



A locally resolved investigation on direct methanol fuel cell uneven components fading: Steady state and degradation local analysis

C. Rabissi^{a,*}, P. Gazdzicki^b, L. Guétaz^c, S. Escibano^c, L. Grahl-Madsen^d, A. Baricci^a, A. Casalegno^a

^a Politecnico di Milano, Department of Energy, via Lambruschini 4, 20156, Milano, Italy

^b German Aerospace Center (DLR), Institute of Engineering Thermodynamics, Pfaffenwaldring 38-40, 70569, Stuttgart, Germany

^c CEA, LITEN, 17 rue des Martyrs, 38054, Grenoble, France

^d EWII Fuel Cells A/S, Emil Neckelmanns Vej 15 A&B, DK-5220, Odense, Denmark

HIGHLIGHTS

- Innovative macro-segmented fuel cell setup applied for the first time to a DMFC.
- Local aging in-situ investigation is coupled with TEM and XPS post-mortem analysis.
- Graphitized carbon support based cathode catalyst layer stability is demonstrated.
- Homogeneous fluorine depletion and particle growth are identified in faded MEA.
- Non-homogeneous water distribution leads to uneven performance loss and aging.

ARTICLE INFO

Keywords:

Direct methanol fuel cell
Heterogeneity
Segmented cell
Local degradation
Post mortem

ABSTRACT

DMFC technology widespread commercialization is still hindered by durability issues. In literature, locally resolved measurements and post-mortem analyses reveal the onset of strong heterogeneous components fading, higher at air outlet region. Local aging mechanisms could be enhanced by DMFC cathode cycling operation in highly uneven presence of water. An innovative PEM macro-Segmented Fuel Cell (mSFC) setup has been developed to investigate DMFC local performance and degradation, coupling electrochemical and ex-situ analyses as TEM and XPS. An MEA based on highly graphitized carbon supported cathode electrode, confirmed in AST to be stable to cycling operation under flooded conditions, has been implemented in DMFC operation. 500 h local degradation test, despite 32% heterogeneous current density distribution, reveals homogeneous ECSA loss, consistent with homogeneous nanoparticles growth from 3.16 to 5.4 nm, which leads to 70% lower degradation rate ($31.2 \mu\text{V h}^{-1}$) than the reference MEA. Water-related limitations, such as dehydration and flooding, are revealed to increase local performance loss by 25% and 100% respectively at cathode inlet and outlet regions, leading to current redistribution and uneven voltage loss. Hence, local optimization of MEA properties is foreseen to permit further important durability improvements.

1. Introduction

Thanks to the employment of a high energy density liquid fuel, stable under a wide range of conditions and permitting convenient and quick recharging [1–3], direct methanol fuel cell (DMFC) technology is interesting for portable electronics, small to medium scale power production and vehicular applications. Some detrimental factors still prevent its large-scale diffusion, mainly related to high cost of the materials together with low efficiency and power density compared with hydrogen proton exchange membrane fuel cells (PEMFC). Above all,

severe performance degradation limits DMFC devices durability [4]; hence, the number of publications investigating this issue is continuously increasing, focusing on both its reversible, or temporary [4–8], and irreversible, or permanent [9–13], components. In the literature, the latter is attributed to permanent alterations of the microstructure of both catalyst layers (CL), gas diffusion layers (GDL) and polymer electrolytic membrane (PEM), attributed to different degradation mechanisms. Particularly, electrochemical surface area (ECSA) loss is mainly due to phenomena such as Ostwald ripening, determining platinum and ruthenium dissolution, migration and

* Corresponding author.

E-mail address: claudio.rabissi@polimi.it (C. Rabissi).

<https://doi.org/10.1016/j.jpowsour.2018.07.034>

Received 29 March 2018; Received in revised form 14 June 2018; Accepted 6 July 2018

Available online 14 July 2018

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recombination, together with carbon support corrosion [13–16].

Recently, locally resolved measurements and local post-mortem analysis [17–21] revealed the development of the onset of heterogeneous degradation in DMFC cells. It is relatively well documented that in DMFC performance is the result of a complex interaction of properties and microstructure of materials, cell design and assembling as well as operating parameters, which are locally varying. Locally non-optimized operating conditions could lead to early localized aging of membrane-electrode assembly (MEA); this represents a critical issue, since the earliest fading area could compromise the durability of the entire device. Hence, a strong effort is being put in properly understanding the determining mechanisms. To enable a local investigation of performance during operation, segmented cell-based works are increasing in number [22], usually basing the investigation on ad-hoc developed hardware or commercial boards able to permit a localized analysis of performance. To the author's knowledge, in literature no work about DMFC degradation combine the analysis of performance distribution during ageing and local degradation measured by ex-situ analysis, i.e. transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). While the former is typically investigated by means of highly locally resolved hardware, which can limit measurements reliability, in other works the latter relies on local post-mortem analysis. This work aims to provide a combined investigation of performance heterogeneity and degradation, correlating local electrochemical and post-mortem methodologies to identify the determining mechanisms of such uneven fading of components.

In a previous work [20], the authors investigated the degradation of a DMFC MEA operated for 1000 h, distinguishing each component contribution. Strong MEA heterogeneous fading was found in post-mortem analysis by XPS and TEM imaging at both sides GDLs and CLs. The study revealed CLs fluorine depletion, indicating ionomer content degradation, together with heterogeneous aging of GDLs hydrophobic properties. Moreover, a stronger particle agglomeration at cathode outlet area, consistent with the Ostwald ripening mechanism, was found to determine an increased localized ECSA loss. Such localization of these phenomena can be related to the higher water content at cathode outlet, both produced by the oxygen reduction reaction (ORR) and back-diffused from anode. High water presence increases Pt ions mobility [23,24] that, after dissolution, can more easily migrate and recombine in bigger, more stable particles, enhancing localized ECSA loss. Moreover, as published in Ref. [25] and confirmed in Ref. [8], hydrogen reference electrodes (RHE) measurements revealed a high cathode potential of DMFC during operation (always over 0.85 V vs RHE). This value is even higher than that of PEMFC, due to the lower current density at which DMFC are operated, limited by the high anode overpotential for methanol oxidation reaction (MOR). Such a high potential enhances Pt oxidation [4–6] that, limiting catalyst surface available for oxygen reduction reaction (ORR), acts as a key mechanism for temporary performance degradation. Hence, as emphasized in Refs. [5–8], cathode potential during DMFC operation is periodically cycled to values below 0.5 V during *refresh cycles*, in order to reduce platinum oxides and restore Pt metal form. However, while hindering ORR activity, superficial oxidized Pt is suspected to be beneficially more stable to dissolution [26,27], acting as a 'protecting' layer from ripening mechanism. Interestingly, in Ref. [8] using external RHEs, a strongly heterogeneous decrease of cathode potential was identified during the *refresh cycle* itself. Indeed, due to inhomogeneous residual oxygen distribution, the potential drop was found to be actually deeper at the air outlet region. This would mean a more effective localized temporary degradation recovery from Pt oxidation, but also a periodical exposure of fresh catalyst back to dissolution during operation without any 'protective' oxide layer, in a region richer in water content, possibly explaining the stronger nanoparticle growth at cathode outlet.

Considering the given interpretation, this work starts from the selection of a stable material for cathode catalyst layer, whose durability is first assessed through a modified accelerated stress test (AST)

protocol simulating DMFC operating conditions. Then, DMFC heterogeneous degradation is investigated by means of an innovative setup, applied to both steady state and 500 h degradation test. Local analysis of the MEA is compared to locally resolved ex-situ analysis, analogously to what published in ref. [20], focusing on eventual uneven fading of MEA components. Elucidating the main mechanisms originating the uneven distribution of current density and its redistribution over time will permit future works to identify possible solutions to homogenize the current density during the operation, aiming to improve cell operation in stability and durability.

2. Experimental methodology

2.1. MEA samples

Experiments performed in this work are carried out on 25 cm² DMFC MEA samples manufactured by EWII Fuel Cells A/S. The membrane is Nafion[®] 115 (127 μm thick), anode and cathode are loaded with 1.8 mg cm⁻² (PtRu alloy) and 1.2 mg cm⁻² (Pt), respectively. Aiming to promote electrode stability during potential cycling in presence of liquid water as discussed in the introduction, a highly graphitized carbon support is adopted for cathode catalyst layer (CCL), with 0.5 Pt:C and 0.6 ionomer:C ratio. The expected hydrophobic behavior and stability under flooding conditions, consistent with the literature [28–30], is assessed in section 3.1 by means of AST testing. On both sides Sigracet[®] SGL35DC GDLs (thickness 325 μm, 20% PTFE content) provided with microporous layer (MPL) are used.

The experimental setup, thoroughly explained in Ref. [20], has been improved to perform local detailed analysis of performance and degradation as described in the following.

2.2. Macro-segmented fuel cell hardware

To perform locally resolved electrochemical measurement, a custom setup has been developed and manufactured, based on a segmented cell-like approach. The so-called macro-Segmented Fuel Cell (m-SFC) is characterized by a lower spatial resolution compared to existing approaches based on shunt or hall sensors matrices [22,31], aiming to an independent control of several macro-area of the cell. Complete electrochemical characterization is locally possible with limited internal border effects, avoiding possible crosscurrent and reciprocal interference between segments. The m-SFC hardware has been developed using materials and geometries as close as possible to the traditional single cell standard [20], ensuring backward compatibility with measurement performed in former works. The resulting design for the first mSFC prototype, represented in Fig. 1, features four segments at both cathode and anode on a triple channel serpentine flow field, suitable for square 25 cm² MEAs. The segmented graphite flow plate, developed by Politecnico di Milano with the cooperation of EWII fuel cells A/S, are kept together with a 0.1 mm layer of inert epoxy resin.

As visible in Fig. 1, the system has three small additional bores facing the GDL to permit external RHE connection as successfully performed in Refs. [7,8].

2.3. Operating conditions and testing protocols

As indicated by the MEA manufacturer, nominal current density and cell operating temperature are respectively 0.25 A cm⁻² and 75 °C. Anode and cathode are respectively fed with 1.0 M methanol solution and air saturated with water at ambient temperature (stoichiometries equal to 6 and 3 respectively at 0.25 A cm⁻²). The mSFC reference operating protocol is galvanostatic: total current is imposed, which is divided by a 4-module electronic load (4x Chroma ATE 63610-80-20) between the segments, aiming to maintain each segment ΔV at the same value. This configuration permits identification of the contribution of each segment to the overall current density in the cell, while operating

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