Modeling Chemical Degradation of a Polymer Electrolyte Membrane and its Impact on Fuel Cell Performance

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Materials durability in state-of-the-art polymer electrolyte membrane fuel cells (PEMFC) is one of the main shortcomings limiting the large-scale development and commercialization of this zero-emission power technology. Typical PEMFC lifetime is only around 300-500 hours under some severe operating conditions representative of automotive applications [1]. Part of the loss of performance is due to a severe electrochemical degradation of the perfluorosulfonated polymer electrolyte membrane (PEM). The origin of these degradation phenomena is partly known and described in the literature [2], but still not on a way which allows predicting the associated impact on the temporal evolution (degradation) of the cell potential.

Despite numerous previous experimental works on the impact of specific PEMFC operation conditions on PEM degradation [3-4], only few modeling work predicting the evolution of the PEM transport properties and addressing the transient behavior of the PEM degradation mechanisms in interaction with other physicochemical aging phenomena have been reported [5].

Franco *et al.* recently proposed a multi-scale modeling framework of PEMFC electrochemical processes [6-8] that allows to understand the detailed mechanisms underlying the PEM degradation under automotive operating conditions. This approach scales up *ab initio* concepts into an elementary kinetic model accounting for: (i) the MEA physicochemistry at the spatial nanoscale (detailed HOR and ORR electrocatalysis, steric and electrochemical double layer effects) and microscale (ionic and reactants transfers), (ii) the intrinsic MEA nanomaterials degradation (e.g. catalyst oxidation/dissolution/ripening, carbon support corrosion, metallic ions migration and catalyst contamination by external impurities).

In this paper a microstructurally resolved model of the PEM degradation is developed, linking the elementary kinetic processes of PEM electrochemical aging with the microstructural evolution (pore size distribution, ionomer chains lengths…) and the evolution of the local physical properties ($H_2/O_2/N_2$ permeation, water diffusivity, proton conductivity).

The microstructure of the PEM is modeled as a time-variant multi-fractal object (Fig. 1). A first fractal dimension captures the micro-channels distribution and a second one, along the PEM thickness and associated to a twirled fractal object (like DNA), captures the channels shape distribution (local tortuosity).

The electrochemical degradation of the PEM is modeled on the basis of an elementary kinetic data (radical production through Fenton's reaction, radical initiation and propagation [9]).

On the basis of finite-element simulations, this model accounts for spatially-resolved transport of protons, water, H_2, O_2, OH, O_2H, H_2O_2 as well as PEM degradation products.

The developed PEM model is coupled with Franco *et al.* electrode models [5-8], allowing to account for catalyst and carbon support degradation within the electrodes. By accounting for the numerical feedback between the calculated instantaneous local conditions (species concentrations etc.) and the degradation phenomena, the model allows predicting the evolution of the PEM aging and its transient impact on the MEA performance degradation (cell potential evolution). Simulations of the transient behavior of the experimental observables (e.g., electrode potential as function of demanded current) have been carried out and compared to dedicated experiments, including Fluorid Emission Rate (FER) measurements, for different operating conditions (OCV, power-cycled, stationary). As an example, Fig. 2 shows the simulated evolution of current-voltage curves for different simulated operation times. It is clearly seen that over time the fuel cell performance cell decreases, in particularly for high current densities. This is due to the decrease of PEM proton conductivity and the increase of the gas permeation coefficients.

In addition, we discuss a general sensitivity study of the PEM degradation to its initial microstructural properties, which can be useful information towards the PEM durability improvement.

REFERENCES

[1] S. Escribano et al, in *Proc. of the16th World Hydrogen Energy Conference*, Paper no. S19–583 (2006).
[2] V.O. Mittal et al, *J. Electrochem. Soc.* **154**, B652 (2007).
[3] T. Xie, C.A. Hayden, *Polymer*, **48**, 5497 (2007).
[4] C. Chen, T.F. Fuller, *ECS Trans.*, **11** (1) 1127 (2007).
[5] A.A. Franco, S. Escribano, O. Lemaire, oral comm. in *215th ECS meeting*, San Francisco (2009).
[6] A.A. Franco et al, *Fuel Cells*, **7**, 99 (2007).
[7] A.A. Franco, M. Gerard, *J. Electrochem. Soc.* **155**, B367 (2008).
[8] A.A. Franco, M. Tembely, *J. Electrochem. Soc.,* **154**, B712 (2007).
[9] T.Xie, and C.A. Hayden, *Polymer,* **48**, 5497 (2007).
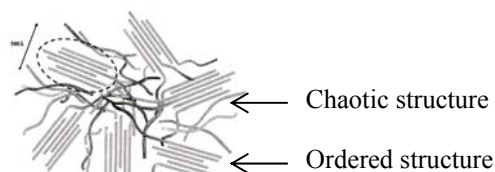[10] L. Rubatat, G. Gebel and O. Diat, *Macromolecules*, **37**, 7772 (2004)

Chaotic structure

Ordered structure

Figure 1: Schematic view of correlated polymeric aggregates domains [10]

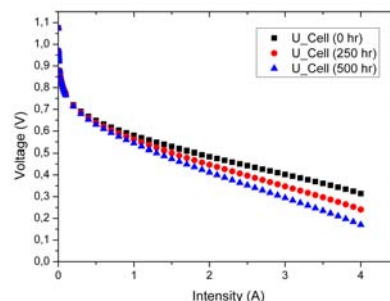**Figure 2:** Calculated potential over current density at the following conditions: T_{cell} = 80 °C, P_{in} = 150 kPa$_{abs}$ (An/Ca). Simulated MEA with a PFSA membrane (initial thickness 25 µm), electrode with 40 % Pt/Vulcan catalyst at 0.1 mg$_{Pt}$/cm² loading on anode and at 0.3 mg$_{Pt}$/ cm² loading on cathode.