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Investigation of the difference between the low frequency limit of the impedance spectrum and the slope of the polarization curve

M. Chandesris[a,*], C. Robin[a,b,d], M. Gerard[a], Y. Bultel[b,c]

[a] Univ. Grenoble Alpes, CEA, LITEN, F-38054 Grenoble, France
[b] Univ. Grenoble Alpes, LEPMI, F-38000 Grenoble, France
[c] CNRS, LEPMI, F-38000 Grenoble, France
[d] Zodiac Aerospace, F-78370 Plaisir, France

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ABSTRACT

Analysis of both polarization curve and Electrochemical Impedance Spectroscopy (EIS) provides meaningful information about the electrochemical behavior of Proton Exchange Membrane Fuel Cells (PEMFC). Nevertheless, the interpretation of the electrochemical responses remains complex without the use of physics-based models. This paper investigates the experimentally observed and unexpected difference between the low frequency resistance of a cell and the slope of the polarization curve. A 0D stirred tank model is proposed to analyze the experimental data and a simple relation is obtained linking the two resistances difference with the air stoichiometry. Furthermore, it is shown that, until moderate current densities, the low frequency loop of the impedance spectra can be associated to oxygen transport limitation due to convective oxygen supply along the channel, without having to resort to diffusion limitations. Finally, the equivalent electrical circuit (EEC) corresponding to this model is built as a tool to process results from other tests.

1. Introduction

Proton exchange membrane fuel cells (PEMFC) constitute a major alternative energy producing system which transforms chemical energy from oxygen and hydrogen to electricity and heat without combustion. The performance of these electrochemical power sources is determined by a complex combination of charge and mass transport, electrode kinetics and water balance. Several methods exist to study and diagnose these systems. Among different techniques, the polarization curve and Electrochemical Impedance Spectroscopy (EIS) are two of the most well-known characterization techniques.

The recording of polarization curves for various operating conditions is the most common method to discuss the performance of the cell. To get a polarization curve, the cell potential is plotted versus the cell current density and the performances of the cell are discussed for the various tested operating conditions. Compared to polarization curves, EIS has been demonstrated to be a powerful non-invasive in situ experimental technique that allows a deeper investigation of the complex processes occurring within thin porous coating electrodes and gas diffusion electrodes, both in half cell [1–8] and entire fuel cell [9–24]. By measuring the dynamic response of the fuel cell to a sinusoidal ac perturbation signal, EIS allows the discrimination of limiting processes having different time scales. As a consequence, EIS has been widely used to understand phenomena that occur within the membrane electrode assembly (MEA) such as the capacitance effect, the transfer resistances as well as gas supply from the channels to the catalyst particles. Nevertheless, the interpretation of EIS measurements remains difficult due to the overlap of processes with similar time scales and the complexity of the underlying physical phenomena.

The impedance spectrum of low temperature PEMFCs fed with air generally exhibits the behavior of a pure ohmic resistance at high frequency, followed by a high frequency loop which is commonly attributed to electrode processes: capacitive effects, electrode charge transfer kinetics and charge transport effects [3,7,11]. For PEMFCs fed with air, a second low frequency capacitance loop appears in the spectrum. The size of this low frequency arc increases with decreasing air stoichiometries [10]. Until recently, this second loop was mostly considered as resulting from oxygen transport limitations within the MEA [3]. The existence of another contribution to the impedance resulting from oxygen concentration oscillations along the air flow channels was not considered before the

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[*] Corresponding author. CEA, LITEN, 17 rue des martyrs, F-38054 Grenoble, France. Tel.: + 33 4 78 24 88; fax: +33 4 38 78 41 39.
E-mail address: marion.chandesris@cea.fr (M. Chandesris).

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Nomenclature

Symbol	
C_{dl}	Double layer capacitance ($F.cm^{-2}$)
C_{O_2}	Oxygen concentration ($mol.m^{-3}$)
e_M	Thickness of the membrane (m)
E_{rev}	Reversible potential (V)
f	Frequency (Hz)
F	Faraday's constant ($C.mol^{-1}$)
I	Total current of the cell (A)
j	Total current density ($A.m^{-2}$)
j_F	Faradic current density ($A.m^{-2}$)
P	Gas pressure (Pa)
Q	Air flow rate ($m^3.s^{-1}$)
R	Perfect gas constant ($J.K^{-1}.mol^{-1}$)
RH	Relative humidity (%)
R_{ohm}	Ohmic resistance ($\Omega.cm^2$)
R_{ct}	Charge transfer resistance ($\Omega.cm^2$)
R_{lf}	Low frequency resistance ($\Omega.cm^2$)
S_e	Surface of the electrode (m^2)
St_{O_2}	Oxygen stoichiometric coefficient (.)
T	Temperature of the cell (K)
U	Cell voltage (V)
V	Volume of the cathode channels (m^3)
x_{O_2}	Oxygen fraction on dry air (.)
κ	Ionic conductivity of the membrane ($S.m^{-1}$)
Ω	Pulsation (rad)

experimental work of Schneider et al. [25,26]. They experimentally prove that the amplitude of oxygen concentration oscillation created as a consequence of the ac current at the air electrode is not zero at the channel/GDL interface and extends into the gas channels. This phenomenon is particularly significant for low oxygen stoichiometries and at the lowest frequencies.

The dependence of the second low frequency loop on the air stoichiometry implies that the low frequency resistance of the cell, R_{lf}, defined as the intercept of the cell spectra with the real axis at low frequencies, strongly increases as the air stoichiometry decreases. However, this strong dependence on the air stoichiometry is not always observed on the direct current resistance, R_{DC}, obtained from the slope of the polarization curve. As the impedance is intrinsic to the cell, at least for low amplitude of the ac measuring signal, the low frequency resistance, which corresponds to the impedance when the frequency tends to the zero, should be equal to the direct current resistance. This is not coherent with experimental observations that one resistance depend on the air stoichiometry, R_{lf}, but not the other one, R_{DC}. Nevertheless, as analytically shown by Maranzana et al. [27], a bias can be observed between these two resistances when the operating conditions of the EIS do not converge to the steady state solutions of the polarization curves as the frequency tends to zero. At the same time, Schneider et al. [25] and Freunberger et al. [28] did not seem to observe a difference between these two resistances. They obtained a good correspondence between the local low frequency resistance and the local direct current resistance for their segmented cell.

If one wants to extract physical properties of the PEM fuel cells using both polarization curves and EIS, a deeper understanding of the difference between these two resistances is crucial. As we will show in this paper, when diffusion effects can be neglected, this difference i) is null when the polarization curves are performed under constant air flow rate and ii) can be related to the oxygen variation with current in the cathode compartment when the polarization curves are performed at constant air stoichiometries.

In this work, we investigate the difference between the low frequency resistance and the direct current resistance of a PEM fuel cell for different air stoichiometries. First, this difference is characterized experimentally on a 8-cell stack. Then, a general analysis of the difference between the two resistances is given in the third section. This general analysis is illustrated using a stirred tank reactor model which allows determining analytically both the electrochemical impedance and the direct current resistance. From this 0D model, a simple relation is given between the two resistances difference and the air stoichiometry. Finally, modeling and experimental results are compared and discussed in the last section.

2. Experimental

2.1. Experimental setup and configuration

An 8-cell stack has been assembled to measure electrochemical impedance spectra (EIS) and polarization curves (V-I curves) for different air stoichiometries. The properties of the Membrane-Electrode Assemblies (MEAs) used in this test are listed in Table 1. Although these MEAs are typical for an operation with reformate H_2, the stack in this test is fed with pure H_2 at the anode and air at the cathode. The MEAs area is 220 cm^2. The bipolar plates are in steel 316L and stamped to get a serpentine flow field. The stack has been run during the whole test with fixed operating conditions: Temperature: 353K, anode and cathode pressure: 1.5bar, anode and cathode relative humidity: 50%, hydrogen stoichiometry: 1.5; except for the air stoichiometry. Four different stoichiometries have been tested successively: St_{O_2} = 1.2, 1.5, 2.0 and 3.0. These stoichiometry values are set and each one of them, together with the desired current value, defines the air flow rate at the inlet according to Faraday's law.

The V-I curves are recorded using current stepwise increment of 0.05 $A.cm^{-2}$ and each current step is held during 2 minutes before measuring the voltage. The electrical load device is a commercial one from TDI Power (product reference Dynaload XBL 100-600-4000) and it has an accuracy of 0.01 V and 0.01 A. The EIS are recorded for cells 3 and 6 at 0.4 $A.cm^{-2}$ and several amplitudes of the AC current (5%, 10%, 20%) are tested for each air stoichiometry. The frequency range during the EIS is 10 kHz to 0.05 Hz.

2.2. Experimental results

2.2.1. Influence of the air stoichiometry on the V-I curves

V-I curves for the different air stoichiometries (1.2, 1.5, 2.0, 3.0) are plotted Fig. 1 for cell 6. Performances are alike for the 4 air stoichiometries for low currents ($\leq$ 0.5 $A.cm^{-2}$). At higher currents though, the air stoichiometry impacts the average cell potential. The best performances are obtained for air stoichiometry values set to 1.5 and 2.0. Conversely, values set to 1.2 and 3.0 give the worst performances. For very high air stoichiometries like 3.0, high current values exacerbate drying phenomena which decreases the potential. On the opposite, for very low air stoichiometries like 1.2, the oxygen diffusion limitation is amplified at high currents (> 0.5 $A.cm^{-2}$), which decreases the performances of the fuel cell as well [7].

Table 1
Properties of the MEAs used for the 8-cell stack test

	Anode	Cathode	Membrane
Area (cm^2)	220	220	220
Type of catalyst	PtRu	PtCo	-
Catalyst loading ($mgPt/cm^2$)	0.520	0.4	-
Type of GDL	SGL 24BC	SGL 24BC	-
Type of membrane	-	-	Nafion@ HP, 20 μm