

The dynamic response of PEM fuel cells to changes in load

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Abstract

The dynamic response of the stirred tank reactor (STR) polymer electrolyte membrane (PEM) fuel cell has been explored over the temperature range of 35–105 °C. When the fuel cell was operated in the autohumidification mode the fuel cell current “ignited” when the membrane water content was greater than a critical level of $\sim 1.6 \text{ H}_2\text{O}/\text{SO}_3$, and it extinguished when the initial membrane water content was below this critical level. Above 70 °C, two stable “ignited” states were observed at intermediate load resistances; these steady states corresponded to different levels of membrane hydration. At low load resistances only a single ignited steady state was observed with high membrane hydration, and at high load resistances only a single ignited steady state was observed with intermediate membrane hydration. Hysteresis between the two ignited states was observed; the steady state selected depended on the initial conditions in the fuel cell. The time constant for the fuel cell current to reach steady state after a change in the load resistance was $\sim 10^3\text{--}10^4$ s. Below 70 °C only one “ignited” state and the extinguished state were observed in the autohumidification fuel cell. After 3000 h of operation the STR PEM fuel cell current and effluent relative humidities oscillated autonomously between two membrane hydration states with a period of oscillation of $\sim 10,000$ s. The oscillations showed abrupt transitions indicative of a capacitive switch. These complex dynamics of PEM fuel cell operation are associated with the membrane water uptake. It is hypothesized that water produced and swells the membrane, altering the interfacial membrane–electrode contact.

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1. Introduction

Polymer electrolyte membranes (PEM) mediate the transport of protons between the anode and cathode in PEM fuel cells. Membrane humidification is essential for ion transport in the fuel cell. If the membrane is not adequately humidified the proton conductivity is low and the power output from the fuel cell is limited. At the other extreme, too much water can flood the electrodes with liquid, hindering gas transport to the catalyst/membrane interface, also limiting the power output from the fuel cell. We previously reported the existence of a critical initial membrane water content capable of “igniting” a PEM fuel cell (Moxley et al., 2003). We demonstrated a positive feedback between water production

and membrane water activity that resulted in multiple steady states in the autohumidification PEM fuel cell.

The essential result from this previous work was that *the PEM is a reservoir for water, and the membrane resistance depends on the water inventory in the membrane*. Changes in the operating parameters of the PEM fuel cell, such as the external load resistance or the fuel cell temperature, alter the balance between water production and water removal, thereby changing the membrane water activity.

This paper reports dynamical results of the differential stirred tank reactor (STR) PEM fuel cell to changes in load and in temperature. This paper is organized as follows: the ignition phenomenon in a PEM fuel cell is reviewed as the starting point for studying dynamics. The dynamical responses to changes in external load resistance are reported, suggesting a coupling of the mechanical properties of the membrane to its chemical and transport properties. This coupling of mechanical and chemical properties gives rise to

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highly unusual responses, including the existence of 5 steady states in PEM fuel cells, and the occurrence of autonomous oscillations with extremely long periods, $\sim 10,000$ s. Lastly, we suggest how our observations may be employed to improve PEM fuel cell design.

2. Experimental

Experiments were carried out in a differential STR PEM fuel cell described elsewhere (Moxley et al., 2003; Benziger et al., 2004). The STR PEM fuel cell is a one-dimensional differential reactor where the only gradients are transverse, across the PEM. The fuel cell can be modeled as two well mixed reactors coupled through the PEM. The membrane-electrode-assembly (MEA) was pressed between two machined graphite plates and sealed with a silicon rubber gasket. Gas flow channels at the anode and cathode were replaced with plenums above the MEA. The plenums were open areas of about $1\text{ cm} \times 0.2\text{ cm}$ deep. There were pillars in the plenums to apply pressure more uniformly across the MEA. The active area of the MEA was $\sim 1\text{ cm}^2$. Hydrogen and oxygen were supplied from commercial cylinders (Airco) through mass flow controllers at flow rates, $Q \sim 1\text{--}10\text{ cm}^3/\text{min}$ (mL/min). The residence times of the reactants in the gas plenums ($V/Q = 1.2\text{--}12\text{ s}$) were greater than the characteristic diffusion time ($V^{2/3}/D = 0.3\text{--}1.0$), ensuring uniformity of the gas compositions at both the anode and cathode. The cell temperature was controlled by placing the graphite plates between aluminum plates fitted with cartridge heaters connected to a temperature controller. The entire fuel cell assembly was mounted inside an aluminum box to maintain temperature uniformity.

Gas pressure was maintained in the cell by placing spring loaded pressure relief valves (Swagelok) at the outlets. Tees were placed in the outlet lines with relative humidity sensors in the dead legs of the tees. The water content of the outlet streams was measured with humidity sensors (Honeywell HIH 3610), and the temperature at the humidity sensors was measured with a thermocouple in the gas line. At a flow rate of $10\text{ cm}^3/\text{min}$ the humidity sensor responded to changes in the humidity at the anode and cathode in $< 2\text{ s}$.

We report here results using an MEA consisting of a Nafion™ 115 membrane pressed between 2 E-tek electrodes (these consist of a carbon cloth coated on one side with a Pt/C catalyst). The catalyst weight loading at each electrode was $0.4\text{ mg-Pt}/\text{cm}^2$. Each electrode was brushed with solubilized Nafion solution to a loading of $\sim 4\text{ mg-Nafion}/\text{cm}^2$ before placing the membrane between them (Raistrick, 1989). The assembly was hot pressed at $130\text{ }^\circ\text{C}$ and 10 MPa . Copper foils were pressed against the graphite plates and copper wires were attached to connect them to the external load resistor.

The current and voltage across the load resistor were measured as the load resistance was varied. A 10-turn $0\text{--}20\text{ }\Omega$ potentiometer was varied to obtain a polarization curve (IV

curve). Current and voltage were both read out by a data acquisition board and stored by computer. For transient studies the current, voltage and relative humidity of the anode and cathode effluents were read out by computer and stored.

The STR PEM fuel cell was normally operated in the autohumidification mode; it performed continuously for hundreds of hours without attention. The data presented in this paper were obtained with three different MEAs. The first MEA was operated for a period of $\sim 2000\text{ h}$; the membrane failed after 2000 h and the open circuit voltage fell to zero. When the fuel cell was opened, a rip was found in the membrane along the sealing surface of the graphite plates. A second MEA was employed with the flow channel plate modified, so it had open plenums at the anode and cathode and no pillars to seal the MEA at the center. The initial performance of this MEA was similar to the first, but the fuel current density at the same operating conditions fell to 25% of the first MEA after 200 h . We replaced that MEA/flow channel plate assembly with a replica of the original design. The third MEA assembly was operated continuously for $\sim 12,000\text{ h}$. During the first 2000 h of operation the open circuit voltage was 0.92 V , comparable to the first MEA. The polarization curves taken with the first and third MEA were reproducible within 0.05 V .

The fuel cell was operated autonomously, without external control. The independent system parameters for the fuel cell are the feed flow rates, feed gas composition, fuel cell temperature and *external load resistance*. We present data with the external load resistance as the independent parameter. This is different from the traditional electrochemistry approach where PEM fuel cells are operated under galvanostatic or potentiostatic control (constant current or constant voltage). We wish to understand the *autonomous* operation of the PEM fuel cell; operation of the fuel cell under galvanostatic or potentiostatic control can distort the autonomous dynamics. The feed flow was also fixed and was not slaved to the current as is frequently done in fuel cell operation. Most experiments were carried out with a hydrogen flow rate of $10\text{ cm}^3/\text{min}$, which limited the current to $\sim 680\text{ mA}$. In most instances the currents in our experiments were $< 200\text{ mA}$.

In the results presented here we have limited ourselves to conditions where liquid water is not present in the fuel cell (relative humidity is kept below 100%). When liquid water condensed in the fuel cell, it operated irregularly. The gas flow would change erratically due to water droplets blocking the effluent. The irregular operation of the PEM fuel cell with liquid water formation is highly relevant to the fuel cell pathology, but it lies beyond the scope of this paper.

The dynamics of the STR PEM fuel cell are much simpler to analyze than experiments performed with a typical fuel cell test station. The STR PEM fuel cell is one-dimensional, so the current, voltage and membrane resistance are all spatially uniform. The water content only varies transverse to the membrane. All the system variables may be directly related to the anode and cathode effluent compositions. No

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