

Mutistability, Nonlinear Transients and Propagation of Current in Self-Humidified Polymer Electrolyte Membrane Fuel Cells

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Introduction

In a world of ever-increasing consumption of oil, the atmospheric pollution and the finiteness of fossil energy resources have recently become major concerns. This situation has triggered an increasing interest toward the development of alternative, reliable and non-polluting power sources. Among these, *fuel cells* appear nowadays as one of the most realistic and feasible solutions. They are very efficient devices, capable of delivering important amounts of energy, and are in addition usually environment-friendly. In particular, polymer electrolyte membrane (PEM) fuel cells based on the $H_2 + O_2$ reaction are seen as the most adequate power source for mobile applications. Because they could be submitted to changes in the environment or the operating parameters, understanding the dynamic response of these devices is of great importance. Note that despite their potential importance time-dependent models for fuel cells are rare in the literature, as the focus is usually placed on steady state properties. In this view, we have recently developed an experimental and theoretical program whose objectives are to understand, model and control the dynamics of such cells.

Experimental Results

Our studies revealed many complex nonlinear kinetic features during cell operation, in particular, when PEM fuel cells are operated in the *autohumidified* mode, i.e. using dry feeds - which is interesting among others because water reservoirs and injection systems are then not needed. These systems display steady state multiplicity in the current and spatio-temporal ignition and extinction phenomena during the startup and shutdown of the cell, respectively. Using a segmented anode fuel cell (see Figure 1), ignition and subsequent spatial propagation of current could be observed (Figures 2a-b). Two types of spatial propagation are found, depending on whether the reactants are injected as co-current or counter-current flows.

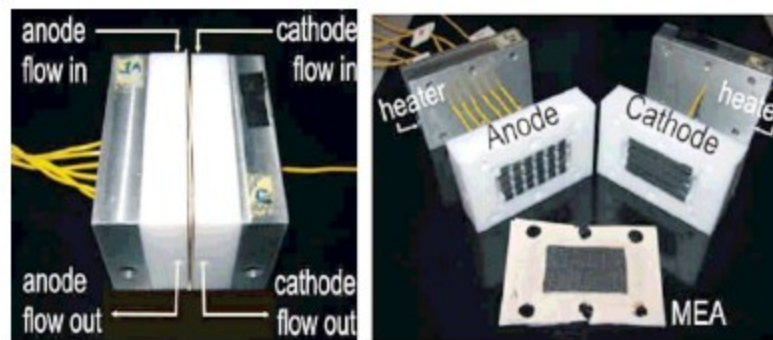


Figure 1: The segmented anode fuel cell. The anode electrode was broken into six individual elements separated by Teflon spacers. Current through each element was measured independently. A membrane-electrode-assembly employing 2 ETEK electrodes with carbon supported Pt catalyst and a Nafion 115 membrane was placed between anode and cathode.

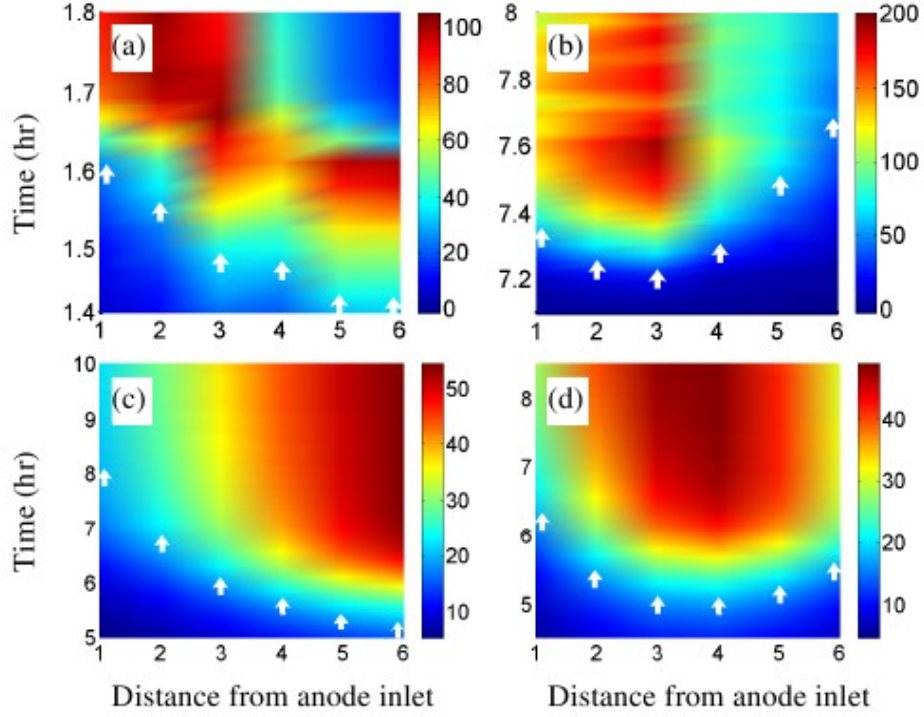


Figure 2: A comparison of the experimental and computed currents for co-current and counter-current flow of hydrogen and oxygen in a segmented anode PEM fuel cell. The color scale is for current through each anode segment in mA. (a) experimental co-current (b) experimental counter-current (c) computed co-current (d) computed counter-current..

Model

These transient dynamics are intensely nonlinear due to a positive feedback loop: we recently demonstrated that water generated in a polymer electrolyte membrane (PEM) fuel cell *increases* proton transport exponentially, which “ignites” the current. We have been able to capture the basic physics of ignition dynamics and front propagation for the segmented anode fuel cell with a simple differential PEM fuel cell model and its extension to a series of differential elements. The water balance in each segment of the membrane is given by Eq. (1) for membrane water activity ($j=1$ to 6 ; $j=0$ is the feed and $a_w(7)=0$); the inventory is balanced respectively by water produced ($1/2$ the proton current), water convected in the gas flow, and longitudinal water diffusion. Eq. (2) is an empirical fit to the number of water molecules associated with each sulfonic acid group as a function of water activity in a Nafion 115 membrane.

$$\left[N_{SO_3} \frac{d\lambda(j)}{da_w(j)} + (V_A + V_C) \frac{P_w^0}{RT} \right] \dot{a}_w(j) = \frac{i(j)}{2\mathcal{F}} + [F_A(j-1) + F_C(j-1)] P_w(j-1) - [F_A(j) + F_C(j)] P_w(j) + k_m [a_w(j+1) + a_w(j-1) - 2a_w(j)] \quad (1)$$

$$\lambda(j) = 14.9 a_w(j) - 44.7 a_w^2(j) + 70 a_w^3(j) - 26.5 a_w^4(j) - 0.446 a_w^5(j) \quad (2)$$

We assume that the total gas pressure is fixed, and the local water activity in the membrane is in equilibrium with the local gas phase. The molar flow rates are given by $F_A(j)=F_A(j-1)-i(j)/4F$ and $F_C(j)=F_C(j-1)$ (F is Faraday's constant). Lastly, we assume the local potential between the anode and cathode is given by the thermodynamic potential - see Eq. (3). This neglects interfacial potential drops, which results in the predicted currents being about 20% larger than found in real fuel cells.

$$V_{FC}(j) = 1.23 - \frac{RT}{4\mathcal{F}} \ln \left[\frac{P_{\text{H}_2}^2(j) P_{\text{O}_2}(j)}{P_{\text{atm}}^3 a_w^2(j)} \right] \quad [V] \quad (3)$$

Based on the equivalent electrical circuit, the differential elements are electrically connected in parallel to each other. The voltage across the external load resistance thus depends on the total current produced by all elements; the local current is given by Eq. (4). The local membrane resistance, $R_M(j)$, depends of the local water content in the membrane. For a Nafion 115 membrane employed in this fuel cell the membrane resistance as a function of water activity is given by Eq. (5). The strongly autocatalytic behavior we mentioned earlier is here especially striking.

$$i(j) = \frac{V_{FC}(j) - R_L \sum_{k \neq j} i(k)}{R_M(j) + R_L} \quad [A] \quad (4)$$

$$R_M(j) = 5 \times 10^5 \exp(-14 a_w^{0.2}) \quad [\Omega] \quad (5)$$

The key features of the model are thus the water inventory in the polymer electrolyte, the transverse proton conductivity from the anode to the cathode and the longitudinal water transport through the membrane. The model captures the ignition and front propagation, though it predicts larger currents than observed experimentally. Figures 2c and 2d show the simulated current profiles for co-current and counter-current flow, respectively. Thanks to the simplicity of the model, we can show that the key elements that account for ignition are (1) the exponential dependence of proton conductivity in the PEM with membrane water content and (2) the dynamics of water uptake into the PEM. Another important conclusion concerns the location of ignition and front propagation, which following our model seem to be a consequence of (1) convection of water produced down stream and (2) diffusion of water upstream through the polymer membrane. We can also study in details how the ratio of the flow rates between the anode and cathode will shift the ignition point. Note that the model can capture the ignition and front propagation, but breaks down at longer times, when liquid water floods the gas diffusion layers and starts entering the flow channels.

Conclusions

We thus here demonstrate how the exponential increase in proton conductivity in polymer electrolyte membranes with water content can lead to ignition of the current in PEM fuel cells. Water can be injected to a fuel cell to ignite the current, just like a match can be struck to ignite a flame. The diffusion of water coupled with the exponential increase in proton conductivity produces current fronts that propagate along flow channels, just like flames propagate. The positive feedback loop between water production and increased proton conductivity of the electrolyte membrane in PEM fuel cells is in this view analogous to thermal ignition and flame propagation with exothermic chemical reactions, but "water fans the flame" in PEM fuel cells! We also show how front propagation depends on flow configurations creating different front ignition and propagation patterns. Understanding the parametric dependence and time scales of these phenomena is an important component of fuel cell design, non-steady state operation and control.