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Hydrogen emission characterization for proton exchange membrane fuel cell during oxygen starvation – Part 1: Low oxygen concentration

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ABSTRACT

Hydrogen emissions during low oxygen concentration appear in the cathode exhaust of a PEM fuel cell stack. In this paper, the hydrogen emission rates for a stack containing cells without hydrogen crossover leaks are characterized. A Ballard 9-cell Mk1100 stack under standard FCvelocity®[1]-HD6 bus module operating conditions is employed, and extensive experiments are conducted under current demand to evaluate individual cell voltages and quantify hydrogen emissions. The results indicate that the emission rates are a strong function of current demands.

In parallel, a model is developed to estimate the amount of hydrogen in the cathode outlet. To illustrate the accuracy of the developed model, the simulation results and the measured hydrogen emission rates in the cathode exhaust are compared for two current demands. It is acknowledged that the proposed model can be a reliable emulator for the hydrogen sensor in the cathode exhaust, where catalytic sensors cannot perform correctly because of the lack of proper oxygen concentrations, or other types of sensor may fail due to wetting or sensor degradation. Moreover, the proposed model provides a user-friendly tool for systems engineers to design reliable start-up procedures for the control of hydrogen emissions.

Introduction

Fuel cells (FCs) are one of the best alternative power sources for future energy demand. They can generate electricity with very low to zero emissions and have been envisaged as an environmentally-friendly power source for future sustainable energy technology. FCs are classified primarily by the type of electrolyte they utilize [1]. The characteristics of the type of electrolyte, in turn, affect the applications for which these cells are most suitable. There are several types of FCs currently under development, each with its own advantages, limitations, and potential applications. Among the various types of FCs, Polymer Electrolyte Membrane fuel cells (PEMFC)

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[2] are used primarily for mobile and some stationary applications. The PEMFC is widely considered one of the best candidates to replace the internal combustion engine in the future, because of its relatively high efficiency, high power density, near-zero emissions and short start-up time [3]. A PEMFC typically consists of a membrane electrode assembly (MEA) sandwiched between reactant-delivering flow-fields. The MEA is composed of an ion conduction polymer integrated with two electrodes (anode and cathode) on both sides, and are often manufactured as one component.

During transient operation for PEMFCs, safety and performance efficiency are among the major concerns. Despite pervasive research on PEMFCs, there still exist drawbacks related to safety and reliability. For FC systems without leaky cells, there exists a body of literature to investigate the analysis, control and monitoring of supply sub-systems and water and thermal management [4–12]. In Ref. [10], the problem of oxygen and hydrogen supply for a high-pressure FC was investigated. The modeling and control of the cathode air stream and hydrogen flow with recirculation in a PEMFC was addressed in Refs. [4,13]. In Ref. [8] a qualitative model-based diagnostic algorithm for anode and cathode low flows was introduced.

Further, despite significant successes for existing approaches in fault detection systems for FCs [6,7,14–20], there remain some sources of concern regarding hydrogen emissions and flammability safety issues in an FC exhausts. In Ref. [6], an approach to quantify overall hydrogen emissions (internal plus external) in a FC stack was introduced. In Ref. [7], given voltage, current, and total pressure measurements, an observer was designed to estimate the hydrogen partial pressure at the inlet and at the exit of the anode channel. In Ref. [17], anode/cathode crossover and anode/cooling compartment leakage are detected using monitoring and analysis of open circuit voltages of cells in different operating conditions. Very recently, a fuel-cell model was developed that represents the dynamics of a cell during oxygen starvation [21].

To comply with standards for safety associated with hydrogen, volumetric hydrogen concentration (VHC) should be maintained at less than 4.6% [22,23], where the lower flammability limit (LFL) of 4.0% (or some fraction of LFL to provide greater margin) is commonly used as an upper operating limit. Although the VHC is typically measured using existing hydrogen sensors directly, sometimes it cannot be measured correctly or accurately due to technical issues; for example, through lack of enough oxygen near the sensor (in the case of catalytic-type sensors), or through sensor degradation due to adsorption and decomposition of siloxanes or other contaminants on sensor catalyst [24,25]. To the best of the authors' knowledge, none of the existing approaches for determination or measurement of exhaust hydrogen concentrations have addressed quantification methods to estimate actual VHC values, or true ignitability in the cathode exhaust [26].

In this paper, the hydrogen emission rates in a PEMFC stack were characterized during oxygen starvation, and a model was developed that permits accurately estimating the observed hydrogen emissions behavior. A Ballard 9-cell Mk1100 short stack was tested in the presence of current (load) demand where not enough oxygen was provided for the cathode, leading to oxygen starvation and hydrogen pumping [27]. Extensive experiments were conducted to measure hydrogen emissions in the cathode outlet during oxygen-starved conditions for a stack with healthy cells. To better understand this air starvation and its effects, two parameters, cathode-outlet hydrogen concentration and individual cell voltages were monitored during the oxygen starvation phenomenon and the hydrogen emission rates were characterized. It is worth mentioning that the Faraday's law predicts consumed reactants' molar rate, while the actual reaction rates and then the relevant VHC can be influenced by other factors say, less recombination rates and mass transportation limitations. The emission rates were quantified in the short stack using a simple model. The model incorporates the operational conditions prescribed for a stack while a current is demanded. Simulation results verified the accuracy of the model for estimation of hydrogen emission rates in the cathode exhaust. The improved model can be utilized as an independent indicator of emissions providing redundancy for the cathode exhaust hydrogen sensor, or as an alternative measure where catalytic sensors cannot perform correctly in the lack of proper concentrations of oxygen. Furthermore, during start-up conditions, the air compressor typically cannot immediately provide enough air and then oxygen to supply the required current for all the electrical components. When the actual current drawn from a cell exceeds the allowable current amount, determined by the provided air flow rates, hydrogen emissions can occur in the cathode exhaust due to hydrogen pumping. The proposed approach can provide a useful guideline for systems engineers to design the start-up procedure properly such that the drawn current is limited and the emission rate can be controlled.

Preliminaries section, in this paper, provides useful information on the relationships among reactant gas flows, gas mixtures, and the role of the current in consuming reactants, while Experimental setup section presents a detailed review of the equipment and testing performed to study cathode exhaust emissions. Hydrogen emissions in a PEMFC short stack section discusses the development of a simple model for predicting hydrogen emissions in the presence of low oxygen concentrations. Results and discussions section presents the results of the use of the model for the estimation of hydrogen emissions for low oxygen concentration or low air flow. Conclusions and future work section summarizes the results of the work and presents the conclusions that can be drawn regarding the accuracy of the developed modeling.

Preliminaries

Oxygen stoichiometric ratio in cathode

In a normally operating FC stack the ratio of reactant supplied to the minimum required reactant is called stoichiometry, and is represented by λ [3]. This stoichiometry is defined for a cathode as

$$\lambda_{cathode} = \frac{\dot{n}_{O_2,feed}}{\dot{n}_{O_2,min}} \quad (1)$$