# Interpretation of Low-Frequency Inductive Loops in PEM Fuel Cell Impedance Data in Terms of Reactions Influencing the Life-Time of Fuel Cell Performance

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#### Abstract

Impedance models were developed to account for reaction mechanisms that may be responsible for the inductive impedance response often seen at low frequencies in PEM fuel cells. Models that incorporate only the hydrogen oxidation and oxygen reduction reactions cannot account for these inductive features. Inductive loops can be predicted by models that account for formation of hydrogen peroxide as an intermediate in a two-step oxygen reduction reaction. Hydrogen peroxide is considered a degrading agent for materials used in the fuel cell components (membrane, electrodes) and its formation under the fuel cell operating conditions is reported in the literature. Inductive loops can also be predicted by models that account for Pt dissolution and associated deactivation of catalytic activity. These interpretations are supported by experimental evidence. Interpretation of impedance spectra in terms of side reactions may prove useful for predicting the life-time of fuel cell performance.

#### 1. Introduction

Impedance spectroscopy is often used to characterize processes in fuel cells, including proton exchange membrane (PEM) fuel cells.<sup>1–5</sup> Low-frequency inductive features<sup>6–8</sup> are commonly seen in impedance spectra for PEM fuel cells (see, for example, Figure 3 reported by Makharia *et al.*<sup>6</sup>). These researchers suggested that side reactions and intermediates involved in the fuel cells operation can be possible causes of the inductive loop at low frequency. However, such low-frequency inductive loops could also be attributed to nonstationary behavior, or, due to the time required to make measurements at low frequencies, non-stationary behavior could influence the shapes of the low-frequency features. In previous work, Roy and Orazem<sup>9</sup> used the measurement model approach developed by Agarwal *et*  *al.*<sup>10,11</sup> to demonstrate that, for the fuel cell under steady-state operation, the low-frequency inductive loops were consistent with the Kramers Kronig relations. This work demonstrated that, independent of the instrumentation used, the low-frequency features could be consistent with the Kramers Kronig relations. Therefore, the low-frequency inductive loops could be attributed to process characteristics and not to non-stationary artifacts.

Some typical results are presented in the Figure 1(a) for the impedance response of a single 5 cm<sup>2</sup> PEMFC with hydrogen and air as reactants. The experimental conditions are reported elsewhere.<sup>9</sup> The result presented as Figure 1(a) was obtained using a Scribner 850C fuel cell test station and the results presented as Figure 1(b) was obtained using a Gamry FC350 impedance instrument coupled with a Dynaload RBL:100V-60A-400W electronic load. The arrow points to the nominal zero-frequency impedance calculated from the slope of the polarization curve, and the solid lines correspond to a fit of the measurement model.

Mathematical models are needed to interpret the impedance data, including the lowfrequency inductive loops, in terms of physical processes. The most quantitative of the impedance models reported in the literature have emphasized detailed treatment of the transport processes, but use of simple electrochemical mechanisms precluded prediction of the inductive loops. As the oxygen reduction reaction (ORR) at the cathode is the ratedetermining step, most models emphasize the reaction kinetics at the cathode. The onedimensional models proposed by Springer *et al.*<sup>2,12</sup> considered the cathode to be a thin film on agglomerated catalyst particles. They studied the role of water accumulation in the gas diffusion layer and oxygen diffusion in the gas phase. These models considered only a singlestep irreversible ORR at the cathode. The impedance models by other researchers<sup>13–15</sup> also treated a single-step kinetics for the ORR.

Several models for the impedance response of PEM fuel cells have considered a more detailed reaction mechanism. The model developed by Eikerling and Kornyshev<sup>16</sup> considered a single-step ORR to be reversible at the cathode. Antoine *et al.*<sup>7</sup> proposed an impedance model with three steps for the ORR kinetics in acidic medium on platinum nanoparticles. Antoine *et al.*<sup>7</sup> proposed the presence of unspecified reaction intermediates and did not consider the kinetics at the anode. They explained that the low-frequency inductive loops were a result of the second relaxation of the adsorbed species involved in the different steps of the ORR. More recently, Wiezell *et al.*<sup>17</sup> considered a two-step hydrogen oxidation reaction (HOR) and have reported low-frequency inductive loops. They have explained that the inductive loops were the result of changing factors such as water concentration, membrane thickness, hydrogen pressure and the HOR kinetics.

The role of intermediates in the ORR is supported by independent observation of hydrogen peroxide formation in PEM fuel cells.<sup>18–20</sup> A rotating-ring-disk-electrode study<sup>21</sup>



(a)



(b)

Figure 1: Impedance data obtained for a PEM Fuel cell that were determined by measurement model techniques to be consistent with the Kramers Kronig relations. Symbols represent experimental data and solid lines represent the measurement model fit. The arrow points to the nominal zero-frequency impedance obtained from the slope of the polarization curve. a) Data collected at  $0.2 \text{ A/cm}^2$  using the Scribner 850C; and b) Data collected at  $0.2 \text{ A/cm}^2$  using the Scribner 850C; and b) Data collected at  $0.2 \text{ A/cm}^2$  using Gamry FC350 impedance instrument coupled with a Dynaload RBL:100V-60A-400W electronic load.

revealed that formation of the peroxide on platinum particles supported on carbon (catalyst used in the fuel cell) is quite possible by two-electron reduction while the formation is not an option on clean bulk platinum. The hydrogen peroxide formed as an intermediate causes chemical degradation of the membrane.<sup>20</sup> Other reactions have also been reported which could potentially account for the low-frequency features observed in the impedance data. Platinum dissolution, for example, has been observed in PEM fuel cells<sup>22</sup> which can lead to the loss of catalytic activity and, consequently, to the degradation of the fuel cell performance.<sup>23</sup> Side reactions and the associated intermediates can degrade fuel cell components such as membranes and electrodes, thereby reducing the lifetime, one of the crucial issues in the commercialization of fuel cells.<sup>24,25</sup>

The influence of side reactions and reaction intermediates on the impedance response is comparatively unexplored. The objective of this work was to identify chemical and electrochemical reactions that could account for the low-frequency inductive impedance response and could therefore be incorporated into mechanistic models of the impedance response of PEM fuel cells. The model responses were compared to the experimental results. Experimental investigations were also conducted to support the possibility of the formation of the intermediates identified in the reaction mechanisms.

#### 2. Experimental

The experimental system, impedance instrumentation, and supporting experimental techniques are presented in this section.

#### 2.1. Materials and Chemicals

The membrane electrode assembly (MEA) employed 0.0308 mm (2 mils) thick Nafion N112. The catalyst layers of the MEA were platinum supported on carbon with a Pt catalyst loading of 0.4 mg/cm<sup>2</sup> on both the anode and the cathode sides. The material of the flow channel used was graphite with a single channel horizontal serpentine flow configuration with the outlet lower than the inlet to facilitate removal of condensed water. Hydrogen gas was used as fuel and compressed air was used as oxidant for experiments. Compressed N<sub>2</sub> was used for purging of the fuel cell before and after experiments. A Barnstead E-Pure Water System was used as a source of deionized water delivered to the anode and the cathode humidifiers. The active surface area was 5 cm<sup>2</sup>.

The 850C fuel-cell test station (supplied by Scribner Associates, Southern Pines, NC) was used to control reactant flowrates and temperatures. The test station was connected to a computer by an interface for data acquisition. The gas flow to the anode was held at temperature of  $40 \pm 0.1$  °C, and the gas flow to the the cathode was held at a temperature of

 $35 \pm 0.1$  °C. The gas flows were humidified to 100 percent relative humidity at the respective temperatures. The cell temperature was held at  $40 \pm 0.1$  °C. The hydrogen flow rate was 0.1 liters/min and the air flow rate was 0.5 liters/min, providing a stoichiometric ratio of 2.

## 2.2. Electrochemical Impedance Measurements

Impedance measurements were performed using two different systems. The Scribner Associates 850C Fuel Cell Test Stand contains both an electronic load and a frequency response analyzer. Impedance measurements obtained with the 850C were compared to impedance collected using a Gamry Instruments FC350 impedance analyzer coupled with a Dynaload electronic load RBL 100V-60A-400W. The two instruments yielded comparable levels of stochastic errors and artifact-free frequency range.<sup>9</sup> All electrochemical measurements were performed with a two-electrode cell in which the anode was used as a pseudo-reference electrode.

The impedance measurements were conducted in galavanostatic mode for frequency range of 1 kHz to 1 mHz with a 10 mA peak-to-peak sinusoidal perturbation. The corresponding potential perturbation ranged from 0.04 mV to 0.4 mV. The frequencies were spaced in logarithmic progression with 10 points per frequency decade. Impedance scans were conducted in auto-integration mode with a minimum of 2 cycles per frequency measured. Each scan required 5 hours for the Scribner system and 3 hours for the Gamry system. The difference in time required can be attributed to differences in impedance settings. Multiple scans of impedance measurements were performed at different points on the polarization curve.

#### 3. Model Framework

The mass-transfer problem was simplified significantly by assuming that the membrane properties were uniform, that issues associated with flooding and gas-phase transport could be neglected, and that the heterogenous reactions took place at a plane, *e.g.*, the interface between the catalyst active layer and the the proton exchange membrane. This preliminary approach does not account for the spatial distribution of the catalyst particles in the catalyst layer, but this simplified treatment is sufficient to explore the role of specific reaction on impedance features, such as low-frequency inductive loops.

The mathematical framework for model development is summarized briefly in this section. The development of impedance models for specific hypothesized reaction sequences is presented in a subsequent section.

## 3.1. Polarization Curve

The current density can be expressed as a function of applied potential V, concentrations of reactants  $c_i(0)$ , and surface concentrations  $\gamma_k$  as

$$i = f(V, c_i(0), \gamma_k) \tag{1}$$

The steady state surface coverage was calculated by a material balance of the intermediates involved in the proposed reaction mechanism. Concentrations of reactants and products at the reaction plane were calculated from the bulk concentrations  $c_i(\infty)$  and the mass-transferlimited current densities  $i_{\text{lim}}$  using

$$\overline{c}_i(0) = c_i(\infty)(1 - \frac{\overline{i}}{i_{\lim}})$$
(2)

where

$$i_{\rm lim} = \frac{nFD_i c_i(\infty)}{\delta_i} \tag{3}$$

 $\delta_i$  is the diffusion film thickness, F is Faraday's constant,  $D_i$  is the diffusivity of the reactant, and n is the number of electron exchanged in the reaction.

The steady-state current for each reaction was calculated as function of overpotential using the values of the steady-state surface coverage and concentrations. The total steady-state current was calculated by adding current contributions from all participating reactions at the cathode, and the total current at the anode was equated to the total current from the cathode to calculate the anode overpotential  $\eta_a$ , *i.e.*,

$$\eta_a = \frac{1}{b_{\mathrm{H}_2}} \log \left( \frac{\bar{i}_{T,c}}{k_{\mathrm{H}_2} c_i(\infty) \left( 1 - \frac{\bar{i}_{T,c}}{i_{\mathrm{lim}}} \right)} \right)$$
(4)

where  $\bar{i}_{T,c}$  is the total cathode current,  $k_{\rm H_2}$  is the rate constant for the HOR,  $c_{\rm H_2}$  is the concentration of the hydrogen, and  $b_{\rm H_2}$  is the Tafel slope for the HOR. The total overpotential  $\eta$  was given by

$$\eta = V_{eq.} - \eta_c - \eta_a - IR_e \tag{5}$$

 $\eta_c$  is the cathode overpotential and  $R_e$  is the frequency-independent ohmic resistance.

#### 3.2. Impedance Response

The Faradaic current density can be expressed in terms of a steady state contribution i and an oscillating contribution  $\tilde{i}$  as

$$i_f = \bar{i}_f + \operatorname{Re}\left\{\tilde{i}_f \exp\left(j\omega t\right)\right\}$$
(6)

where  $j = \sqrt{-1}$ , t is time, and  $\omega$  is the frequency in units of s<sup>-1</sup>. A Taylor series expansion of equation (1) about the steady-state value yields

$$\widetilde{i}_{f} = \left. \frac{\partial f}{\partial V} \right|_{c_{i}(0),\gamma_{k}} \widetilde{V} + \left. \frac{\partial f}{\partial c_{i,0}} \right|_{V,c_{j\neq i}(0),\gamma_{k}} \widetilde{c}_{i}(0) + \left. \frac{\partial f}{\partial \gamma_{k}} \right|_{V,c_{i}(0),\gamma_{j\neq k}} \widetilde{\gamma}_{k} \tag{7}$$

where  $\widetilde{V}_{i}, \widetilde{c}_{i}(0)$  and  $\widetilde{\gamma}_{k}$  were assumed to have small magnitudes such that the higher-order terms in the expansion can be neglected.

An expression for  $\tilde{c}_i(0)$  was found in terms of  $\tilde{i}_f$  using

$$\widetilde{i_f} = nFD_i \frac{\partial c_i}{\partial y} \tag{8}$$

or

$$\widetilde{c}_i(0) = \frac{\widetilde{i}_f \delta_i}{nFD_i} \left( -\frac{1}{\theta'_i(0)} \right) \tag{9}$$

where  $\theta'_i(0)$  represents the dimensionless gradient of the oscillating concentration  $\theta = \tilde{c}_i/\tilde{c}_i(0)$ . Under the assumption that mass transfer is through a Nernst stagnant diffusion layer,

$$\frac{-1}{\theta_i'(0)} = \frac{\tanh\sqrt{jK_i}}{\sqrt{jK_i}} \tag{10}$$

where

$$K_i = \frac{\omega \delta_i^2}{D_i} \tag{11}$$

The total current was found by summing the interfacial charging current and the Faradaic current, *i.e.*,

$$i = i_f + C_0 \frac{dV}{dt} \tag{12}$$

where  $C_0$  is the interfacial capacitance. For a small-amplitude sinusoidal perturbation, the total current was written as

$$\widetilde{i} = \widetilde{i}_f + j\omega C_0 \widetilde{V} \tag{13}$$

An analytical expression for impedance was calculated for each model using

$$Z = \frac{\widetilde{U}}{\widetilde{i}} = R_e + \frac{\widetilde{V}}{\widetilde{i}} \tag{14}$$

where  $R_e$  is the frequency independent ohmic resistance, U is the cell potential, and V is the cell potential. The Faradaic current was calculated by summing contributions from all the reactions in accordance with the reaction stoichiometry.

#### 4. Impedance Response for Proposed Reaction Mechanisms

Three impedance models were investigated for the interpretation of low-frequency inductive loops. Model 1 incorporates a single-step ORR at the cathode and a single-step HOR at the anode. Model 2 treats hydrogen peroxide formation in a two-step ORR at the cathode along with a single-step HOR at the anode, and Model 3 includes the single-step ORR coupled with the platinum catalyst dissolution at the cathode along with a single-step HOR at the anode. For the present work, the surface concentration of the proton was assumed to be constant and was therefore incorporated into the effective reaction rate constant.

#### 4.1. Model 1: Simple Reaction Kinetics

The reaction sequence for model 1 can be expressed as an equivalent circuit as shown in Figure 2(a) where the boxes represent Faradaic impedances that are to be determined for the specific assumption reaction mechanisms.

The ORR

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{15}$$

was assumed to take place at the cathode. The steady-state current density expression corresponding to this reaction was assumed to be

$$i_{O_2} = -K_{O_2} c_{O_2}(0) \exp\left(-b_{O_2} \eta_{O_2}\right) \tag{16}$$

where  $K_{O_2} = nFk_{O_2}$ ,  $k_{O_2}$  is the rate constant, *n* is the number of electron exchanged in the reaction,  $b_k = \alpha_k F/RT$ ,  $\alpha_k$  is the apparent transfer coefficient for reaction *k*, *R* is the universal gas constant, *T* is absolute temperature, and *F* is Faraday's constant.

The single-step HOR

$$\mathrm{H}_2 \to 2\mathrm{H}^+ + 2\mathrm{e}^- \tag{17}$$

was assumed to take place at the anode. The corresponding steady-state current expression was

$$\bar{i}_{\rm H_2} = K_{\rm H_2} \bar{c}_{\rm H_2}(0) \exp\left(b_{\rm H_2} \eta_{\rm H_2}\right) \tag{18}$$

where  $K_{\text{H}_2} = nFk_{\text{H}_2}$ ,  $k_{\text{H}_2}$  is the rate constant, and *n* is the number of electron exchanged in the reaction.

#### 4.2. Model 2: Hydrogen Peroxide Formation

The mathematical framework for Model 2 can be represented as the equivalent circuit presented in Figure 2(b). The ORR was assumed to take place in two steps in accordance to the reaction scheme as discussed in the literature.<sup>19</sup> The first reaction

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{19}$$



Figure 2: Equivalent circuit diagrams for proposed reaction sequences where the boxes represent Faradaic impedances that are to be determined for the specific assumption reaction mechanisms: a) Model 1; b) Models 2 and 3.

involves formation of hydrogen peroxide  $(H_2O_2)$  which reacts further to form water, *i.e.*,

$$H_2O_2 + 2H^+ + 2e^- \to 2H_2O$$
 (20)

The steady-state current for reaction (19) can be expressed as

$$i_{\rm O_2} = -K_{\rm O_2} c_{\rm O_2}(0) \left(1 - \gamma_{\rm H_2O_2}\right) \exp\left(-b_{\rm O_2} \eta_{\rm O_2}\right) \tag{21}$$

where  $K_{O_2} = nFk_{O_2}$  with the same notations defined for Model 1 and  $\gamma_{H_2O_2}$  is the fractional surface coverage of hydrogen peroxide. The current density corresponding to the reaction (20) can be expressed as

$$i_{\rm H_2O_2} = -K_{\rm H_2O_2} \Gamma \gamma_{\rm H_2O_2} \exp\left(-b_{\rm H_2O_2} \eta_{\rm H_2O_2}\right)$$
(22)

where  $K_{H_2O_2} = nFk_{H_2O_2}$ . The electrochemical reaction at the anode was given as reaction (17), and the corresponding current expression was given as equation (18).

# 4.3. Model 3: Platinum Dissolution

A general equivalent circuit for model 3 is presented in Figure 2(b). Platinum dissolution was proposed by a reaction scheme similar to that reported by Darling *et al.*<sup>22</sup> which takes place in a two-step reaction scheme according to an electrochemical reaction

$$Pt + H_2O \leftrightarrow PtO + 2H^+ + 2e^-$$
(23)

in which PtO is formed, followed by a chemical dissolution reaction

$$PtO + 2H^+ \leftrightarrow Pt^{+2} + 2H_2O \tag{24}$$

The current density corresponding to the reaction (23) was given by

$$i_{\rm Pt} = K_{\rm Pt,f} (1 - \gamma_{\rm PtO}) \exp\left(b_{\rm Pt,f} \eta_{\rm Pt,f}\right) - K_{\rm Pt,b} \gamma_{\rm PtO} \exp\left(-b_{\rm Pt,b} \eta_{\rm Pt,b}\right)$$
(25)

where  $\gamma_{PtO}$  is the fractional surface coverage by the PtO. The dissolution of the PtO was assumed to occur according to

$$r_{\rm PtO} = K_{\rm PtO} \gamma_{\rm PtO} \tag{26}$$

and the corresponding material balance for the PtO was expressed as

$$\Gamma \frac{\partial \gamma_{\rm PtO}}{\partial t} = -i_{\rm Pt} - r_{\rm PtO} \tag{27}$$

where  $\Gamma$  is the maximum surface coverage.

The formation of the platinum oxide was proposed to have an indirect influence on the ORR at the cathode by changing the effective rate constant for the reaction. Thus,

$$K_{\rm eff} = K_{\rm Pt} + (K_{\rm PtO} - K_{\rm Pt})\gamma_{\rm PtO} = f(\gamma_{\rm PtO})$$
(28)

where  $k_{\text{Pt}}$  is the rate constant on a platinum surface and  $k_{\text{PtO}}$  is the rate constant on a platinum oxide surface. It was assumed that  $k_{\text{PtO}} \ll k_{\text{Pt}}$ . The ORR was assumed to take place according to reaction (15) with a steady-state current density given by

$$i_{\rm O_2} = -K_{\rm eff} c_{\rm O_2}(0) \exp\left(-b_{\rm O_2} \eta_{\rm O_2}\right) \tag{29}$$

where  $K_{\text{eff}}$  is defined by equation(28).

A mechanism that involves Pt dissolution is supported by CV measurements which reveled a reduction in the electrochemically active surface area and by the detection of trace amounts of platinum in the effluent from the fuel cell.

## 5. Results and Discussions

Mathematical expressions were developed for the impedance response of a fuel cell that accounted for the reaction mechanisms described in the previous sections. These models were compared to the experimental polarization and impedance data. The method employed was to calculate the polarization curve that matched closely the experimental results and then to use the same parameters to estimate the impedance response at different currents. Direct regression was not employed as the model does not account explicitly for the non-uniform reaction rates caused by the serpentine flow channels. Sample results are presented here. A more complete presentation of the results is in preparation.

Constant values were assumed for the double layer capacitance, the Tafel slope, the ionic resistance in the catalyst layer, the membrane resistance, and the Oxygen permeability with values taken from the literature.<sup>2</sup> The impedance response for all simulations corresponded to a frequency range of 10 kHz to 0.001 mHz. The low frequency limit was used to explore more fully the low-frequency inductive features.

## 5.1. Response Analysis of Model 1

The polarization curve generated from model 1 is compared to experimental data in Figure 3. The low current region was controlled by kinetics, the intermediate current region was controlled by ohmic processes and the high current region was controlled by mass transport processes. To map the overall behavior of the fuel cell, the impedance responses were generated at several steady-state points on the polarization curve. The polarization behavior



Figure 3: A comparison of the polarization Curve generated by Model 1 with experimental data.

of the fuel cell is broadly divided in three regions: the low current region is under kinetics control, intermediate current region is ohmic control and the high current region is mass transport control. The results presented in the present work are for the intermediate current region.

The model impedance response is compared to experimental results at an intermediatecurrent (1A or  $0.2 \text{ A/cm}^2$ ) in Figure 4. Model 1 provides a reasonable representation of the capacitive loops, but cannot account for the inductive loops seen at low frequency. Similar agreement was seen at both lower and higher current densities. The model that accounts for only the hydrogen oxidation and oxygen reduction reactions cannot explain the inductive behavior at low frequencies.

## 5.2. Response Analysis of Models 2 and 3

The impedance response for the model with the hydrogen peroxide formation (Model 2) consisted of one high-frequency capacitive loop and one low-frequency inductive loop. The impedance response for the model accounting for platinum dissolution (Model 3) also consisted of one high-frequency capacitive loop and one low-frequency inductive loop. The polarization curve generated with these models is presented in Figure 5. The presence of the side reactions in the model has no discernable influence on the polarization curve as



Figure 4: A comparison of the impedance response generated at an intermediate current density by Model 1 with the corresponding experimental data.



Figure 5: A comparison of the polarization curves generated by Models 2 and 3 with experimental data.



Figure 6: A comparison of the impedance response generated at intermediate current density with Models 2 and 3 with experimental data.

these reactions are assumed to be taking place at a low rate as compared to the dominant hydrogen oxidation and oxygen reduction reactions. As shown in Figure 6 for the intermediate current density, impedance measurements are much more sensitive to the presence of the side reactions. Both models 2 and 3 were found to be capable of yielding low-frequency inductive loops. Similar results were found at lower and higher current densities.

## 6. Conclusions

Three analytic impedance models were derived from consideration of specific reaction sequences proposed to take place in PEM fuel cells. The model that accounted only for hydrogen oxidation and oxygen reduction could not explain the low-frequency inductive loops observed in experimental data. Models that accounted for additional reactions, *i.e.*, formation of hydrogen peroxide and formation of PtO with subsequent dissolution of Pt, could predict low-frequency inductive loops. These results show that either of these reaction mechanisms could account for the experimentally observed low-frequency inductive loops.

The formation of intermediates in the proposed reaction mechanism were confirmed by experimental investigations including analysis of the outlet water from the cathode by the ICP-MS, estimation of the hydrogen crossover through membrane by CV, and estimation of electrochemically active area by LSV. The decrease in the electrochemical active area of the catalyst observed by the LSV experiment confirmed platinum deactivation, and detection of Pt in the effluent by ICP-MS confirmed Pt dissolution. The substantial hydrogen crossover through the membrane estimated by CV experiments confirmed peroxide formation. Thus, both reaction sequences 2 and 3 are likely in the PEM fuel cell under study, and both reaction sequences 2 and 3 were found to yield low-frequency inductive loops in the impedance response. This work suggests that quantitative analysis of low-frequency inductive loops may provide a useful characterization of reactions which reduce the efficiency and operating life-time of PEM fuel cells.

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