

Multistability, nonlinear response and wave propagation in self-humidified PEM fuel cells

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ABSTRACT

A simple tanks-in-series model is presented, which allows for the understanding of the basic physics behind complex spatiotemporal behaviors observed in self-humidified polymer electrolyte membrane (PEM) fuel cells. Our approach is focused on how the intrinsically nonlinear dynamics of water formation couples with water transport, leading to multistability, inhomogeneous steady state current profiles through the cell and other nonlinear phenomena. We show in particular how the operating parameters determine the location of high current spots and the subsequent propagation of current waves throughout the cell during the ignition procedure. We also reproduce and explain transient current increases seen during the extinction of the cell and the unusual aspect of the polarization curves. Implications for the efficiency of self-humidified PEM fuel cells are highlighted, and possible ways to improve their performances are discussed on these bases.

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1. Introduction

Fuel cells promise to be an efficient, realistic and reliable environment-friendly alternative to the traditional combustion engine (Martin, 2005; Fronk, 2005). The conversion of chemical into electrical energy in these devices does not suffer from the Carnot limitations associated with heat engines, so that fuel cells are typically capable of delivering energy with a high efficiency. Polymer electrolyte membrane (PEM) fuel cells, in which protons traverse a proton exchanging membrane separating the anode from the cathode, are seen as the most attractive solution for automotive transportation.

Fuel cells differ from the traditional batteries, in the sense that they are not closed systems but open ones, due to a constant exchange of reactants and products with the environment. They are, in effect, *chemical reactors* with the voltage associated with chemical potential difference across the electrolyte being the driving force for reaction, and the current being a measure of the reaction rate. Through the last several years we have been developing an experimental and theoretical program centered around a “reaction engineering” approach of simplified PEM fuel

cells based on the H_2/O_2 reaction. In the case of small self-humidified cells (dry feeds), which can be seen as stirred tank reactors (STRs), complex dynamical features were observed, including multistability, current ignition and extinction, etc. (Moxley et al., 2003; Chia et al., 2004). These phenomena could be traced back to the intrinsically autocatalytic character of such cells: water created by the reaction humidifies the PEM, which reduces its resistance with respect to proton conduction, which in turn increases the current flowing through the cell and hence the rate of H_2O formation (Benziger et al., 2004, 2005). This is remarkably analogous to the positive feedback occurring for exothermic chemical reactions in a STR (Luss, 1997; Marwaha and Luss, 2003; Marwaha et al., 2004).

In this work we focus on *spatially extended* PEM fuel cells. Indeed, we recently developed a modified cell with a segmented anode, allowing for the real-time monitoring of the current as a function of the distance from the gas inlets. As was reported earlier (Benziger et al., 2007b), we observed a wave-like propagation of the current throughout these “plug-flow”-like cells which can be thought of as analogous to propagating flames observed in combustion processes. It should be emphasized that Nazarov and Promislow (2006) had at this time presented numerical simulations showing front propagation and associated long time constants on the basis of some of our previous results, i.e. before we reported the existence of such waves. The simulated temporal response of the current, however, strongly differed qualitatively from our observations, and the reasons behind this discrepancy

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remain unclear. The complexity of this model also did not allow for a clear understanding of the main parameters governing the formation of these patterns. In order to clarify the origin of the observed waves, we proposed a simple, semi-quantitative model focusing on the basic physicochemical mechanism behind these phenomena (Benziger et al., 2007b). This study revealed the central role played by water formation and transport in the emergence and subsequent propagation of “wet spots” in the cell. Since then, more sophisticated models have been proposed for self-humidified PEM fuel cells (Hanke-Rauschenbach et al., 2008; Grötsch et al., 2008) but they mainly focus on current–voltage characteristics and bifurcation analysis of spatially lumped models.

In this work, we perform a systematic parametric study (bifurcation analysis) of our previously introduced, spatiotemporal model and compare the predictions made in different flow configurations with newly available experimental data on the shutdown dynamics and electrochemical properties of the cells (Benziger et al., 2007a). As will be shown, the simple model qualitatively reproduces the main features of the real system. The steady state global current and current profile through the cell, the spatiotemporal propagation of the reaction and the electrochemical properties of the cell (i – V curves) are predicted semi-quantitatively. Thanks to the simplicity of the model, an intuitive explanation can be given as to how and why the presence of current patterns could affect the efficiency and the dynamic response of self-humidified PEM fuel cells. We show in particular what parameters affect the time necessary to ignite or extinguish the cell, the location of current “hot spots” and their subsequent propagation. We also assess, on the basis of this model, the possibility to run the cell in “extreme” conditions, for example at relatively high temperatures.

The paper is organized as follows. We first briefly present the experimental setup allowing for the study of the spatiotemporal dynamics of our simplified PEM fuel cells. We then present and discuss the kinetic model that will form the theoretical basis of our investigation. In the following section we present the steady state properties of the model, along with the corresponding results from experiments. We also discuss the spatiotemporal behavior of the system under consideration, including the polarization curves (Section 5). In the last section, we discuss the potential implications of these specific kinetics for a fuel cell operating under realistic conditions, as well as its behavior under feedback control. We also point to possible experimental and theoretical extensions of this work.

2. Experiments

In order to relate our modelling/computational results with the physics of the problem, it makes sense to include here a brief description of the apparatus used in Benziger et al. (2007a, 2007b) which we are here trying to model. As illustrated in Fig. 1, the cell consists of two compartments or flow channels, the anode and the cathode, between which a membrane–electrode assembly is sandwiched (two ETEK electrodes with carbon supported Pt catalyst and a Nafion™ 115 membrane). Flow channels (1.6 mm wide \times 3.2 mm deep \times 75 mm long) were machined out of polycarbonate. At the cathode the channel was lined with a split stainless steel electrode along the length of the channel. The anode was lined with six split segmented electrodes. The reactant gases are dry hydrogen and oxygen, respectively, with inlet flow rates F_A and F_C maintained with mass flow controllers. Two types of setups will be considered in this work: in the *co-current* mode, hydrogen and oxygen flow in parallel and follow the same direction (vertically, from top to bottom); in the *counter-current*

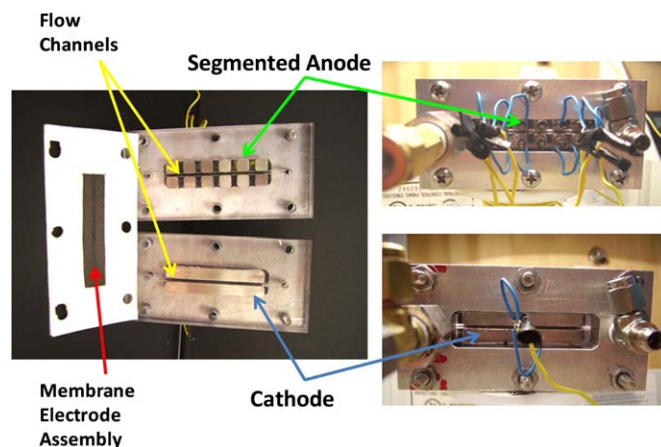


Fig. 1. A picture of the segmented anode fuel cell. The membrane electrode assembly consists of two ETEK electrodes with carbon supported Pt catalyst and a Nafion™ 115 membrane.

setup, the two reactants are flowing in anti-parallel directions: hydrogen flows up while oxygen flows down. These two configurations permit gravity to remove liquid water drops at the cathode; operation in horizontal configurations leads to very complex dynamical features, which were discussed in a previous publication but are beyond the scope of the present work (Kimball et al., 2008). The cell is kept at the desired operating temperature T through the use of two aluminium heating blocks.

The anode was broken in six equivalent segments separated by insulating spacers in order to record independently the current through each segment and the voltage drop across the external load resistor as a function of time (the lead wires from each anode segment being connected individually to a 0.1Ω sensing resistor). The reactor was designed with the lateral separation between anode segments more than 10 times larger than the transverse separation between the anode and cathode, so that the transverse current is large compared to the lateral currents. Each of these segments has a total area of 0.5 cm^2 . Note that the different segments are electrically connected *in parallel* with each other, as shown in the equivalent circuit (Fig. 2).

We will now turn to the simple physicochemical model we used to rationalize our results and compare its predictions with the actual experimental data.

3. The kinetic model

The basic mechanism of water formation in PEM fuel cells is now well understood. The H_2 molecules are adsorbed and dissociate at the anode, and the H atoms are subsequently oxidized to protons that are transferred to the PEM. At the level of the cathode, the O_2 molecules are adsorbed, they dissociate, and they subsequently react with the protons coming from the membrane to produce water. The electrons are transferred from the anode to the cathode through an external load resistance R_L . A voltage difference V_L is generated between the anode and cathode, which drives a current i reflecting the rate of water production. The membrane plays a central role in such a device, since protons must be transferred through it in order for the reaction to take place. As was mentioned, we use Nafion™ membranes, which are partially substituted perfluorosulfonic acid ionomers. The transport of protons in such polymers can be greatly enhanced by the presence of absorbed water, ionizing the sulfonic groups and thus allowing for a proton hopping mechanism between fixed ions. Because of this, the membrane resistance strongly depends on the

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