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In situ activation procedures applied to a DMFC: Analysis and optimization study

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ABSTRACT

A direct methanol fuel cell (DMFC) needs to be activated to achieve its maximum performance. The activation procedure includes a pre-treatment and an in situ activation procedure. Along the activation procedure the membrane electrode assembly (MEA) experiments significant changes that are studied by electrochemical impedance spectroscopy (EIS), polarization curves and methanol crossover measurements. It is shown that the activation procedure makes the proton conductivity of the PEM to increase as well as the catalyst area and activity. The DMFC power density increases from 8.8 mW cm^{-2} to 22.4 mW cm^{-2} at 55 °C along the activation procedure. The Design of Experiments (DoE) methodology was then applied to optimize the in situ activation, where loading cycles were employed. The factors considered for the experimental design were the temperature, the loading and the cathode air pressure. The maximum power density response was optimized using a central composite design (CCD). It was also verified that the potential was the most significant factor. Finally, the in situ loading cycles procedure was critically compared with other in situ activation procedures reported in the literature. It was concluded that the hydrogen conditioning and the in situ loading cycles procedure led to the best performance of the DMFC.

1. Introduction

Due to their near zero pollutants emission and potentially high energy efficiencies, polymer electrolyte fuel cells (PEFCs) are growing of interest, assuming a crucial role on the research and development of new energy production systems [1]. In particular, direct methanol fuel cells (DMFCs) are promising candidates for portable power applications because they do not require fuel processing and allow simple and compact designs [2]. Although, DMFCs are being deeply studied, challenging issues still to overcome, such as the most effective procedures for starting-up or restarting DMFCs – the so-called activation procedures.

Whenever a membrane electrode assembly (MEA) is inserted in a DMFC, it does not reach the best performance immediately after starting up. It is well known that DMFCs undergo a gradual increase in performance before reaching a stabilized power density output [3]; the MEA needs to be activated. Activation procedures can be understood as all the actions that can bring the MEA to its highest and stabilized performance. In this study we distinguish between pre-treatment and in situ activation procedures. Pre-treatment procedures include all actions carried over a fresh MEA, including the proton exchange membrane (PEM) and electrodes, while in situ activation procedures are actions used to improve the performance of a MEA when the fuel cell is on a working state.

Activation procedures can be applied during the start-up or after resting periods (restarting) and are common to both hydrogen and methanol fuel cells [4,5]. Regarding pre-treatment procedures, several approaches are discussed in the literature [3,6–9]; Kho et al. [3] proposed that the MEA should either be immersed in water or methanol aqueous solution for hours prior to use. These authors claim that a significant increase on the DMFC performance is observed due to the attainment of higher levels of hydration, both in the membrane and in the electrodes. Silva et al. [6] observed a considerable increase on the PEM proton conductivity and DMFC performance when the PEM is boiled in water during 1 h. Other studies indicate that higher levels of hydration are achieved when immersing the MEA in ethanol, ethanol aqueous solutions or even in aqueous solutions of diluted sulfuric acid at elevated temperatures [7–9].

In situ conditioning procedures are also reported, namely the so-called hydrogen evolution [10], where the air feed to the cathode is replaced by nitrogen, while pure hydrogen is fed to the anode. It seems that forcing hydrogen to cross the membrane with the help of an external power source leads to possible structural changes in the catalyst layer, namely in porosity and tortuosity. The same authors reported other two procedures to enhance and accelerate the PEMFC start-up. One method refers the exposing of the MEA to elevated conditions of temperature and pressure. It

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is claimed that the resistances of both membrane and catalyst are reduced and that the effect is long-lasting [9]. Another approach considers submitting the catalyst surface to a CO poisoning and subsequence CO oxidation. It seems that this procedure increases the electrode active surface area [11]. Sometimes, DMFC anodes are activated running the cell under H_2/O_2 prior to the use. It is believed that this activation procedure is speeded up due to the high current densities obtained [12]. Indeed, the easiest way to activate a MEA should be based on the application of loading periods [12,13], using either hydrogen or methanol as a fuel. Rice et al. [14] presented a different approach named current conditioning. The current conditioning procedure considers the operation of the MEA with a current of polarity opposite to the normal use. This leads to an electrochemical generation of hydrogen at the PtRu electrocatalyst, reducing the surface oxides that might exist there.

This paper analyzes the behavior of a MEA (DMFC) along an activation procedure aiming to understand how this activation affects the PEM and the catalyst. The activation procedure comprehends six in situ loading cycles. The polarization curve, the impedance spectrum and the methanol crossover measurement were obtained along the activation loading cycles.

The effect of the temperature, load and pressure along the activation procedure is also studied using a design of experiments. Later, the pre-treatment and activation procedure based on loading cycles was compared with other known procedures, such as the anode hydrogen conditioning and the hot-methanol conditioning.

2. Experimental

2.1. MEA pre-treatment

In this work it was used a PEM of Nafion 112. This membrane was boiled during 1 h before being assembled and used in the fuel cell, in order to improve its protonic conductivity. The backing and catalyst layers were also boiled during 1 h for improving the catalyst performance.

2.2. MEA activation protocol

The MEA activation protocol consists in submitting it to six loading cycles at 55 °C, interrupted by a set of electrochemical measurements. These measurements are the polarization curve, impedance vs dynamic hydrogen electrode (DHE) at 300 mV and methanol crossover. It was allowed the MEA to rest at open circuit for 30 min before applying a new characterization technique.

Each loading cycle lasted 180 min at 200 mV. The activation procedure, including the open circuit periods, load periods and different electrochemical tests had lasted of ca. 30 h. It should be pointed out that during the electrochemical measurements the cell was also gradually activated.

2.3. Characterization methods

2.3.1. Methanol crossover measurements

The current density that results from the methanol that crosses the electrolyte, $I_{crossover}$, is intimately related with the anode mass-transport limiting current density, $I_{\lim}$, by the following equation [15]:

$$I_{crossover} = I_{OCV,crossover} \times \left(1 - \frac{I}{I_{\lim}}\right) \tag{1}$$

where $I_{OCV,crossover}$ is the methanol crossover current density at the *OCV* and *I* is the operation current density. As shown by this equation, that assumes a direct relation between the actual current and the methanol crossover, the parasitic current density due to the methanol crossover at any current value is obtained evaluating the parasitic current density at open circuit voltage and the limiting current density. To evaluate the parasitic current density at open circuit, the DMFC cell was operated with a methanol aqueous solution (12 mL min^{-1} at 55 °C, 1.5 M and 2.5 bar) at the anode side and with hydrogen on the cathode chamber (200 mL_N min^{-1} at 55 °C and 2.5 bar). Scans were performed at a scan rate of 3 mA s^{-1} between 0 and 0.8 V vs the reference electrode, in the galvanostatic mode. Finally, the limiting current density was obtained measuring the polarization curves to 0 V.

2.3.2. Electrochemical impedance spectroscopy

Impedance spectra were obtained operating the DMFC cell with a methanol aqueous solution (12 mL min^{-1} at 55 °C, 1.5 M and 2.5 bar) at the anode side and a dry hydrogen stream (200 mL_N min^{-1} at 55 °C and 2.5 bar) on the cathode chamber. The cathode side worked as a dynamic hydrogen electrode (DHE) and the applied voltage was 300 mV between the anode and the cathode. In this way, only the anode impedance behavior was studied. The electrochemical impedance measurements were performed using a Zahner IM6e workstation coupled with a potentiostat (PP-240, Zahner). Impedance spectra were also recorded at ten points per decade by superimposing a 5 mV ac signal over the frequency range from 100 kHz to 10 mHz.

2.3.3. DMFC tests

The studied MEA was prepared by hot pressing the membrane sample, Nafion 112 from GEFC, between two ElectroChem electrodes at 90 °C and 150 bar for 150 s. Supported PtRu (1 mg cm^{-2} and 1:1 molar ratio) and Pt (0.5 mg cm^{-2}) were used on the anode and cathode, respectively. Single cell measurements were performed in a 25 cm^2 effective area cell. The DMFC was operated with a methanol aqueous solution (backpressure of 2.5 bar, 12 mL min^{-1}, 1.5 M) at the anode side and with humidified air (backpressure of 2.5 bar, 1000 mL_N min^{-1}, 100% relative humidity) at the cathode side. The cell temperature was maintained at 55 °C.

2.4. Design of experiments applied to the in situ activation procedure

To evaluate the DMFC response along the in situ activation procedure, it was followed a DoE approach and selected a simple central composite design with three factors with axial values in orthogonal positions. It was used a commercial software (JMP 7.0 from SAS) that indicated 17 experiments. Temperature, loading and cathode air pressure were selected as input factors and the maximum power density as the response. All other operating conditions were kept constant (a methanol aqueous solution at 12 mL min^{-1} and 1.5 M at the anode side and humidified air at 1000 mL min^{-1} and 100% relative humidity at the cathode side). Each parameter range was selected taking into account the normal operating conditions associated to low–medium temperature DMFC operation but also to previous screening experiments where only one parameter was varied (data not shown). The ranges of the parameters given are in Table 1.

3. Discussion and results

3.1. Polarization and power curves

The activation procedure described in the experimental section was applied at 55 °C comprehending a set of six loading cycles performed at 200 mV.

Fig. 1 plots the potential (a) and power density (b) as a function of the current density and the activation cycle. It can be seen that