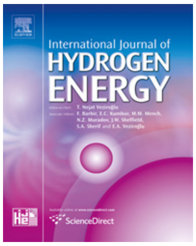
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 35 (2010) 2586–2590

Available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/he



# Diagnosis of performance degradation phenomena in PEM fuel cells

*M.A. Rubio**, *A. Urquia*, *S. Dormido*

*Departamento de Informática y Automática, UNED, Juan del Rosal 16, 28040 Madrid, Spain*

ARTICLE INFO

*Article history:*
Received 23 March 2009
Accepted 29 March 2009
Available online 5 May 2009

*Keywords:*
Diagnosis
Impedance spectroscopy
Electrochemical parameters
CO poisoning
Flooding
Membrane drying

ABSTRACT

A novel diagnosis methodology for characterizing the cathode flooding, the membrane drying and the anode catalyst poisoning by carbon monoxide is proposed in this manuscript. This diagnosis methodology is intended to be used in portable control systems. Two equivalent-circuit models for PEM fuel cells (PEMFC) with a low computational cost are proposed. The first model describes the dynamic behavior of the PEMFC during its normal operation, and also during the cathode flooding and the membrane drying processes. A method to estimate the parameters of this model is proposed. The experimental procedure for data acquisition does not interfere significatively with the cell operation, and the measurement equipment is easily portable and inexpensive. The second model reproduces the cell dynamic behavior when the anode catalyst is poisoned by carbon monoxide. The relationship among the parameters of these equivalent-circuit models and PEMFC electrochemical parameters is stated.

## 1. Introduction

The performance of PEM fuel cells (PEMFC) is negatively affected by several physical–chemical phenomena that take place during the cell operation: anode catalyst poisoning by carbon monoxide [1,2], membrane humectation [3–5], cathode flooding [6,7], freezing [8], drying phenomena [9,7], absorption of contaminants into the membrane [10], etc.

Some of these physical–chemical phenomena can irreversibly degrade the cell performance (e.g., corrosion, membrane degradation due to mechanical phenomena or chemical contamination, and cell degradation produced by freezing). Studies of PEMFC durability include [11–15]. Other phenomena are reversible (e.g., the anode catalyst poisoning by carbon monoxide, the membrane drying and the cathode flooding), tending to accelerate the gradual degradation process of the cell performance.

The PEMFC diagnosis task addressed in this manuscript consists in estimating: a) the effect on the cell performance of the irreversible degradation processes; and b) the value of those PEMFC electrochemical parameters which are relevant to identify and to characterize the reversible processes that take place within the cell.

## 2. PEMFC performance degradation phenomena

The physical–chemical phenomena that negatively affect the PEMFC performance can be classified according to their time scale. Most relevant short-time-scale phenomena (minutes–hours) include the cathode flooding, the membrane drying, the anode catalyst poisoning by carbon monoxide and the absorption of contaminants into the membrane. Long-time-scale

---

* *Corresponding author.*
E-mail addresses: marubio@dia.uned.es (M.A. Rubio), aurquia@dia.uned.es (A. Urquia), sdormido@dia.uned.es (S. Dormido).

0360-3199/$ – see front matter © 2009 Professor T. Nejat Veziroglu. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.ijhydene.2009.03.054

phenomena (hours–days–years) are chemical processes with a slow reaction rate, such as the membrane degradation and the corrosion of the electrical conducting parts. On the other hand, mechanical phenomena including membrane breakage, fluid leak within the fuel cell and stack structure deformation, produce immediate degradation of the cell performance.

The relative increment over time of the PEMFC internal resistance ($\Delta R$) due to different performance degradation phenomena is shown in Fig. 1. The experimental data has been extracted from the bibliography. The relative increment of the cell internal resistance has been calculated from Eq. (1), where $R_0$ is the initial value of the cell internal resistance. The internal resistance ($R$) of the cell is calculated from Eq. (2), where $V_{OC}$ is the open-circuit voltage of the cell, and $V$ and $I$ are the cell voltage and current, respectively.

$$\Delta R = 100 \cdot \frac{R - R_0}{R_0} \tag{1}$$

$$R = \frac{V_{OC} - V}{I} \tag{2}$$

Data from nine experimental studies is represented in Fig. 1: (1) cell under dehydration, constant current density: 0.1 A $cm^{-2}$ [16]; (2) cell under dehydration at 70 °C, constant current density: 0.180 A $cm^{-2}$ [17]; (3) cathode flooding, constant current density: 0.470 A $cm^{-2}$ [7]; (4) anode catalyst poisoning by carbon monoxide: 100 ppm of CO in $H_2$ at 80 °C, constant cell voltage: 700 mV; (5) cathode flooding, cell surface: 25 $cm^2$, load: 66 mΩ [6]; (6) hydrogen crossover due to the MEA degradation [15]; (7) constant current density: 0.300 A $cm^{-2}$, cell voltage decrement as a result of the cell degradation: 20 $\mu V h^{-1}$ [12]; (8) constant current density: 0.400 A $cm^{-2}$ [18], linear cell voltage decrement as a result of the cell degradation; and (9) constant current density: 0.500 A $cm^{-2}$, cell voltage decrement as a result of the cell degradation: 0.5 $\mu V h^{-1}$ [11].

The reversible and irreversible degradation phenomena considered in Fig. 1 exhibit clearly differentiated time scales. The time scale of the reversible phenomena is below $10^5$ s, whereas the time scale of the irreversible phenomena is above $10^6$ s. On the other hand, the increment over time of the cell resistance ($\Omega s^{-1}$) due to the irreversible degradation phenomena can be considered a constant for each type of cell.

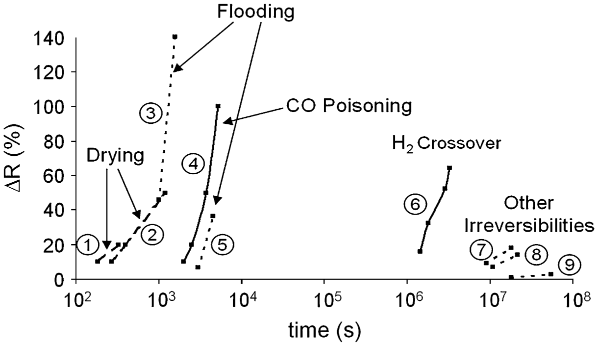


**Fig. 1 – The relative increment over time of the PEMFC internal resistance due to different performance degradation phenomena.**

## 3. Operating point

The value of the cell electrochemical parameters is strongly dependent of the voltage–current operating point. As a consequence, the cell nominal operating curves need to be known in order to perform the cell diagnosis.

In order to illustrate this dependence, the I–V curves corresponding to three different stages of the cathode flooding process are shown in Fig. 2a. These curves have been calculated simulating the operation of a 25 $cm^2$ PEMFC. The model has been composed using the *FuelCell*Lib Modelica library [19] and it has been simulated using the Dymola modeling environment. The corresponding internal resistance, calculated from Eq. (2), is plotted in Fig. 2b. The internal resistance, and consequently the electrochemical parameters, depends strongly on the current for a certain stage of the cathode flooding. The impedance spectrum and the internal resistance curve intersect when the frequency tends to zero (see Fig. 2c).

## 4. Diagnosis procedure

The PEMFC internal resistance increases approximately at constant rate due to the irreversible degradation phenomena [12,18,11]. As a consequence, the contribution of the irreversible phenomena to the internal resistance can be modeled by means of a term proportional to the time. Once this model has been estimated for a particular type of cell, it allows decoupling the effect on the internal resistance of the reversible and irreversible degradation phenomena that take place simultaneously in the PEMFC.

Two equivalent-circuit models of the PEMFC are proposed in this section, and the relationships among the parameters of these models and the cell electrochemical parameters are stated. The first equivalent-circuit model allows reproducing the dynamic behavior of the cell under normal operation, and also under cathode flooding and membrane drying conditions. Once estimated from the experimental data, the value of the electrochemical parameters and their evolution over time allow determining whether any of these degradation processes is ongoing. The second model allows reproducing the cell dynamic behavior when the anode catalyst is poisoned by CO. Good fitness of the experimental data to this model indicates the occurrence of this kind of poisoning process.

### 4.1. *Normal operating conditions, cathode flooding and membrane drying*

The equivalent-circuit models of the cell impedance shown in Fig. 3a and b were proposed in [6]. The second one is obtained from the first one by approximating the Warburg impedance as described in Eq. (3). $R_1$, $R_2$, $C_1$ and $C_2$ are parameters whose value is estimated in [6]. Five electrochemical parameters intervene in the cell model shown in Fig. 3b: the diffusion resistance ($R_d$), the charge transfer resistance ($R_p$), the diffusion-related time constant ($\tau_d$), the membrane resistance ($R_m$) and the double layer capacitance ($C_{dl}$). This model is intended to reproduce the cell dynamic behavior under normal