



On the effect of gas diffusion layers hydrophobicity on direct methanol fuel cell performance and degradation



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HIGHLIGHTS

- The lack of anode MPL and a reduction of GDL hydrophobicity leads to DMFC cathode flooding.
- Cathode electrode flooding does not determine a variation of cathode active area loss mechanisms rate.
- Cathode flooding effect has a worsening effect on the performance loss during a degradation test.
- Permanent cathode water balance modification occurs in the very first part of the degradation test (<100 h).

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ABSTRACT

Degradation and mass transport phenomena management are two of the main issues hindering direct methanol fuel cell commercialization. Water and methanol crossover through the membrane, regulated by both anode and cathode gas diffusion layers hydrophobic properties, is widely studied in the literature, while the effect of mass transport phenomena evolution on the direct methanol fuel cell degradation has not been investigated yet. This work aims to present a combined experimental and modeling analysis on the effect of the gas diffusion layers hydrophobicity on DMFC degradation, through the comparison of performance characterization and degradation tests of two different fuel cells. In one of them, the lower diffusion layer hydrophobicity and the absence of anode microporous layer determines the onset of cathode flooding, negatively affecting performance and degradation. However, the cathode surface area loss is similar between the two fuel cells, meaning that flooding does not involve modifications in cathode permanent degradation mechanisms, but it mainly determines the amplification of the cathode surface area loss effects.

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1. Introduction

Direct methanol fuel cell (DMFC) is a promising technology for both remote stationary and portable applications mainly due to the use of a high energy-density liquid fuel [1–3]. Among the technical issues that still hinder the DMFC commercialization, mass transport phenomena management and a severe performance degradation are two of the mainly investigated [4–7]. DMFCs are fed with a liquid mixture composed by water and methanol; both of them flow through the membrane from the anode to the cathode. Water crossover through the membrane may cause problems such as cathode flooding and anodic water depletion. The former decreases oxygen diffusivity at cathode, determining a lower cell voltage,

while the latter enhances methanol crossover through the membrane, implying fuel waste and performance loss. During the last years, both water and methanol crossovers in DMFCs have been extensively studied [5,9]. It has been found that the design of gas diffusion layer (GDL), usually coated with an additional microporous layer (MPL), plays an important role in the management of mass transport phenomena. However, the investigation of DMFC mass transport phenomena evolution during lifetime and the effect of GDL configuration on DMFC degradation are only rarely presented [4].

DMFC degradation consists in two different components [6]: a temporary degradation, which can be recovered by means of appositive procedures, and a permanent one. Mass transport phenomena through a DMFC play a key role regarding various temporary degradation mechanisms already highlighted in the literature, such as both cathode electrode flooding and dehydration

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[10] or CO₂ gas-phase transport through the anode porous media [11] and along the anode flow field [12].

DMFC permanent degradation is attributed both to the electrodes and to the membrane; different degradation mechanisms have been highlighted, mainly from ex-situ investigations [6,7,13,14]. Electrochemical surface area (ECSA) loss can be due to phenomena such as platinum dissolution, ruthenium dissolution and crossover, carbon corrosion; besides, delamination and thinning of the membrane are sometimes highlighted as other interesting mechanisms. However, the influence of the mass transport phenomena evolution, caused by degradation phenomena, or variations, due to modifications in the MEA structure, on the DMFC permanent degradation mechanisms occurrence has not yet been investigated.

This work aims to investigate experimentally the effect of the GDL hydrophobic properties on DMFC performances and degradation, coupling mass transport and electrochemical measurements during two analogous degradation tests on similar MEA's provided by different GDL's. Moreover, a previously developed DMFC model [9,15] is used to support and integrate the interpretation of the experimental results.

2. Experimental methodology

2.1. Experimental setup and MEAs

The experimental setup for single DMFC characterization and degradation tests (both for overall and anode operation) is described in Ref. [4], where the set of equations governing mass transport and the recent improvements to the experimental setup are explained in details.

All the MEA's used for this work are manufactured by IRD Fuel Cell A/S. The reference MEA's (named "M–M") used for this work are commercial 25 cm²: membrane is Nafion115, with catalyst loading of 1.8 mg cm⁻² (PtRu) at the anode electrode and 1.2 mg cm⁻² (Pt) at the cathode electrode. Both anode and cathode diffusion layer are Sigracet[®] SGL35DC (thickness 325 μm, 20% PTFE content, with MPL). The benchmark MEA's (named "G–M"), with the same active area, membrane and electrodes, presents differences from the reference one in the diffusion layers characteristics: anode GDL is Sigracet[®] SGL24BA (thickness 190 μm, 5% PTFE content, without micro-porous layer), while cathode diffusion layer is Sigracet SGL25B (thickness 235 μm, 5% PTFE content, with MPL).

During galvanic operation 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 both calculated at 0.25 A cm⁻². Instead, during anode operation tests, cathode is set as a dynamic hydrogen electrode, as explained in Ref. [11], feeding it with 3.5 Nml min⁻¹ of dry hydrogen. Nominal current density is 0.25 A cm⁻² and 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. As a proxy for methanol crossover, CO₂ measurements are performed at the cathode exhaust with a Vaisala sensor GMP70 (uncertainty 50 + 2% ppm) in a vessel of 0.5 dm³ 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 CO₂ concentration, thus the uncertainty of the final measurements is evaluated to be 70 + 2.8% ppm [22]. An heat exchanger to warm up the cathode exhaust to

evaporate eventual liquid water and a thermo-hygrometer (Vaisala HMT333) 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. [9]. The uncertainty associated to the measurement of water flow is evaluated equal to 7% in the whole investigated range [9].

2.2. Preliminary characterization

Prior to the degradation test characterization, a first sample of G–M MEA has been characterized, obtaining several polarization curves in various operating conditions; just few of them are reported in the followings for the sake of shortness. The same tests have been carried out on the M–M MEA acting as a reference, in order to highlight the effect of the modifications introduced in the GDL configuration. The preliminary characterization also allows ensuring the degradation tests results reliability, by means of a results repeatability evaluation.

The polarization curve acquisition is composed of 9 single measurement points, collected increasing current densities following one-way curves, as explained in Ref. [8]. Each polarization curve is performed with reactants at constant flow rates in order to ensure the steady state operation, in order to obtain high reliability of methanol crossover, water content in cathode outlet and EIS measurements.

Electrochemical impedance spectroscopies (EIS) are executed during the diagnostic polarization curves, at 0.1 and 0.25 A cm⁻² steps, and periodically during the degradation tests, using a potentiostat/galvanostat (Autolab PGSTAT30) provided with a frequency response analysis 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 [17,18]; thus, the imposed amplitude 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.

2.3. Degradation test

As explained in Refs. [19,20], a DMFC cannot work in continuous operation due to an excessive degradation rate and, for this reason, suitable operating strategies are adopted. 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] to limit temporary degradation, consisting in an operation break during which a sequence of periods of OCV (about 0.8 V) and cathode air interruption (less than 0.3 V) are performed; as the operation restarts, a significant positive effect on performances is noticeable [19].

Besides, about every 100 h of this discontinuous degradation testing, a one-day interruption for diagnostic is performed. The diagnostic interruption is preceded and followed by a long break period (about 16 h) with the anode fed with a minimal fuel flow and the cathode closed; this procedure allows a complete removal of temporary degradation effects.

During the diagnostic operation interruptions, the DMFC degradation is evaluated performing polarization curves, EIS and, finally, 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

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