



A combined in-situ and post-mortem investigation on local permanent degradation in a direct methanol fuel cell



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HIGHLIGHTS

- Permanent and temporary degradation rates are equal to 59 and 21 $\mu\text{V h}^{-1}$.
- ECSA loss effect is 9 and 31 $\mu\text{V h}^{-1}$ for anode and cathode respectively.
- Membrane and mass transport degradation effects are 4 and 15 $\mu\text{V h}^{-1}$ respectively.
- ECSA loss is due to heterogeneous particle growth, Ru crossover and ionomer loss.
- Anode CL and GDL degradation is due to Ru dissolution and PTFE decomposition.

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ABSTRACT

Performance degradation is one of the key issues hindering direct methanol fuel cell commercialization, caused by different mechanisms interplaying locally and resulting in both temporary and permanent contributions.

This work proposes a systematic experimental investigation, coupling in-situ diagnostics (electrochemical and mass transport investigation) with ex-situ analyses of pristine, activated and aged components (X-ray photoelectron spectroscopy and transmission electron microscopy), with an in-plane and through-plane local resolution. Such a combined approach allows to identify on one hand the degradation mechanisms, the affected components and the presence of heterogeneities; on the other hand, it allows to quantify the effect of the major mechanisms on performance decay. Thanks to a novel procedure, temporary (21 $\mu\text{V h}^{-1}$) and permanent degradation (59 $\mu\text{V h}^{-1}$) are separated, distinguishing the latter in different contributions: the effects of active area loss at both at anode (9 $\mu\text{V h}^{-1}$) and cathode (31 $\mu\text{V h}^{-1}$), mass transport issue (15 $\mu\text{V h}^{-1}$) and membrane decay (4 $\mu\text{V h}^{-1}$). The post-mortem analysis highlights the effect of degradation mechanisms consistent with the in-situ analysis and reveals the presence of considerable in plane and through plane heterogeneities in: particle size growth in catalyst layers, Pt/Ru and polymer content in catalyst and diffusion layers, Pt/Ru precipitates in the membrane.

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1. Introduction

The direct methanol fuel cell (DMFC) technology is a promising energy source for portable and automotive applications, mainly due to the direct use of a liquid fuel, quick recharging and low operating

temperature [1–3]. In the last decades the research activities on DMFC have been mainly focused on the development of innovative materials in order to improve performance [4–7], as, for example, reducing methanol crossover [8,9] and increasing the effectiveness of the catalysts [10,11]. However, further critical issues still must be overcome to reach market competitiveness, among which severe performance degradation is one of the most relevant [12–15]. Therefore, the number of experimental investigations of DMFC degradation is continuously increasing [16–20] and recently a

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thorough review has been published [21].

DMFC performance loss can be partially recovered by interrupting the operation for diagnostics or by using appropriately developed procedures. Cha et al. characterize this behaviour defining a permanent and a temporary contribution [22], but the latter is not definitely explained. Several studies attribute the performance recovery to the cathode, probably due to the reduction of platinum oxides [23] or to the removal of water accumulation (i.e., flooding) [24]. Instead, other studies propose the galvanic/electrolytic operation of the DMFC as temporary degradation mechanism, due to hydrogen generation at the anode side [25,26]. These works [23–27] demonstrate that an interruption of both operation and cathode air feeding determine a positive effect on DMFC performance. For this reason, the focus on operating strategies that allow reducing temporary degradation mainly regards DMFC cathode [28,29]. Instead, temporary degradation of the DMFC anode has been firstly identified in Refs. [30], where it has been attributed to CO₂ accumulation in both catalyst layer (CL) and gas diffusion layer (GDL), as confirmed by the reduction of methanol crossover during degradation tests [31]. However, DMFC temporary degradation minimization is not extensively investigated in the literature since permanent and temporary contributions are not effectively distinguished.

In the literature, permanent degradation is attributed to both the electrodes and to the membrane and different degradation mechanisms are highlighted. Electrochemical surface area (ECSA) loss can be due to phenomena such as platinum dissolution, ruthenium dissolution and crossover and carbon corrosion [16–18], while membrane delamination and thinning are sometimes highlighted as other mechanisms. However, permanent degradation itself is seldom identified [22] from the temporary one and its quantification is not performed in standard and repeatable operating conditions.

DMFC shares some permanent degradation mechanisms with hydrogen polymer electrolyte membrane fuel cell (PEMFC), like typical platinum degradation mechanisms involving an average catalyst particle size increase, such as dissolution and re-deposition [17,22,32,33], highlighted for example by X-ray diffraction (XRD) and transmission electron microscopy (TEM) observations. Moreover, membrane degradation due to pinholes, crystallinity increase [13,32] seems to occur mainly next to the cathode side [17], while GDL degradation is mainly investigated with scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) showing a general polymer loss [19,34]. Among the main DMFC degradation mechanisms, the literature focuses on the instability of the ruthenium nanoparticles resulting in ruthenium dissolution and crossover to the cathode investigated mainly through EDS [17,28,35]; however, no work presents the investigation of the heterogeneities related to the different DMFC permanent degradation mechanisms in the different regions such as reactants inlet and outlet, while a deep focus on the degradation heterogeneities in PEMFC has been already presented in Refs. [33,36]. Moreover, the coupling between the measurements obtained during the DMFC operation and the post-mortem analysis is seldom carried out [28]. From the literature analysis emerges that a direct relation between each degradation mechanism and the corresponding voltage decay is missing, as also highlighted in Ref. [21].

The aim of this work is to separate and quantify the effect of each component degradation on voltage decay. Periodic in-situ diagnostic measurements, assisted by modelling analysis, allow to distinguish the effects of active area loss at both at anode and cathode, mass transport issue, membrane decay and reversible degradation. Ex-situ analyses on pristine, activated and aged components (with in-plane and through-plane local resolution) allow to identify the major degradation mechanisms and the

related heterogeneities. Finally, the consistency of the results from in-situ and ex-situ analyses are discussed in details to provide a further insight on DMFC degradation.

2. Experimental methodology

2.1. DMFC sample and experimental setup

The DMFC membrane electrode assemblies (MEAs) used in this work, both for the preliminary tests on *full refresh* procedure and for the long term test, are commercial 25 cm² manufactured by IRD Fuel Cell A/S. The membrane is Nafion[®] 115, anode catalyst loading is 1.8 mg cm⁻² (PtRu) and cathode catalyst loading is 1.2–1.4 mg cm⁻² (Pt). Both anode and cathode diffusion layers are Sigracet[®] SGL35DC (thickness 325 μm, 20% PTFE content, with microporous layer (MPL)). Nominal current density is 0.25 A cm⁻² and fuel cell temperature is maintained at 75 °C. During testing, unless differently indicated, anode and cathode are fed respectively with 1.0 M methanol solution (with stoichiometry equal to 6 at nominal current density) and air, saturated by water at ambient temperature (with stoichiometry equal to 3 at nominal current density).

The experimental setup utilized in this work is explained in detail in Ref. [37].

2.2. Operating strategy description

As explained in Refs. [31,38], a DMFC cannot work in continuous operation due to an excessive degradation rate and consequently they are usually operated by means of discontinuous operating strategies. For the long term degradation test, the DMFC has been operated by cycles of 20 min followed by 1 min of *refresh* cycle. About every 120 h of operation, an interruption for diagnostic is performed to evaluate permanent degradation.

The *refresh* cycle is an IRD Fuel Cell confidential procedure that consists of a sequence of OCV and cathode air feeding interruption,¹ similar to that reported in Ref. [24], which allows recovering the temporary degradation. In the *refresh* cycle, as the air feeding is switched off, cathode potential drops to less than 0.3 V and when the operation restarts a significant positive effect on performances is obtained. A preliminary interpretation of the positive effect of *refresh* cycles on DMFC performance has been already presented in Refs. [29,39], where temporary degradation turned out to be caused on one end by a gradual increase of CO₂ content in the anode porous layers that hinders reactant transport to active sites, on the other hand by Pt oxides formation in the cathode catalyst layer due to operation at high cathode potential. The *refresh* cycle proposed in Ref. [29] permits to lower the CO₂ content at the anode interrupting its operation while flowing the reactant and to reduce the Pt oxides at cathode lowering its potential thanks to an interruption of air feeding. However, despite this operating strategy results in a lower temporary degradation than the one occurring during continuous operation, it does not entirely eliminate the temporary decay. Therefore, a *full refresh* procedure, able to fully recover temporary degradation, has been developed and utilized before carrying out diagnostic measurements. The details are reported in Appendix A1.

2.3. In-situ electrochemical diagnostic measurements

The following diagnostic measurements have been periodically performed to characterize permanent degradation, once the

¹ The details cannot be provided for confidential agreement.

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