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Detecting proton exchange membrane fuel cell hydrogen leak using electrochemical impedance spectroscopy method

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HIGHLIGHTS

- EIS is able to detect the hydrogen leak through an MEA.
- Impedance signature increases with the increasing rates of leaks.
- The mass transport region increased due to the recombination of oxygen at the cathode.
- EIS cannot detect the leak if it is low or located at the downstream of the MEA.

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ABSTRACT

When a proton exchange membrane (PEM) fuel cell runs short of hydrogen, it suffers from a reverse potential fault that, when driven by neighboring cells, can lead to anode catalyst degradation and holes in the membrane due to local heat generation. As a result, hydrogen leaks through the electrically-shorted membrane-electrode assembly (MEA) without being reacted, and a reduction in fuel cell voltage is noticed. Such voltage reduction can be detected by using electrochemical impedance spectroscopy (EIS). To fully understand the reverse potential fault, the effect of hydrogen crossover leakage in a commercial MEA is measured by EIS at different differential pressures between the anode and cathode. Then the signatures of these leaky cells were compared with the signatures of a no-leaky cells at different oxygen concentrations with the same current densities. The eventual intent of this early stage work is to develop an on-board diagnostics system that can be used to detect and possibly prevent cell reversal failures, and to permit understanding the status of crossover or transfer leaks versus time in operation.

1. Introduction

Fuel cells transform chemical energy into electrical and thermal energy by electrochemical reaction that takes place in between electrodes and an electrolyte. In proton exchange membrane (PEM) fuel cells, hydrogen oxidation takes place on the anode side while oxygen reduction occurs at the cathode. After oxidation, hydrogen protons move from the anode to the cathode with the help of a thin layer of ion-conducting catalyst and electrons flow out of the cell to produce energy. In order to come up with enough power to satisfy the load, fuel cells are usually stacked in series.

Ballard Power Systems uses 6th generation FCvelocity™-HD6 Modules that utilize state of the art automotive Proton Exchange Membrane (PEM) stacks to power many buses around the world. Fuel cell system design targets optimum operating conditions and efficient systems to insure sufficient humidification, and air and fuel supplies. However, if the reactant feed does not respond to the current demand quickly enough, such as during sudden load increases and/or start-up/shutdowns, full or transient fuel starvation may occur causing cathode or anode degradation. Cells containing transfer or crossover leaks are at greater risk of fuel starvation.

Full fuel starvation can result in reverse potential faults, where normal operating cells push current through the fuel starved cell. This causes a rise in the anode potential to the potential required to oxidize water and the anode catalyst carbon support (Equations (1) and (2)). The protons then pass through the membrane to the cathode to produce hydrogen (equation (3)).

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad (1)$$

$$C + H_2O \rightarrow CO_2 + 2H^+ + 4e^- \quad (2)$$

$$2H^+ + 2e^- \rightarrow H_2. \quad (3)$$

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During shut-down periods hydrogen is consumed by air that diffuses to the anode catalyst layer. Upon start-up, hydrogen mixes with the stagnant air and creates transient starvation of cells as the hydrogen supply is replenished at the anode. This causes a spike in both the cathode and anode potentials, resulting in oxidation of water and the cathode catalyst carbon support, as described by Equation (2). Tang et al. [1] studied the effect of fuel starvation on the fuel cell during start up and noticed a reduction of the catalysts surface areas.

Carbon oxidation of the catalyst support reduces the catalyst active area due to agglomeration and reduces the catalyst layer thickness, which often causes mass transport degradation. N. Yousfi-Steiner et al. [2] reviewed the causes and consequences of fuel cell starvation faults in detail.

During the reverse potential fault, the safe threshold of hydrogen leaks through the fuel cells can be detected using hydrogen sensors in the downstream cathode exhaust. Unfortunately, those sensors are expensive and not reliable over long periods of time. Thus, a more reliable diagnostic technique is required to monitor hydrogen leakage through fuel cells. Wu et al. [3] reviewed several diagnostic techniques that can be used to detect fuel cells faults. The Cell Voltage Monitoring (CVM) technique measures the voltage of each cell in the stack. However, it cannot be used to detect the voltage on board due to reliability issues. Electrochemical impedance spectroscopy (EIS) is an experimental technique that can be used to perform impedance measurements over a wide frequency range for DC power generation devices. The main advantage of EIS is the possibility to resolve, in the frequency domain, the individual contributions that affect the overall PEM fuel cell performance under load conditions [4].

The authors of this paper are not aware of any EIS study that has been conducted to show the effect of hydrogen leaks through PEM fuel cell. In this study the effect of hydrogen leaks on a single cell were evaluated using an EIS method. In order to increase our understanding of the impedance behavior at different hydrogen leak rates, we compare it with the impedance signatures of reduced oxygen concentrations in the cathode. These faulted impedance signatures will be used in the future to detect reverse potential faults in a stack or the outcomes thereof.

2. Process modeling

2.1. An overview of EIS

EIS usually employs a frequency response analyzer (FRA) to apply either a small AC voltage or current perturbation signal to a cell, and measures its output signal for a wide frequency range. The impedance is calculated by dividing the voltage by current, in the form of a magnitude and phase angle, at each specific frequency.

Impedance spectroscopy has the ability to characterize many of the electrical properties of materials and their interfaces with electrodes. This ability has made the EIS technique widely used in modeling and diagnostics of PEM fuel cells, where individual contributions affecting cell performance can be distinguished by fitting the impedance spectrum into parameters of an equivalent circuit model. Electrical circuits with different configurations, components, and degree of complexity have been proposed in the literature.

The basic equivalent circuit often used to represent fuel cell operation is the Randles circuit shown in Fig. 1, where C_{dl} is the double layer capacitance of the catalyst surface, R_{HF} describes the movement within a conducting media and illustrates the sum of contribution from contact resistance between components and high frequency resistance of the cell components, and R_{ct} is the resistance that occurs when electrons transfer at the electrode/electrolyte interface. R_{ct} decreases when overpotential increases due to the faster oxygen reaction rate. Kang et al. [5] noticed an increase in R_{ct} with increasing the degree of the reverse potential fault in a fuel cell caused by fuel starvation.

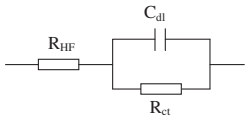

Fig. 1. Randles model.

Nyquist plots show the resistance versus reactance at multiple frequencies, as obtained by the EIS measurements, Fig. 2. The high frequency region of the impedance spectrum represents the high frequency resistance whereas the low frequency region represents the high frequency resistance and charge transfer resistance respectively [6]. At high frequency, the C_{dl} is short circuited and the R_{HF} is measured. As frequency decreases, the impedance becomes a combination of resistance and reactance from the capacitive element. At low frequency, C_{dl} acts like a blocking diode and the total resistance is equal to R_{HF} and R_{ct}.

2.2. Electrical circuit model

More complicated circuits than the Randles circuit are proposed in the literature for different purposes. Others [4,7,8] have added additional to the Randles circuit to include mass transfer effects series connections represent subsequent events while parallel connections represent simultaneous events.

Makharia et al. [9] used a transmission line circuit to include the catalyst layer resistance. Cano-Castillo et al. [10] compared the transmission line circuit with a circuit similar to the ones used by Refs. [4,7], where they added a resistive and capacitive element to the Randles circuit. Both the transmission line and the modified Randles circuit gave reasonable fit with the experimental data.

Andreasen et al. [11] used two circuits, the modified Randles circuit described above, and the other with a constant phase element (CPE) instead of a capacitor in the second circuit. The authors showed that using the circuit with the CPE fitted better to their impedance data. Others [12–14] also replaced capacitive elements with CEPs to adapt their models with the deformed impedance arc. This deformation results from the porous structure of the electrodes where the electron charges are not distributed evenly inside the electrode.

Another equivalent circuit variant [15] represented the mass transport phenomena with a Warburg impedance element in series with the Randles circuit.

In this study it was sufficient to represent the impedance spectra with the modified Randles equivalent circuit shown in Fig. 3, utilizing resistive and capacitive elements to describe both kinetic and mass transport phenomenon. More specifically, R_{mt} describes the oxygen diffusion resistance, while C has been used to describe the

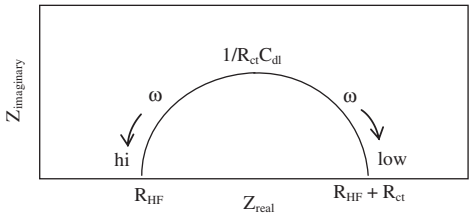

Fig. 2. Nyquist plot of a fuel cell.