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Study of anode and cathode starvation effects on the impedance characteristics of proton exchange membrane fuel cells

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ABSTRACT

The anode and cathode starvations in proton exchange membrane fuel cells are studied using the electrochemical impedance spectroscopy. The impedances are measured while the anode and cathode feeding gasses are diluted using helium and nitrogen, respectively, and the Nyquist plots are compared against the normal operating conditions. It is shown that the cathode starvation significantly inflates the mid-frequency (MF) arc; while similar anode starvation does not affect the Nyquist plots of the measured impedances. These results are in agreement with the trends predicted from the process model presented.

1. Introduction

The starvation phenomenon in proton exchange membrane (PEM) fuel cells can be defined as a state in which there is not enough fuel (hydrogen) in the anode or oxygen in the cathode. Starvation can occur if the flow rates of the feeding gasses decrease; it can also be the result of flooding that can clog the anode and cathode porous electrodes hindering the transport of the reactants to the reaction sites. While the starvation can easily be suppressed by increasing the fuel and air flow rates, it is not an economically efficient approach to improve the fuel cell performance. One of the major problems with starvation is the possibility of reaching to corrosive potentials in the anode which can considerably decrease the durability of the electrode [1]. The anode starvation can also result in carbon corrosion in the cathode [2].

Starvation and flooding phenomena can be studied in PEM fuel cells using the electrochemical impedance spectroscopy (EIS) method. There are two ways to create starvation in the electrode: flooding or decreasing the stoichiometry ratio of reactants. The effect of latter has been studied by O'Rourke et al. [3] who measured the Nyquist plots of a PEM fuel cell in different cathode and anode stoichiometry ratios. They showed that the change in the cathode stoichiometry ratio clearly affects the medium and low frequency arcs; while the change in the anode stoichiometry does not change the Nyquist plot. The effects of the anode and cathode stoichiometry on the Nyquist plot were also studied by Danzer and Hofer [4]. They also reported that while the cathode stoichiometry affects the medium and low frequency parts of the Nyquist plots, the anode stoichiometry has a minimal effect on the plot. Yan et al. [5] also reported similar effects of the cathode stoichiometry on the impedance characteristics of the cell. While these experimental results are normally used to study the starvation effects on the Nyquist plots, there are still debates regarding these cases. As the stoichiometry ratio of the feeding gas changes, the gas flow rates and velocity profiles are also altered which change the flow structure in the channels and also water management in the cell. Consequently, the results captured could be affected by these sideline phenomena. Moreover, the impedance comparisons could be questioned as the operating conditions (specifically, the water transport in the cell) were not precisely similar. As a result, a new experimental approach is needed which changes the stoichiometry while keeping the flow rates and velocities unchanged. Moreover, if the channels are not designed as dead-ended, the stoichiometry is not always a reliable factor for the starvation assessment. In fact, the stoichiometry measures the ratio of the needed reactants (fuel or oxygen) in the catalyst layer to the fed reactants in the channel. Considering the complex transport phenomena from the channel towards the catalyst layer through the gas diffusion layer (GDL), it is reasonable to expect having (at least partial or local) starvation in the catalyst layer (e.g., when the transport coefficient in the GDL is considerably low) even when the stoichiometry is considerably high.

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Nomenclature

D	Diffusion coefficient
F	Faraday's constant
M_M	Membrane equivalent weight
R	Ideal gas constant
T	Temperature
Z	Impedance
$Z_{act.}$	Impedance of the activation overpotential
$Z_{ohm.}$	Impedance of the ohmic overpotential
Z_{tot}	Overall impedance
$Z_{trans.}$	Impedance of the mass transport overpotential
$c_{H^+,s}$	Actual adsorbed proton concentration
$c_{O,s}$	Actual adsorbed oxygen atom concentration
f	Flooding coefficient
i	Imaginary unit ($\sqrt{-1}$)
j	Current density
j_0	Exchange current density
l	Thickness
n	Number of electrons transferred in reaction ($n=2$)
Γ_{H^+}	Surface density of the protons
α	Defined parameter ($=2.5/(22F)$)
α_C	Cathode transfer coefficient
β	Defined parameter ($=\rho_M D_M/M_M$)
ε_s	Dielectric permittivity
η_{ch}	Channel efficiency
λ	Water content
ρ_M	Membrane dry density
σ_M	Membrane electrical conductivity ($=(0.519\lambda_M-0.326)\exp(1268(1/303-1/T))$)
ω	Angular frequency
$(\ )^w$	Water
$(\ )^0$	Reference value
$\bar{(\cdot)}$	Value prior to perturbation
$(\ )_A$	Anode
$(\ )_C$	Cathode
$(\ )_{CL}$	Catalyst layer
$(\ )_{GDL}$	Gas diffusion layer
$(\ )_M$	Membrane

Another factor that can potentially lead to starvation is flooding, as mentioned before. Flooding is in fact undesirable as it causes partial or local starvation. The reported impedance characteristics obtained under the flooded and normal conditions in PEM fuel cells [e.g., [6–13]] do not normally distinguish the flooding in the anode and cathode electrodes or those are not discussed individually. Therefore, these reported impedances cannot be used to study separately the anode and cathode starvation.

Furthermore, the starvation studies reported in literature and reviewed above, are not performed using a 'process model'. The differences between the process modeling and the measurement modeling approaches are discussed in Ref. [14]. In summary, the process model results in an equivalent circuit with elements that are analytical functions of the physical and chemical parameters of the cell. On the other hand, the measurement model results in an equivalent circuit which has similar impedance characteristics as the measured impedance of the cell. As a result, the elements of a measurement-model-based equivalent circuit are not necessarily representative of the physicochemical properties of the cell. The importance of using an accurate process model in this study can be explained as follows. To study the effect of the starvation on the impedance of the cell, the impedances in two 'identical' operating conditions in normal and starved cases have to be compared. Clearly, when the cell is starved, the current density of the cell in the same potential is decreased. As a result, there is no equivalent operating point in the starved case which has the same current density and potential as the normal case. The process model can show that between the potential and current density (or any combinations of them) which one is the dominant parameter in the impedance characteristics of the cell and has to be kept constant. In other words, using the process model, one can produce an 'imaginary' identical point which has the same operating conditions as the normal case and then use this imaginary point for the comparison with the normal case. It is worth mentioning that while it is clear that starvation causes a decrease in the current density in a constant potential (which can be seen in the polarization curve), this decrease cannot be considered as the indicator of the starvation phenomenon, as starvation is not the only phenomenon which causes a decrease in the current density (e.g., membrane dehydration can also result in a decrease in the current density).

The experimental approach used in this paper enables measuring the impedance of a PEM fuel cell in different stoichiometry ratios in the anode and cathode while the flow rates are kept constant. To decrease the anode and cathode stoichiometry, the hydrogen and air are mixed with helium and nitrogen, respectively, and the impedances are measured and discussed. The measured impedances are then compared against the trends observed by the process model presented recently [15] and summarized in the Appendix A. Similar to the process model predictions, the comparison will prove that the cathode starvation can easily be captured from the mid-frequency (MF) arc; while similar anode starvation cannot be captured by impedance characteristics.

It has to be mentioned that the cathode flow dilution using gasses were used before [16] as a way to study the diffusion in the cathode. While the measured impedances depicted the effects of the cathode flow dilution on the impedance characteristics of the cell, the model presented could not predict the measured impedances with an acceptable accuracy. The importance of having an accurate model is rediscussed in Section 4.

2. Experimental setup

A 7.98-cm^2 PEM fuel cell consisting of two SGL-25BC gas diffusion layers for the anode and cathode and an XL-3BP-318 membrane electrode assembly is used. The details of the cell were described before [15]. The cell is monitored using the Arbin fuel cell test station while the impedance characteristics are measured using VERSASTAT 4 electrochemical system (Princeton Applied Research). The impedance measurement sweeps the frequency span of 10 kHz – 10 mHz at the rate of 10 points per decade in the potentiostatic mode. The cell and the anode and cathode flow temperatures are kept at 70 °C; while the relative humidities of the reactants are 90%. The Nyquist plots are measured at potentials of 0.75 V and 0.7 V.

The cell is fed with high flow rates of 1.42 SLPM (standard litres per minute) for the cathode and 0.55 SLPM for the anode (equal stoichiometry ratios) in the normal state to guarantee that the cell has enough fuel and oxygen in this situation. In the next step, the anode is fed by a mixture of hydrogen and helium with the volumetric ratio of 1 to 10. The same process is used for studying the cathode starvation; i.e. the cathode is fed by a mixture of 2% oxygen and 98% nitrogen. This decreases the stoichiometry to one tenth in both cases of the anode and the cathode starvations while the gas flow rates and velocity distributions in the channels and the gas diffusion layers and the transfer rates remain unchanged. The polarization curves for the normal and starved cases are then compared. The (partial) starvation is approved if the differences between the polarization curves are recognizable. Then, the Nyquist plots are compared.

It has to be mentioned that the difference between the heat capacities of hydrogen and helium may influence the temperature distribution inside the cell and hence the results. However, this effect does not seem to be considerable as sensitivity analysis reveal that temperature changes less than 5 °C do not change the Nyquist plots of the measured