to avoid the anode performance to be the limiting one. In the first part of the test, the cathode flow is equal to the reference one, leading to a stoichiometry equal to 7.5 and to a very high degradation rate. Around the 50th h, the cathode airflow is halved, leading to an air stoichiometry equal to 3.75. Two effects are evident from the time–voltage curve just after cathode airflow variation:

- a sudden increase of DMFC performance;
- a significant decrease of the slope of the voltage decay.

The EIS performed during the test, related and marked into the Fig. 10, are reported in Fig. 11. The progressive increase in the DMFC total resistance is coherent with the progressive performance loss, but it is also clearly related to the decrease of oxygen content in the cathode outlet, due to the reduced airflow. In these conditions, since the methanol feeding remains constant, the crossover effect at low air feeding determines an increase of the total resistance.

However, despite a worse cathode operation, an increase of performance is evident with the lowering of cathode airflow. From the zoom on the high frequencies zone of the EIS, reported in the detail of Fig. 11, a significant change in the membrane ohmic resistance is highlighted. During the 40 h of high cathode air feeding, the membrane resistance significantly increases; the halving of the airflow determines its quick and significant recover, returning close to the value seen at the beginning of the test, due to the lower water removal
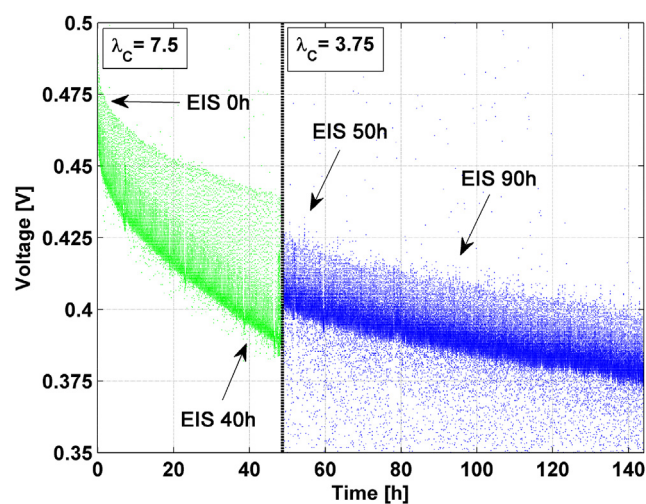
Fig. 10 – DMFC Voltage decay at 0.1 A cm^{-2} with constant anode stoichiometry (15), 75 °C and two different cathode air stoichiometries.
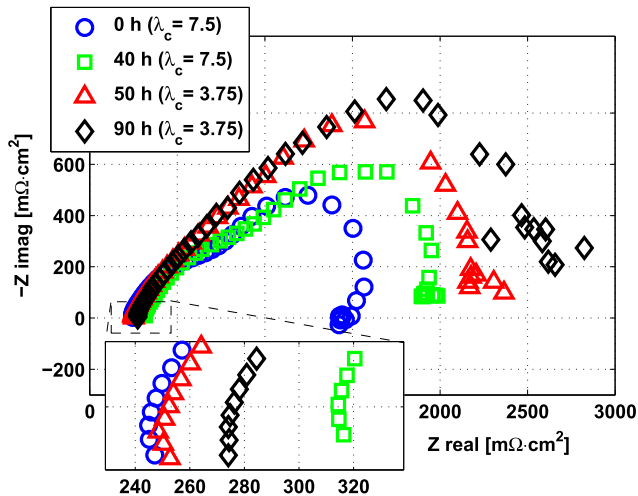
Fig. 11 — EIS at 0.1 A cm^{-2} during the test reported in Fig. 9. The enlargement reveals the membrane ohmic resistance.

from the cathode. Furthermore during the 40 h of high cathode air feeding, an extension of the 45° linear branch, approximation of the electrode proton resistance, is evident. Hence, the strong and quick performance recovery, observable after the airflow reduction, is probably due to both a membrane re-hydration and cathode electrode re-hydration, which cannot be clearly identified by the EIS because of the cathode mass transport limitations due to methanol crossover effects. During the second part of the test, the membrane ohmic resistance progressively shows a slight increase that is coherent with what reported in Ref. [21].

The experimental results shows that both the membrane and cathode electrode dehydration can be responsible for the DMFC temporary degradation; despite the membrane dehydration effect on DMFC voltage is quantifiable by means of the Ohm's law (and it is not very important in comparison with the observed performance losses), the cathode electrode dehydration cannot be quantified.

Furthermore its effect can be recovered during the refresh cycles in the air break phase when, with the continuous anode feeding and the cathode air flow interruption, the electrode ionomer hydration increases again, leading to a performance gain not immediately distinguishable from the Pt oxides reduction effect.

Fully humidified tests

To separate the effects of Pt oxides formation/reduction and electrode dehydration, two tests with an important rise in the humidification of the cathode air feeding are performed. Increasing the air saturation temperature from room temperature to DMFC temperature should result in modifications in the water balance through the membrane; the high water content in the cathode feeding avoids the cathode electrode dehydration. To avoid the opposite risk of flooding, the air saturation temperature has been kept 5 °C lower than the DMFC temperature, and so equal to 70 °C.

Fig. 12 reports the comparison of the voltage evolution of two tests where the only difference is the refresh cycle

structure; a reference refresh (OCV and Air-Break) degradation test is compared with an OCV-only operating strategy (1 min of OCV without air-break every 20 min of operation), in these conditions of high cathode air humidification. The effectiveness on temporary degradation of the air break can be evaluated by comparing the complete, standard refresh to an OCV-only operating strategy.

From this comparison it is possible to point out that, under the assumption of full hydration of the cathode electrode, the important difference between the humidified OCV-only (voltage decay rate: 510 μV h^{-1}) and reference refresh tests (voltage decay rate: 260 μV h^{-1}) shows that the role of platinum oxides, related to air break, is very important as a mechanism for DMFC cathode temporary degradation. Theoretically the difference between the OCV and refresh could be in part associated to the anode electrode hydrogen production during the air-break, discussed in the following paragraph. However, from the anode degradation test performed in Ref. [10] it seems negligible.

The performances obtained with the rise in the cathode humidity corresponds to the highest performances ever acquired during all the experimental work, meaning that the modifications in the water balance, leading to a decrease in membrane and electrode resistivity, can act as a tool for a better DMFC operation.

Electrolytic hydrogen evolution

Another interesting DMFC anodic effect, which could be a temporary degradation mechanism, is the so-called "Electrolytic hydrogen evolution"; it has been independently and simultaneously reported from two research groups, one from Hong-Kong university [23] and one from Julich Research Center [24]. They demonstrated that, when the external load is removed and the oxygen supply is interrupted, the DMFC could be divided into two regions that operate in different ways: galvanic and electrolytic. As long as the methanol solution feeding is maintained, the methanol crossover reduces the oxygen content in the cathode electrode and part of the DMFC could suffer from lack of oxygen availability, starting to operate in electrolytic mode [23,24]. The galvanic zone provides the current for the electrolytic operation of the other region, which results in hydrogen production at the anode, which could determine temporary better performances.

The anode exhaust gas-phase composition has been analyzed during continuous operation and refresh operating strategy but, in the first case, no hydrogen has been identified in the anode exhaust. The analysis of the anode exhausts composition during the DMFC operation with refresh cycles is reported in Fig. 13; hydrogen peaks are 20 min periodic, synchronous with the operation interruptions. Hence, it is confirmed that the refresh cycle determines a slight production of hydrogen at the DMFC anode, which is carried to the μGC by mean of the CO$_2$ produced after the refresh, when the current is drawn again. However, increasing the refresh time from 1 min to 20 min, the hydrogen peak become very low, also after the end of the refresh cycle. This is basically due to the continuous methanol feeding and to the lack of CO$_2$ production: in these conditions, in fact, the hydrogen is continuously removed by mean of the methanol, and the extremely
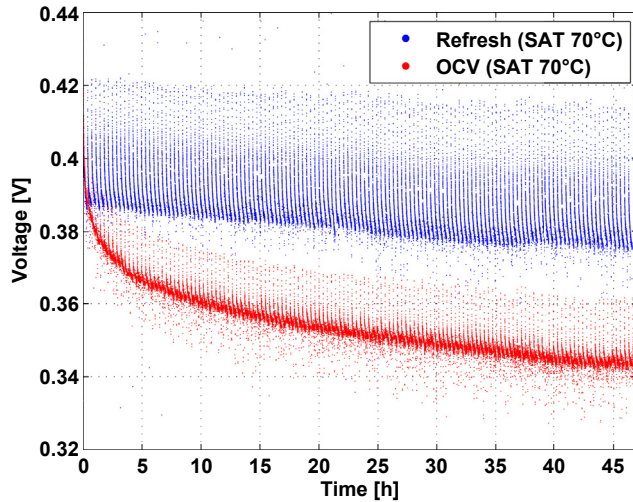
Fig. 12 − **Voltage decay comparison in fully humidified DMFC tests based on refresh and OCV operating strategies, performed in reference conditions.**

small quantity does not permit a correct measurement by the μGC. While the presence of hydrogen at the anode electrode is confirmed with the discontinuous DMFC operation, the evaluation of its effect on anode performance can be found in Ref. [10], where its effect is stated as negligible on DMFC anode performance, and so on the anode temporary degradation phenomena. However, increasing the duration of the interruption periods, the performance recovery progressively increases as highlighted by the long operation interruptions for diagnostic performances, which corresponds to strong performance recoveries as showed in Fig. 4; since the hydrogen production is related to the cathode channel oxygen consumption, it tends to be depleted in a short time implying that the anode hydrogen evolution cannot be responsible for the strong performance recovery observed during the long interruptions.
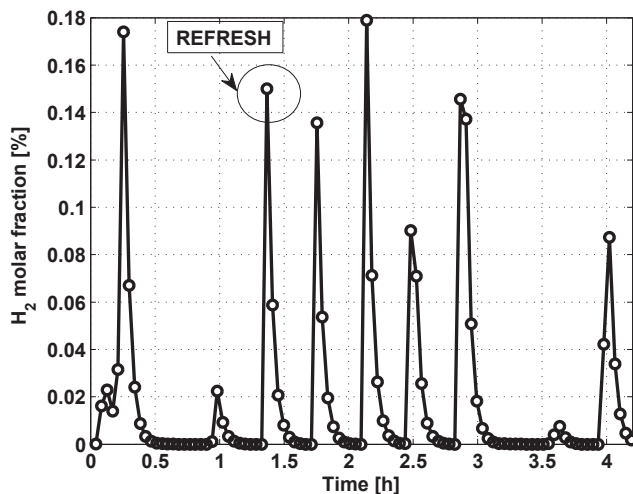
Fig. 13 − **Hydrogen concentration measurements at the anode outlet during refresh operating strategy.**

Table 2 − **Summary of the decay rates of different DMFC degradation tests.**

Degradation test description	Voltage decay rate
1 min Refresh every 20 min, room temperature saturated air, 0.25 A cm^{-2} (reference condition), see Fig. 5	330 μV h^{-1}
1 min Refresh every 20 min, DMFC temperature saturated air, 0.25 A cm^{-2}, see Fig. 12	260 μV h^{-1}
1 min OCV every 20 min, DMFC temperature saturated air, 0.25 A cm^{-2}, see Fig. 12	510 μV h^{-1}
1 min OCV every 20 min, electrolytic (anode) operation, 0.25 A cm^{-2}, see Fig. 5	147 μV h^{-1}
500 h long-term degradation test − reference operating strategy, see Fig. 4	~ 40 μV h^{-1} (Permanent degradation)

The Table 2 reports the different decay rates calculated during the different tests. Most of the temporary degradation is attributable to the cathode electrode: platinum oxides formation and electrolyte dehydration result as the major causes. The permanent decay rate (last line of Table 2), calculated from voltage values at 0 h and 500 h, is one order of magnitude lower than temporary one, coherently with manufacturer data.

Further work is necessary to quantify rigorously the contribution of different phenomena; specific experimental and modeling activities, devoted to a detailed interpretation of impedance spectra taking into account methanol crossover phenomenon and to increase the understanding of Pt/Ru oxides role on temporary degradation, are in progress.

Conclusions

This work proposes an experimental investigation of DMFC temporary degradation through performance characterization, a 600 h degradation test and additional experimental tests.

The main conclusions regarding DMFC temporary degradation are the following:

- the anode contribution to temporary degradation is not sufficient to explain the overall temporary degradation magnitude, confirming the existence of DMFC cathode temporary degradation;
- at the cathode, a slight contribution to the temporary degradation is attributable to electrode dehydration, due to the drying effect of the air flow. The air break phase of the refresh cycle helps the rehydration of the electrode;
- the most severe cathode temporary mechanism seems to be the platinum oxides/hydroxides formation, which occurs with the operation, due to the high cathode potential. Lowering the cathode potential with an air feeding interruption during the refresh cycle, leads to the reduction of the oxidized platinum implying a performance recovery;

- hydrogen evolution is confirmed to occur during the air break period of the refresh cycle in galvanic operation, but its effect on performance seems negligible.

Acknowledgments

R E F E R E N C E S

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