Start-up/shut-down model for Polymer Electrolyte Membrane Fuel Cell

G. Maranzana[a,b], A. Lamibrac[a,b], J. Dillet[a,b], S. Didierjean[a,b], O. Lottin[a,b]

[a] **LEMTA, Université de Lorraine**
Vandoeuvre-lès-Nancy, France

[b] **LEMTA, CNRS**
Vandoeuvre-lès-Nancy, France

During the start-up of a PEMFC, the anode compartment is divided momentarily into an upstream part occupied by fresh hydrogen and a downstream part filled with the gas which was used to flush the anode: air or nitrogen. The boundary between the downstream and the upstream parts moves from the inlet to the outlet of the anode compartment with a velocity that is governed by the hydrogen flow rate. Start-ups occur generally under OCV conditions so that positive and negative internal currents appear between the anode and the cathode, which can be observed thanks to segmented cells [1]. The origin of these currents was attributed to the double layer capacitances charge (or discharge) and to faradic reactions. In the inlet (active) part of the cell, hydrogen is oxidized at the anode and oxygen is reduced at the cathode. However, the outlet (passive) part the cell -not yet filled with hydrogen in the anode compartment- is subjected to reverse currents: some species are oxidized at the cathode whereas others are reduced at the anode. These reactions are responsible from cathode degradation mechanisms including carbon and catalyst oxidation.

To better understand these degradations and in an attempt to quantify them, a model was built. It is based on a 1D generic electrode model that is combined in slices to constitute the cell as shown in figure 1.

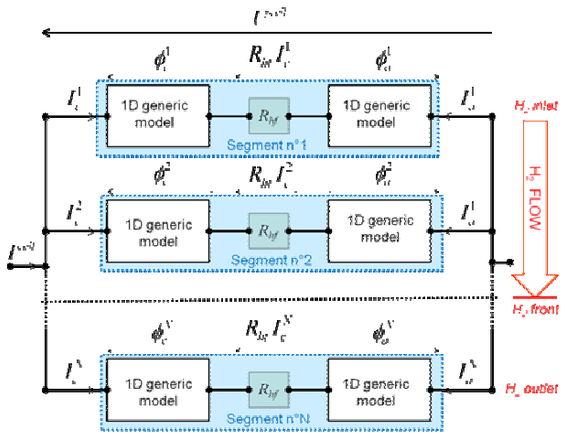

Figure 1: model for the study of start-up. N segments are considered between hydrogen inlet and outlet. Each local electrode (anode or cathode) is treated as the same 1D generic model.

For the generic electrode model, capacitive currents and several faradic contributions were considered in parallel, as shown in figure 2. As shown on figure 2, two kinds of platinum atoms were considered: platinum on the surface Pt_s and on the sub-layer Pt_b. The platinum oxidation kinetic law was adapted from the model of Darling and Meyers [2]. Transient mass transfer was solved considering oxygen, hydrogen and water diffusion through the GDLs and the membrane. Nevertheless, for the sake of simplicity, the GDLs were assumed purely resistive for mass transfer without any storage effect. Mass transfer and kinetic parameters were fitted thanks to polarization curves, cyclic voltamograms and CO_2 emissions. Once 1D generic models were combined, start ups and shut-downs could be simulated by as a function of the gas concentration variation along the channels. This yields internal currents profiles shown in figure 3 that correspond well to the experimental ones. This model can also predict the CO_2 emissions during start-ups or shut-downs. It can be used to test different oxidation mitigation strategies load connection, drying up, or the use of catalysts limiting oxygen reduction at the anode or enhancing water splitting at the cathode. Oxygen and hydrogen permeation of the membrane are also important factors to consider.

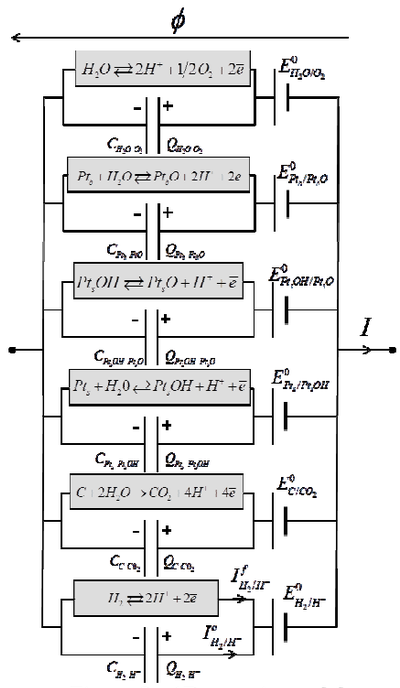

Figure 2 : 1D generic model

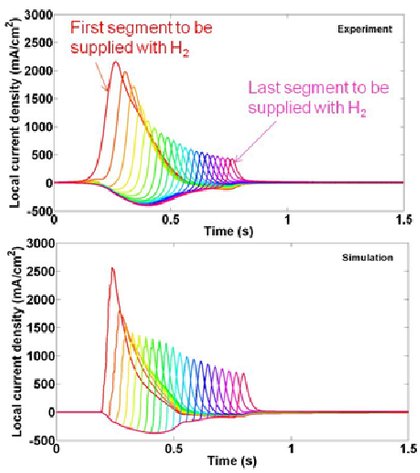

Figure 3. Experimental and numerical internal currents during a start-up by injection of hydrogen in air.

References:

1. A. Lamibrac et al., Journal of Power Sources, Vol. 196, N°22, pp. 9451-9458, 2011.

2. R. M. Darling et al., J. Electrochem. Soc., vol. 150, no 11, p. A1523, 2003