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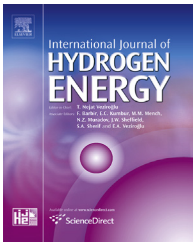

Diagnosis of hydrogen crossover and emission in proton exchange membrane fuel cells

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ABSTRACT

When hydrogen leaks through holes in membrane-electrode assemblies (MEAs) in proton exchange membrane (PEM) fuel cells, it recombines directly with air. This recombination results in a reduction in oxygen concentration on the cathode side of the MEA. In this paper, the signatures of electrochemical impedance spectroscopy (EIS) are analyzed in different multi-cell stack configurations to show the relation between hydrogen leak rate and reduced oxygen concentrations. The reduction in concentration was made by mixing oxygen with nitrogen at different rates, and the increase in hydrogen leak rate was made by controlling the differential pressure (dP) between anode and cathode. To analyze the impedance signatures, we fit the data of oxygen concentration and dP with the parameters of a Randles circuit. The correlation between the parameters of the two data sets allows us to understand the change in impedance signatures with respect to reduction of oxygen in the cathode side. To have a better insight on the effect of insufficient oxygen at the cathode, a model that establishes a relationship between impedance and voltage was considered. Using this model along with the impedance signatures we were able to detect the reduction of oxygen concentrations at the cathode with the help of fuzzy rule-base. However, resolution of detection was reduced with the reduction of leak rate and/or increases in the stack cell count.

Introduction

When the fuel cell starves of hydrogen, its anode and cathode potentials rise and drop respectively. In such a fault, the voltage of a single starved cell is dropping to zero [1]. If a hydrogen starving cell was placed in a stack, its voltage drops to negative values due to the high anode potential [2]. When the cell is air starved however, its voltage drops to almost zero with its anode potential little higher than the cathode [3]. Zhang et al. [1] studied the effect of fuel and air starvation on the voltage along a single PEM fuel cell. Reducing the air stoich to 1.5, the cell voltage drops due to the lack of oxygen concentration. As concentration drops along the flow channel, lower local current density was observed at the downstream of the cell. Running the cell at lower hydrogen stoich, the current density dropped sharply to zero at the downstream of the cell due to the insufficient hydrogen along the cell.

In a similar study, Schneider et al. [4] considered the effect of air starvation on the impedance along a 63 cm^2 single PEM

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fuel cell. At normal air stoich, the impedance spectra had two frequency loops. They suggested that the presence of the second loop, related to the mass transfer region, indicates significant losses associated with oxygen diffusion through nitrogen in the gas diffusion layer (GDL) [5]. However, the loop increases in size with increasing the depletion of oxygen toward the air outlet. When the air stoich was reduced from 3.5 to 1.4, this second loop increased sharply toward the end of the cell outlet. In a previous study done by our group [6] we observed similar behavior of the impedance signature of a single cell with either decreasing oxygen concentration or increasing leak rates. However, the reduction in impedance due to air starvation was not observed, where the impedance measurement collapsed at zero voltage. To avoid this problem, we measured in this study the impedance of a multi-cell stack while driving it to air starvation.

At a stack level, Yan et al. [7] measured the impedance of a 20 cell stack with an MEA active area of 270 cm^2 at reduced air stoich. They noticed that as the stoich reduced to 1.5, the impedance enlarged. However, further reduction of air stoich creates improper conditions that effect the fuel cell operation and measurements. Thus, in this study we reduced oxygen concentrations while keeping constant cathode flow. This gave us a better understanding of the relationship between oxygen concentration and transfer leak rate where in both cases lesser oxygen was available at the cathode. We analyzed this relationship by fitting the impedance signatures with an equivalent electrical circuit.

Toward an understanding of the impedance signatures, we used a Randles circuit to fit our experimental data. More precise fits can be achieved by using a constant phase element (CPE) instead of the capacitance [8]. However, the lack of physical interpretation of CPE elements has limited its use in the literature. Fouquet [9] replaced the CPE with an increased order of the Randles model by adding R and C elements of the transmission line. This resulted in a better fit to the impedance data compared to the normal Randles model. However, more computational power was needed due to the complexity of the model. Because of the complexity in using the CPE element, some researchers have used a double layer capacitance (C_{dl}) instead [10,11]. In our study, the use of a basic Randles circuit in fitting the impedance signatures made the understanding of the impedance behavior easier. The fitting was made by using Zplot software.

While increasing the amount of hydrogen leak rate we noticed no hydrogen emission at the stack cathode outlet. However, the existence of hydrogen at the cathode outlet was detected at air starvation. This hydrogen existence at the cathode agrees with the literature that when the fuel cell starves of oxygen, hydrogen protons pass through the MEA and combine directly with electrons at the cathode side [12,13] in a phenomena that is called hydrogen pumping (Equations (1)–(2)) [14].

$$H_2 \rightarrow 2H^+ + 2e^- \tag{1}$$

$$2H^+ + 2e^- \rightarrow H_2 \tag{2}$$

At a scarcity of oxygen concentration, the stack pumps large amount of hydrogen rates that might pass the critical threshold of acceptable cathode hydrogen emissions. Using the impedance signature and the stack voltage we were able to recognize this fault precisely.

Fuzzy logic (FL) is about representing an *approximate* knowledge that cannot be represented by conventional, crisp methods [15]. Using membership functions, the crisp value is represented by a fuzzy degree between [0–1] which reflects the belonging of the crisp value to the function. By the means of membership functions, crisp values are illustrated linguistically in the fuzzy rule-base that demonstrates the expert knowledge in the form of if-then rules. D. Hissel et al. [16] used FL to control detect drying and flooding in a FC vehicle. J.O. Schumacher [17] used FL in water management of miniature FC stack. J. P Torreglosa et al. [18] used FL in energy management of a battery-FC hybrid tramway system. In this paper, we proposed to use FL in detecting internal leak rate and hydrogen emission for a multi-cells stack.

Fuzzy logic background

In a fuzzy logic system, human knowledge is represented by *If-then* rules in which an input–output relationship is linguistically represented and characterized by continuous membership functions. Appling those membership functions, the crisp measurement is fuzzified for a value between 0 and 1. Then inference mechanism finds the match between the fuzzy value $u(x)$ and its corresponding rule. Once the compositional rule applied, the control action is defuzzified to a crisp value $u(y)$, see Fig. 1.

Similar to the NN, FL is often used when the exact mathematical model is too complex. However, the ability of FL to represent the inexactness in the system widened its applications in the literature where the crisp value is represented by a fuzzy degree $\mu_X(x)$ in the interval [0–1]. $\mu_X(x)$ reflects the belonging of the crisp value to the fuzzy set X. The fuzzy set can be represented graphically by the means of membership functions. A membership function of either zero or one respectively means that the corresponding element does not belong or definitely an element of the set. A membership function in between 0 and 1 corresponds to non-crisp element that fall in the fuzzy boundary of the set, see Fig. 2.

The inference mechanism describes the fuzzy logic reasoning in the form of *if-then* rules where the premise and consequent are illustrated respectively. The premise part represents the fuzzy set X of the input x and the consequent part represents the fuzzy set Y of the output y, (Equation (3)). Both parts are antecedent linguistically; i.e. has been

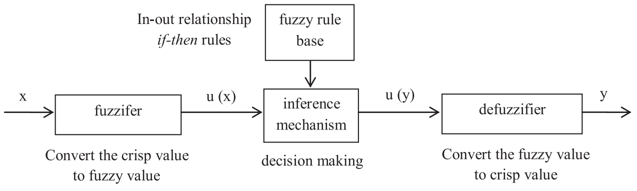

Fig. 1 – Schematic of fuzzy logic system.