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Nonlinear analysis of voltage dynamics in a polymer electrolyte fuel cell due to two-phase channel flow

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HIGHLIGHTS

- Non-linear analysis of chaotic polymer electrolyte fuel cell voltage.
- Correlation dimension, Kolmogorov entropy, & Hurst and Lyapunov exponents.
- Non-linear statistic related to operating condition and two-phase flow regime.
- Computationally efficient reduced-order statistics identified.
- Future applications feedback for embedded fuel cell controllers.

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ABSTRACT

More efficient water management techniques are required to decrease the cost of polymer electrolyte fuel cell (PEFC) systems while maintaining robust performance. In this study, we use nonlinear statistical analysis of experimental data to characterize PEFC dynamics under conditions where water accumulation in the cathode air-delivery microchannels causes decreases in performance accompanied by chaotic fluctuations. Using experimental PEFC voltage signals, we estimate chaotic invariants indicative of the degrees of freedom of the dynamics (the correlation dimension) and the instability of the dynamics (the Kolmogorov entropy). We find that these invariants decrease with increasing gas flow commensurate with greater fuel cell current and air stoichiometric ratio, and that they are indicative of the channel two-phase flow regime. We correlate the Lyapunov exponents of the one-dimensional voltage return map and the Hurst exponents of the voltage time series with the chaotic invariants for use in future PEFC water management and control strategies. In addition, we examine the relationships between the invariants estimated from the voltage signal and the two-phase friction multiplier calculated from measured cathode pressure drop in order to distinguish the distinct dynamics of two-phase channel flow.

1. Introduction

Polymer electrolyte fuel cells (PEFCs) are electrochemical engines that convert hydrogen and oxygen to electricity, with byproducts of water and heat. The ability of sustainably- and renewably-produced hydrogen to provide low emission electricity makes it an attractive alternative to the combustion of limited-supply, carbon-based fuels like petroleum and coal. Because PEFCs offer high power density and quick startup owing to their sub 100 °C operating temperature, they remain promising for use in transportation applications.

While the product water exhaust makes PEFCs attractive as clean engines, it also poses water management problems that reduce system efficiency and hinder robustness of operation [1]. In the PEFC cathode, water is produced according to the oxygen reduction reaction in which oxygen, usually provided by air flow, combines with hydrogen ions and electrons. A certain amount of water is desirable to hydrate the polymer electrolyte membrane, thereby decreasing its ionic resistance [2]. However, too much water can increase the resistance to oxygen diffusion, leading to oxygen starvation and large mass transport overpotentials.

The ability to effectively remove surplus water from the cathode with a low parasitic cost is confounded by the air delivery mechanism and two-phase flow effects under certain operating conditions. State of the art air delivery flow fields are composed of arrays of parallel microchannels which deliver oxygen to the active fuel cell area and remove excess water. To achieve low parasitic costs, it

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is desirable to use low air flow rates in channels with low hydraulic resistance. However, the air momentum that makes positive contributions to the hydraulic resistance also removes liquid water through nonlinear momentum transfer. Hence, low air flow rates allow water to accumulate in the microchannels, thereby reducing the effective cathode active area and the fuel cell power output.

For high current densities, neutron radiography visualization has shown that the water accumulation in the cathode microchannels is relatively insensitive to the air stoichiometric ratio ξ [3], which is the ratio of the air flow rate delivered to that required for the reaction. At low current densities, however, the water accumulation and PEFC performance become more sensitive to ξ because the two-phase flow regime in the microchannels tends towards slug/plug flow when the channel superficial air and water velocities (u_g and u_l, respectively) are low [4,5]. In arrays of parallel channels, the complete blockage of individual channels by water plugs allows air flow to divert from plugged channels to open channels, following the path of least resistance [6]. The diverted flow leaves flooded channels plugged until enough pressure builds up to clear them, resulting in voltage instability and fluctuations, and power loss [7,8] (see Fig. 1). While the channel plurality [8] in a single lab-scale fuel cell may prove manageable, the large numbers of parallel channels present in fuel cell stacks used to power an automobile (>10,000) introduce many additional degrees of freedom and instability into the system's dynamics.

To avoid detrimental instability from water accumulation, operation in the slug flow regime is minimized in favor of annular film flow [5], which can be aided through geometric and material flow field design optimization. Different geometric flow field designs have been investigated, and while interdigitated channels have been shown to effectively remove liquid water [9], they produce much larger pressure drops than the conventional parallel/serpentine channel flow fields. To promote stable liquid water removal via annular film or corner flow, hydrophilic flow field materials may be used [10,11] as well as smaller channel dimensions that increase the gas velocity. Even with these flow field design optimizations, effective water removal is driven by supplying excessive air flow rates at multiple times the stoichiometric flow rate, resulting in high parasitic load on the fuel cell output, especially during the low-power idling and startup conditions.

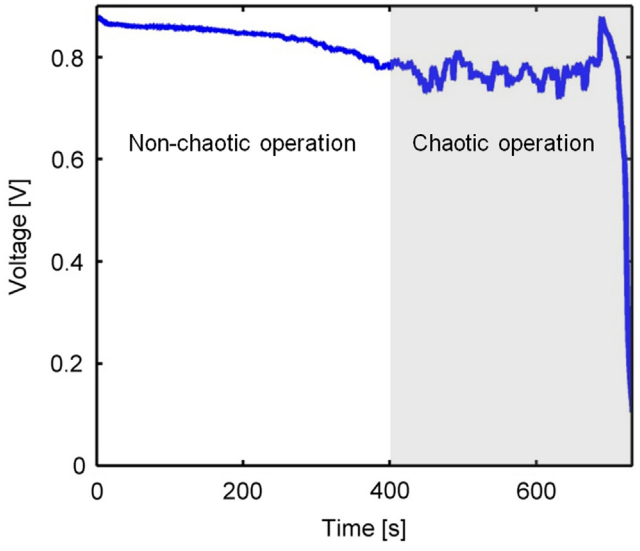

Fig. 1. Voltage signal of an operating PEFC beginning from a purged condition. As water accumulates, voltage output decreases and chaotic voltage fluctuations are introduced (around 400 s) before the cathode completely floods and voltage is lost (around 700 s).

One class of PEFC water management techniques uses fault detection. Output indicative of fuel cell health is monitored, and corrective water purging action is taken when the output indicates that the cathode is flooded. Many different diagnostics have been proposed for fault detection. One such linear fault detection scheme monitors the levels and oscillation frequencies of fuel cell voltage and resistance, stack voltage, pressure drop, and load [12]. When any of these signals breaches a predefined threshold, the air flow rate is pulsed to drive out liquid water. The amplitude response of voltage to small output pressure oscillations, indicated by the voltage variance, has also been proposed as a diagnostic for cathode flooding [13]. Additionally, electrochemical impedance spectroscopy has been employed to indicate cathode health [14]. Fuel cell dehydration shows a strong impedance response across a broad frequency range, while cathode flooding shows a much weaker impedance response across a limited frequency range. Both of the last two techniques require additional hardware to periodically excite the PEFC system, with the latter also requiring frequency response analysis electronics.

To improve upon such fault detection techniques, the signal being monitored and the threshold values can be optimized in a way that is consistent with the nonlinearities of PEFC water accumulation and removal dynamics. Nonlinear chaotic behavior has long been observed in chemical reaction kinetics, like the classic Belousov–Zhabotinsky reaction [15]. The complex PEFC water balance involves two-phase flow in parallel microchannels with electrochemical feedback, resulting in highly nonlinear and chaotic dynamics. While linear indicators like voltage oscillation frequency and magnitude may indicate changes in the PEFC dynamics, they do not account for potential nonlinear differences (*e.g.* in stability) between dynamics with similar linear oscillation characteristics. To address the shortcomings of linear analysis, nonlinear techniques have been used to analyze similar chaotic systems. For instance, calculation of chaotic invariants like Kolmogorov entropy has been shown to indicate two-phase flow regime changes [16], and nonlinear statistics have been shown to provide early defluidization warning in a fluidized bed [17]. Thus, instability induced by changes in system parameters with long dynamical timescales, such as fuel cell temperature and pressure, is potentially detectable using nonlinear statistics before it is apparent from linear statistics. It is also possible to stabilize unstable dynamics with minimal effort using chaos control techniques without changing the system parameters [18]. Bubbling has been controlled with chaos control in a fluidized bed [17], and chaos has been observed and controlled in electrochemical reactions [19].

The purpose of this paper is to provide a framework for understanding the nonlinear, chaotic dynamics of PEFC water management. We apply the first nonlinear time series analysis to PEFC instabilities to investigate how the presence of two-phase flow affects invariant quantities indicative of the degrees of freedom and the stability of the dynamics. We also propose new nonlinear voltage statistics that indicate the dynamical stability and are much less expensive to compute than the traditional chaotic invariants.

2. Method

This section presents the nonlinear analysis methodology that we used in this work and insight into its physical interpretation. Our implementation of the equations and algorithms has been validated on well-characterized nonlinear and stochastic systems like the Lorenz system [20] and Brownian motion, respectively.