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Experimental investigation of methanol crossover evolution during direct methanol fuel cell degradation tests

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HIGHLIGHTS

- The methanol crossover during different DMFC degradation tests decreases.
- The water transport during different DMFC degradation tests remains nearly constant.
- The methanol crossover decrease in time presents both temporary and permanent contributions.
- The methanol crossover evolution could mitigate the degradation effect on DMFC efficiency.

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ABSTRACT

Methanol crossover and severe degradation are two of the most critical issues hindering the commercialization of direct methanol fuel cells. The experimental investigations found in the literature show that degradation has both permanent and temporary contributions; the latter can be recovered thanks to a suitable operation interruption. This work reports the experimental characterization of methanol crossover and water content in cathode exhaust during different degradation tests performed in continuous and cycling operation modes. Such investigation evidences a reduction of methanol crossover during the DMFC degradation tests that can be partially restored. Methanol crossover reduction presents both temporary and permanent contributions: the latter could be related to membrane degradation. Moreover the effect of both methanol crossover and electric power reduction on fuel cell efficiency are discussed.

1. Introduction

Direct methanol fuel cell (DMFC) is a very promising technology as a power source for portable and uninterruptible power supply applications, due to the direct use of a high energy density liquid fuel [1–3]. However, the fuel is also the cause of its main drawbacks: lower efficiency and performance than polymer electrolyte membrane fuel cell (PEMFC) fed with hydrogen. This is due to the slower electrochemical methanol oxidation and to methanol crossover through the polymeric membrane.

In the literature methanol crossover has been extensively studied both experimentally and theoretically [4–8]. It has been widely demonstrated that it is closely related to membrane structure, morphology and thickness and to DMFC operating conditions such as temperature, pressure, and methanol concentration. Nowadays the main research activities are focussing on developing innovative materials to reduce methanol crossover [9,10], in order to reach market competitiveness. However other technical issues must be still overcome to enter into the market, among which the severe performance degradation.

In the literature the experimental investigations of DMFC degradation are continuously increasing [11–18], but generally, they focus only on catalyst characterization before and after the degradation test [12–15]. DMFC performance loss can be partially recovered interrupting the operation for diagnostics or by utilizing the appropriately developed procedures. Cha et al. characterize this behaviour and define a permanent and temporary contributions [17]. The former is due to irreversible degradation mechanisms, such as catalyst agglomeration, ruthenium dissolution and membrane delamination, while the latter is not fully understood nor systematically investigated. In Refs. [19–22] some operating strategies are presented in order to reduce the effect of temporary degradation, but the influence of operating conditions is seldom investigated.

Indeed methanol crossover is a technical issue of fundamental significance, because it determines a strong reduction of cathode

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potential, lowering DMFC performance, and a waste of fuel, decreasing system efficiency [23,24]. The analysis of methanol crossover behaviour during degradation tests is crucial, because the variation of both performance and efficiency is closely related to such phenomenon. In the literature there is a lack of *in situ* mass transport measurements during DMFC durability tests. Both methanol crossover and water transport in DMFC strongly depend on membrane and gas diffusion layer (GDL) properties [25,26] that may fade during operation. In Ref. [27] the analysis of water transport during a durability test is presented, but up to our knowledge no work proposes an investigation of methanol crossover evolution during degradation tests.

This work aims to investigate the evolution of methanol crossover during degradation tests, performed on two different Membrane Electrode Assemblies (MEAs), evaluating the influence of two operating strategies and anode methanol concentration. Moreover the effect of such methanol crossover variation on DMFC efficiency is investigated.

2. Experimental setup

2.1. Experimental equipment

The experimental setup for single cell DMFC characterization is described in Ref. [26], where the set of equations governing mass transport and the recent improvements to the experimental setup are explained in details. CO_2 measurement at cathode outlet is commonly accepted and used as a proxy for methanol crossover quantification. Data are acquired at a 0.5 Hz frequency and collected by mean of an *ad-hoc* developed Labview® software.

In this work electrochemical measurements are added to the experimental setup in order to improve the degradation characterization. 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. The voltage of the fuel cell is simultaneously measured by the electronic load, the milliohmeter and also by a high precision acquisition board (NI 6218, estimated uncertainty: 1 mV) directly connected to the fuel cell, in order to have multiple readings.

Cathode exhaust composition has been measured by an SRA R-3000 μGC analyzer equipped by three columns and preceded by a liquid–gas gravity separator at room temperature. The first column is a nitrogen fed Molsieve for the hydrogen identification, the second one is a helium fed Molsieve for nitrogen, oxygen and CO identification while the third one is a helium fed PlotU for the CO_2 and light hydrocarbons identification such as methanol.

2.2. MEAs description

The first MEA used in this work is a commercial 22 cm^2 MEA: membrane is Nafion117, anode catalyst loading is 3 mg cm^{-2} (PtRu), cathode catalyst loading is 1.2–1.4 mg cm^{-2} (Pt). Anode diffusion layer is Sigracet® SGL10CA (thickness 400 μm, 10% PTFE content, without microporous layer), while cathode diffusion layer is Sigracet® SGL10CC (thickness 415 μm, 10% PTFE content, with microporous layer). During testing anode and cathode are fed respectively with 1.0 M methanol solution with stoichiometry equal to 3 and dry air with stoichiometry equal to 4. Nominal current density is 0.15 A cm^{-2}. The fuel cell temperature is kept at 60 °C by mean of a proportional, integral and derivative (PID) temperature controller.

Instead the second MEA used in this work is a 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 microporous layer). During testing, unless differently indicated, anode and cathode are fed 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} and the fuel cell temperature is kept at 75 °C.

3. Continuous operation

3.1. Mass transport measurements on the first MEA

The test performed on the first MEA is composed of two continuous operation periods at constant current density interspersed with an interruption when diagnostic is performed, as reported in Fig. 1. The following procedure, named as “long refresh”, is performed before each test: OCV is hold for few seconds with air feeding, then the air supply is switched off, while the methanol solution circulation is kept for 5 h. This procedure allows recovering most of the temporary degradation resulting in a considerable voltage recovery, but the reasons are still not fully understood [19,20,28].

In Fig. 1 the two components of the DMFC degradation can be clearly distinguished: the temporary one, that can be recovered, and the permanent one, that appears as a downward shift of the performances between the two tests.

Permanent degradation, calculated as in Ref. [22], is equal to 148 μV h^{-1}, a small part of the overall degradation, 770 μV h^{-1}, calculated as the difference between the initial and final voltages of the first test divided for the test duration; in fact the voltage drop associated with the first test is considerably higher than the downward shift between the two tests. Some researchers attribute DMFC temporary degradation to mass transport issues in cathode GDL and platinum oxide formation on cathode electrode [29]. An anode contribution to temporary degradation has been recently described in Ref. [30] and attributed to the reduction of methanol and water concentrations in the anode GDL and electrode.

Fig. 2 shows the measurements of CO_2 and water content in cathode exhaust during the two consecutive degradation tests; they highlight a decrease of CO_2 content during each test and a considerable recovery after operation interruption. Such reduction could be due to two possible reasons:

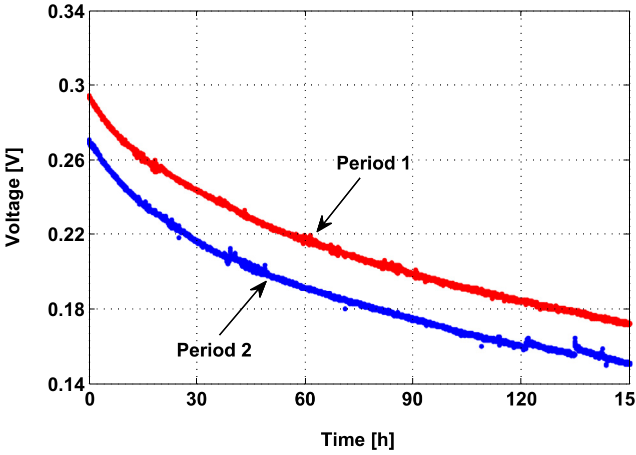

Fig. 1. Voltage decay during two consecutive tests in continuous operation performed on the first MEA at 0.15 A cm^{-2}.