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A mathematical model to study the performance of a proton exchange membrane fuel cell in a dead-ended anode mode

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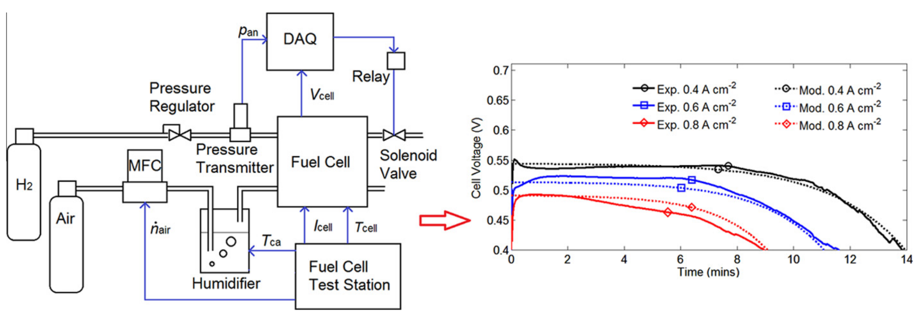
HIGHLIGHTS

- This model can predict the performance of a single cell in a dead-ended anode mode.
- The hypothesis of how current density affects nitrogen accumulation is proposed.
- The model was calibrated and validated by experiments.
- Nitrogen concentration is regarded as a parameter for anode purge strategy.

GRAPHICAL ABSTRACT



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ABSTRACT

When a proton exchange membrane fuel cell (PEMFC) system is operated in the dead-ended anode mode, nitrogen will gradually permeate from the cathode to the anode. The accumulation of nitrogen in the anode causes a performance drop, which can be recovered by purging. The purge strategy depends on operating conditions of the PEMFC. To investigate the effect of operating conditions on the performance of a PEMFC with a dead-ended anode, a mathematical model is developed to estimate the nitrogen crossover and accumulation in the anode of the PEMFC, especially for varying-load operations. The effect of operating current density on nitrogen crossover is coupled in the model. Parameters in the model are calibrated according to experimental data. The experiments are designed to measure the voltage variations of the single cell with dead-ended anode at different operating current densities. The effect of current density on purge frequency and voltage variation is shown. Simulation results by this calibrated model agree well with experimental data. The transient of hydrogen concentration in the anode is investigated by the model. A purge strategy is suggested at the end of this study.

1. Introduction

PEMFCs electrochemically combine hydrogen and oxygen to generate electricity. They have the advantages of high power density, high efficiency, low operating temperature, and low emission. Thus, they are considered as potential power sources of electrical vehicles for the future. For the transportation applications, on-board hydrogen storage is still one of the most challenging to the widespread commercialization. Since the volumetric energy density of hydrogen is much lower than that of gasoline and there is limited space in a vehicle for hydrogen storage tank, the hydrogen utilization is a key issue in fuel management.

Fuel managements of a PEMFC system can be classified as flow through mode, recirculation mode, and dead-end mode [1]. In the flow through mode, excess hydrogen is supplied to the anode to remove water diffused from the cathode, resulting in lower hydrogen utilization. The flow through mode is usually used for testing

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Nomenclature

a_{ij}	tuned parameters
A	area (m^2)
d	thickness (m)
D	gas permeability in membrane ($mol\ m^{-1}\ s^{-1}\ Pa^{-1}$)
E	activation energy ($kJ\ mol^{-1}$)
F	Faraday's constant (96,485 $C\ mol^{-1}$)
i	current density ($A\ m^{-2}$)
$\dot{N}$	molar flow rate ($mol\ s^{-1}$)
$\dot{n}$	molar flux ($mol\ s^{-1}\ m^{-2}$)
p	pressure (Pa)
$\bar{R}$	universal gas constant (8.314 $J\ mol^{-1}\ K^{-1}$)
R	resistance (ohm)
t	time (s)
T	temperature (K)
V	voltage (V) or volume (m^3)
x	molar fraction
y_{O_2}	percentage of oxygen in the air (0.21)

Greek

ϕ	relative humidity
ζ	stoichiometric ratio

Subscripts

act	activation
air	air
an	anode
ca	cathode
cell	single cell
ch	channel
conc	concentration
consumed	consumed
diff	diffusion
H_2	hydrogen
H_2O	water
in	inlet
N_2	nitrogen
O_2	oxygen
ohm	ohmic
PEM	proton exchange membrane
rev	reversible
sat	saturation
v	vapor

fuel cells in a laboratory. In the recirculation mode, non-reacted residual hydrogen is recirculated back to the supply line by a pump or an ejector. These configurations may not be suitable for a small portable fuel cell system or one in which there is limiting space to install the recirculation system. Thus, a simple dead-end mode is another solution to the hydrogen management for a small fuel cell system. In the dead-end mode, a pressure regulator is installed at the inlet of the anode to reduce the pressure of hydrogen from a gas tank, while a solenoid valve is placed at the outlet to seal the anode.

In the dead-ended anode operating condition, the cell voltage gradually decreases with time. The voltage drop may be caused by the accumulation of impurities in the anode, resulting in low hydrogen concentration. The hydrogen starvation could cause reverse-current, resulting in carbon corrosion of the catalyst and degradation of the fuel cell [2–4]. Dumercy et al. [5] investigated the voltage variation of a 3-cell stack operating in the dead-ended anode mode. In their experimental results, the voltage drop was not obvious when the current density of the fuel cell stack was lower than 0.4 $A\ cm^{-2}$, whereas when the current density was higher than 0.4 $A\ cm^{-2}$, anode purge was required for voltage recovery. They suggested that the purge frequency should be dependent on current density but did not provide a purge strategy. Moçotéguy et al. [6] studied the dynamic behavior of a 5-cell stack operating in the dead-ended anode mode. They developed a model and conducted experiments to investigate the voltage response to a step current change. Their results indicated that the cell located at the gas inlet showed higher performance and this was due to lower water accumulation and higher gas partial pressure. Siegel et al. [7] observed water accumulation of a single cell under dead-ended anode operation using a neutron radiography technology. Their experiments showed that when the liquid water in the anode was purged out, the cell voltage increased. Lee et al. [8] designed a transparent cell to observe water accumulation in the anode side of a single cell operated in dead-ended anode mode and investigated the effects of operating parameters on the voltage variation of the cell. Mokmeli et al. [9] developed a model to simulate the voltage drop of a single cell at the dead-ended anode operation. In their model, voltage loss was attributed to accumulation of impurity from hydrogen gas.

In the dead-ended anode mode, nitrogen can diffuse across the membrane due to a partial pressure gradient between the anode and cathode sides. Hikita et al. [10] conducted an experiment to analyze the gas composition in the anode side of a fuel cell operated in a dead-ended anode condition. The experimental results showed the presence of nitrogen inside the anode. Baik et al. [11] used a mass spectrometer to estimate nitrogen crossover under various operating conditions, including cell temperature and relative humidity of reactants. The experimental results showed that nitrogen crossover was larger at the higher temperature and relative humidity. Other operating conditions, such as current density and stoichiometric ratio of hydrogen flow also affected nitrogen crossover.

Manokaran et al. [12] measured the current distribution along the flow channels of a single cell at a dead-end mode to quantify the evolution of inert gas in the anode channel. The results showed that nitrogen accumulated first at the anode outlet and propagated toward the channel inlet. Boillot et al. [13] experimentally studied the effect of hydrogen/nitrogen ratio on the cell performance. Their results suggested when the nitrogen concentration was larger than 20%, the cell voltage showed significant decrease. Yesilyurt et al. [14] supplied a gas mixture with different ratios of oxygen to nitrogen to the cathode of a fuel cell operated at the dead-end mode. The experiments indicated the cell voltage did not drop in 20 min when the ratio was larger than 40%. Ahluwalia et al. [15] studied the buildup of nitrogen in the anode channels of a pressurized PEMFC stack for transportation applications. They concluded that the nitrogen buildup depends on operating conditions. At a lower purge rate, the nitrogen concentration could reach 50–70%, while at a higher purge rate, it could be reduced to 5–20%. Choi et al. [16] installed a pulsation device at the anode outlet to increase anodic purge interval and fuel efficiency. Their experimental results showed that anodic pulsation reduced partial pressure of water vapor and increased the purge interval by approximately three times. Zhai et al. [17] developed a dynamic model and conducted experiments to study the effects of purge