

**ASSESSING CELL POLARITY REVERSAL DEGRADATION
PHENOMENA IN PEM FUEL CELLS BY ELECTROCHEMICAL
IMPEDANCE SPECTROSCOPY**

M.A.Travassos¹, V.L.Lopes², A.Q.Novais², C.M. Rangel^{1*}

¹ Fuel Cells and Hydrogen Unit

² Energy Systems Modeling and Optimization Unit

LNEG, National Laboratory for Energy and Geology,

Estrada do Paço do Lumiar, 22, 1649-038 Lisboa, Portugal

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Abstract

The mechanisms of fuel cell degradation are multiple and not well understood. Irreversible changes in the kinetic and/or transport properties of the cell are fostered by thermal, chemical and mechanical issues which constrain stability, power and fuel cell lifetime. Within the *in-situ* diagnostics methods and tools available, *in-situ* electrochemical impedance spectroscopy (EIS) is within the most promising to better understand and categorize changes during fuel cell ageing.

In this work, the degradation phenomena caused by cell polarity reversal due to fuel starvation of an open cathode 16 MEA (membrane-electrode assembly) -low power PEM fuel cell (15 W nominal power) is reported using EIS as a base technique. A frequency response analyzer from Solartron Model 1250 was used connected to an electrochemical interface also from Solartron, Model 1286. The range of covered frequencies spans from 37000 Hz to 0.01Hz. Hydrogen is supplied from a metallic hydride small reactor with a capacity of 50 NL H₂ at a pressure of 0.2 bar.

Measuring the potential of individual cells, while the fuel cell is on load, was found instrumental in assessing the “state of health” of cells at fixed current. Location of affected cells, those farthest away from hydrogen entry in the stack, was revealed by the very low or even negative potential values. EIS spectra were taken at selected break-in periods during fuel cell functioning.

The analysis of impedance data is made using two different approaches: using an *a priori* equivalent circuit describing the transfer function of the system in question -equivalent circuit elements were evaluated by a complex non-linear least square (CNLS) fitting algorithm, and by calculating and analyzing the corresponding distribution of relaxation times (DRT) -avoiding the ambiguity of the *a priori* equivalent circuit and the need for provision of the initial fitting parameters.

A resistance and two RQ elements connected in series are identified as describing the impedance response of the cell during normal functioning. A constant phase element (CPE) was chosen to describe the impedance observed behavior. The quality of the fit was evaluated by analysis of the residuals between the fit result and the measured data at every single point. Consistency and quality of the impedance data were established by Kramers-Kronning validation.

With continuous operation, using a reduced hydrogen flow, an inversion of polarity was observed in the 16th cell of the stack, evident in the potential measurement of individual cells as a result of insufficient hydrogen to reach the last cells. EIS data analyses suggest that water electrolysis happens at the anode judging by the appearance of an intermediate semicircle associated to a marked change in resistance and capacitance values. The presence of an inductive loop at low frequencies is now evident, which cannot be explained by the relaxation of reaction intermediates involved in the oxygen reduction reaction [1]. It is to be noticed that when the incursion into the negative potential values is not too marked the phenomenon is partially reversible, so it is suggested that the relaxation is due to intermediates in the water electrolysis process. The anode potential rose to levels compatible with the oxidation of water. Once the phenomenon is made irreversible and when water is no longer available, oxidation of the carbon support is favored accelerating catalyst sintering. *Ex-situ* MEA cross section analysis, under a scanning electron microscope, confirmed it. Electrode thickness reduction and delamination of catalyst layers were observed as a result of reactions taking place during hydrogen starvation. Carbon corrosion and membrane degradation are analyzed, according to evidence by SEM.

[1] S.K. Roy, M.E. Orazem, B. Tribollet, "Interpretation of Low Frequency Inductive Loops in PEM Fuel Cells", J. Electrochem. Soc., 152(12) B1478-1378 (2007).