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DYNAMIC MODELLING AND CONTROL OF POLYBENZIMIDAZOLE FUEL CELLS

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ABSTRACT

A dynamic fuel-cell model for high-temperature PEM fuel cells with PBI membranes has been developed in Simulink. In such models it is common to use the current density as input variable, but this model uses a different approach. The current density is regarded as an unrealistic control variable, since it cannot be controlled directly. Instead, it is possible to simulate the effect of changing the characteristic of the external circuit, a more realistic manipulated variable, with resistances or MOSFET transistors. Experimental runs have been executed to confirm the theoretical development. To measure the parameters needed for the model, impedance tests on the fuel cell are considered an effective way to extract parameters by means of parameter regression: the model has therefore been extended and reimplemented to produce simulated impedance plots, that show good agreement with experimental measurements on fuel cells.

INTRODUCTION

Research in fuel cells has shown a rapid growth. The relatively minor interest for their dynamics has recently increased as a topic in its own merit and as a prerequisite for control analysis and controller design. However, many models provided in the literature [1, 2, 3, 4, 5] were not intended for control studies, and in that context they are often "flawed" because they consider *current density* as an input to the system. This is unrealistic from a process-control perspective, because in reality the current is determined by the characteristics of the fuel cell and of its external load, and is not set directly by the control system.

Currently, most PEM fuel cells are based on electrolytes that rely on liquid water for protonic conduction, binding them to an operating temperature below 100 °C (unless pressurized). In polybenzimidazole (PBI)-based fuel cells, water is produced in gaseous form, and since the membrane relies on phosphoric acid to function, the water management issue is removed. Finally, high-temperature PEM fuel cells based on PBI electrolyte exhibit a high tolerance to carbon monoxide [6].

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The parameters used in the model need to be measured appropriately. Impedance tests are measurement of the impedance of the fuel cell at various frequencies. By applying the proposed model structure to calculate the impedance of the fuel cell, a plot of clear resemblance to experimental results is obtained. The fundamental theory about impedance spectroscopy can be found in many textbooks, for example in Macdonald [7].

The objective of this paper is to show the development of a model using the external circuit's characteristic as an input, and how this model is able to explain experimental results observed on a PBI fuel cell. Another objective is making the point that dynamic models for control-design purposes should make use of proper manipulated input variables, instead of using either voltage or current as an input. Furthermore, the usefulness of impedance measurements in determining the model parameters will be demonstrated.

EXPERIMENTAL METHODS

Experiments were carried out on a PBI fuel cell, previously assembled in the laboratory of the Depart-

ment of Materials Technology at NTNU, to determine the transient response of the cell to a variable load. The load itself was assembled as a variable-resistance board, with two resistances in parallel; in series with one of these resistances, a switch could be opened and closed manually. The PBI fuel cell was kept at a constant temperature of 150 °C by an external electric heater. The fuel cell ran on industrial-grade hydrogen and oxygen at atmospheric pressure.

EXPERIMENTAL RESULTS

The results obtained switching from an initial resistance to a smaller one and back are shown in figure 1. It can be seen how the operating point moves from a resistance's characteristic to the other along parallel lines. As a reference, the steady-state polarization curve is plotted as well. Since some hysteresis was experienced in its measurement, the polarization curve is not an entirely precise reference.

Looking carefully at figure 1, it is clear that in the descent to steady-state some transients are faster than others; this can be seen by the number of markers on the trajectory in the *V*-*I* plane. It appears that the electrochemical transient to 12.88 Ω is slower than the one to 5.47 Ω, which is in turn slower than the one to 2.85 Ω.

There is therefore an indication that the electrochemical transient can have *different time constants* depending on both the start and the end point. This behavior could be related to the one observed in a Master's thesis written at NTNU [8], where the same proportional controller, applied on a PBI fuel cell, performed too aggressively in some operating ranges and too mildly in others.

MODELLING

To model the behaviour presented in the previous sections and in figure 1, we actually only need to consider a simple differential equation referred to the cathode of the cell: it is basically a charge balance of a capacitor (3). This capacitor represents what is known in electrochemistry as the *charge double layer*, but also other electrically charged species. At this point we are neglecting the anodic overvoltage and concentrating instead on the cathodic one, but this assumes we do not have any catalyst poison (as CO) on the anode side. Butler-Volmer's equation (1) is implemented with an iterative loop to find the value of the overvoltage, using Tafel's approximation as an initial value for the iterative algorithm[1]. A scheme of the model is provided in figure 2.

A preliminary analysis was run to establish the influence of diffusion transients on the response of fuel cells. The results indicated diffusion transients in the order of 0.01–0.1 seconds, which is faster than the control bandwidth of interest[2]. Furthermore, the gas concentration at the reaction sites has a significant effect only when near to the mass-transfer limit, where oxygen cannot diffuse fast enough from bulk to the reaction surface. Because of these considerations, the model will assume that diffusion transients settle instantaneously, and also that all partial-pressure profiles are linear from bulk to reaction site. The model has later been extended to incorporate the simulation of the anodic overvoltage, but this will be useful only when a reliable simulation of the dynamics of CO poisoning in PBI fuel cells has been developed; without CO poisoning, the anodic overvoltage is negligible for most practical purposes.

The activation overvoltage η of an electrode can be calculated for a given reaction current density i_r and an exchange current density i_0, according to the Butler-Volmer equation:

$$i_r = i_0 \left(\mathrm{e}^{\alpha \frac{nF}{RT} \eta} - \mathrm{e}^{-(1-\alpha) \frac{nF}{RT} \eta} \right) \qquad (1)$$

The reversible potential E^{rev} can be found with well-known thermodynamic data, and the ohmic loss is $r_{cell}\, i$. The cell voltage is then found as:

$$V = E^{rev} - \eta - r_{cell}\, i \qquad (2)$$

During transients, the reaction current density i_r is different from the current density i, which we calculate dividing the current in the circuit by the fuel cell's area. Looking at the following differential equation [1], it is obvious to see that the difference $i - i_r$ is actually the driving force of the transient behaviour of the activation overvoltage:

$$\dot{\eta} = \frac{i - i_r}{C} \qquad (3)$$

[1] Using Tafel as an initial approximation accelerates the algorithm signifi cantly.

[2] We are assuming that the bandwidth of interests begins from time constants of 0.2 seconds, as is typical for automotive applications [9].

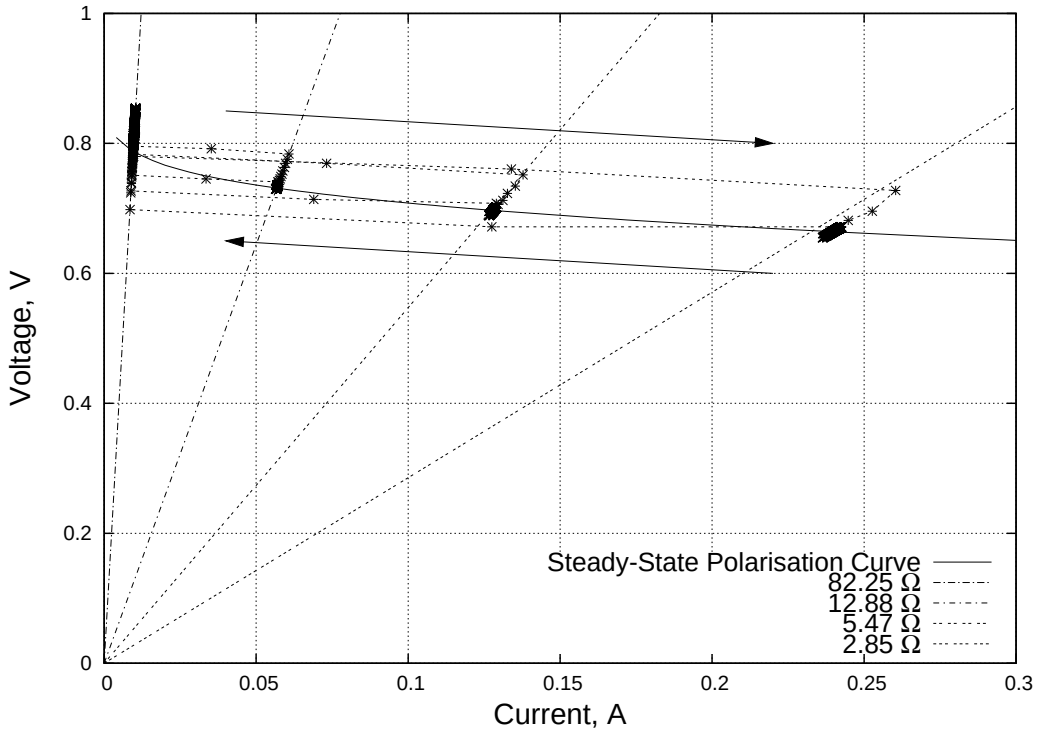

Figure 1: Operating points' path in the V-I diagram after step changes in the external circuit's resistance, starting from 82.25 Ω and switching back. The arrows indicate the path in the I-V plan.

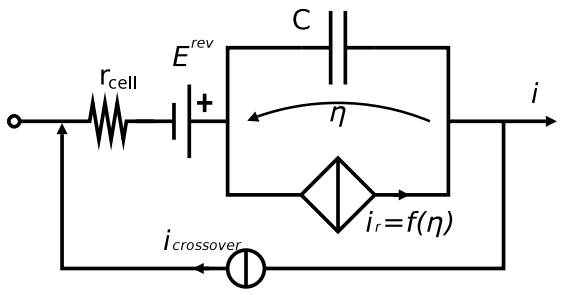

Figure 2: Diagram of the cathode-only fuel-cell model.

This is the only differential equation that we will be considering in order to compute the transient of the fuel cell. The cell's load in the model is generally allowed to vary with time, and is described by a function in the form $I = f(V,t)$.

The model can be expressed in an electrical-circuit diagram, as shown in figure 2. There, one can see the internal resistance r_{cell}, the reversible potential E^{rev}, the capacitor C and its voltage η. The bipole in parallel with the capacitor is a nonlinear voltage-controlled current generator, that enforces the Butler-Volmer law, and imposes a current i_r as a function of η (and many other parameters). This last bipole is often also modelled as a nonlinear resistance [10], or a linearized value in an area of interest. Incidentally, the ideal generator E^{rev} and the resistance r_{cell} in series with it can be viewed as a Thevenin equivalent circuit. Finally, a crossover current density (representing either electronic conductivity of the membrane or permeation of hydrogen molecules) is modelled with a current generator, and given a constant value; PBI fuel cells usually have small values for crossover current density, and a typical value is 5 A/m^2.

The actual integration of differential equation 3 is not very simple, since i_r is a function of many parameters, and also of η itself, through the Butler-Volmer equation (1). An iterative loop is therefore necessary to calculate i_r at all integration steps, and this is the major computational cost of the simulation. The resulting layout for the fuel-cell model in Simulink is shown in figure 3.

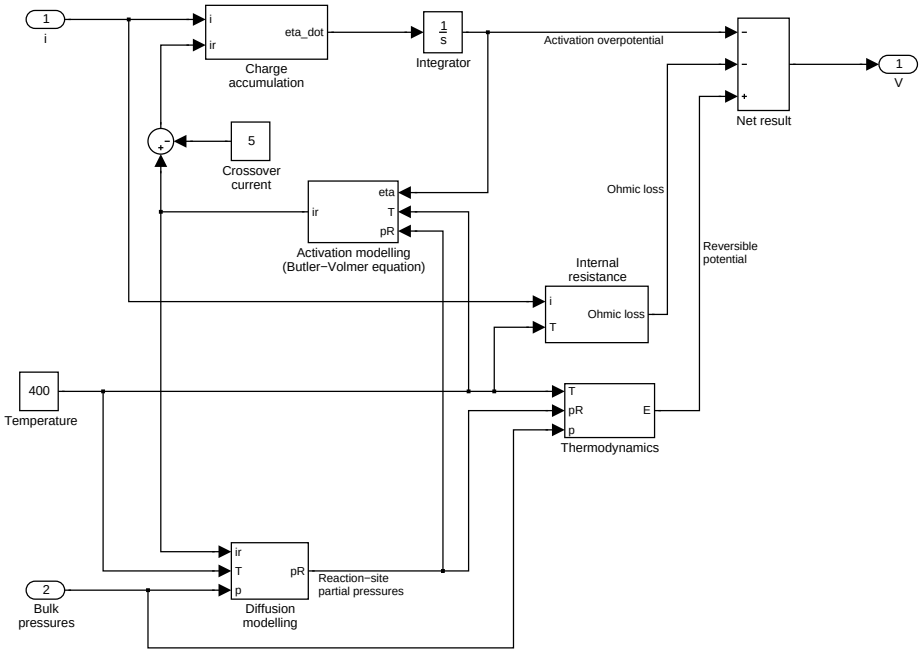

Figure 3: The Simulink implementation of the fuel-cell model, with only the cathode overvoltage being modeled.

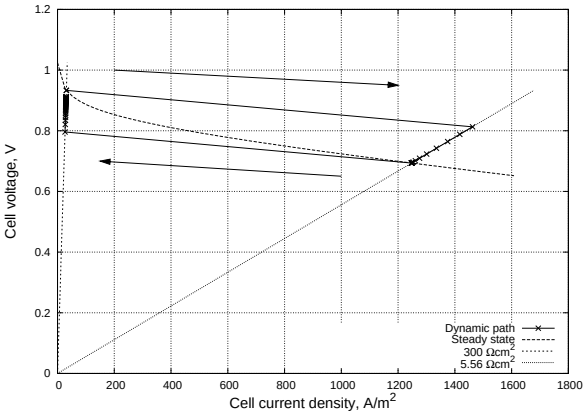

Figure 4: A typical output of the model: a simulation of a transient from a steady-state operating point to a new value of the external resistance, and back. Assumed temperature is 150 °C. The markers are spaced by 0.01 s.

MODEL RESULTS AND INSIGHTS

The cause of the sudden "kick" in the dynamic path diagram, as can be seen in the simulation in figure 4 and in experimental results in figure 1, is caused by the simple fact that the operating point *must* always lie on the load's characteristic, when the load is purely resistive. It is possible to determine to *which coordinates* on the load's characteristic the operating point will jump, considering that the activation overvoltage η varies *continuously* with time; when a step change in the outer load happens at time t_0, η will therefore be the same for times t_0^+ and t_0^-.

Using the load characteristic as the model's input has allowed to simulate real laboratory results, and has given the possibility of simulating the implementation of MOSFETs as manipulated variables in control of fuel cells. Pulse-width modulation (PWM) has also been implemented.

Looking at figure 4, it is clear that the drawn part of the polarization curve is closer to the characteristic of the higher resistance, when distance is measured along the i axis. Since $\dot{\eta}$ is proportional to the distance between the intersections of the instantaneous characteristic with the polarization curve and the external resistance along the i axis, i.e. $i - i_r$, it follows that the transient to the lower resistance will be faster than the one coming back, because of the higher val-

ues of $i - i_r$ along that path; this is confirmed by the experimental measurement shown in figure 1.

An analytic expression for the time constants has been found. Assuming that C and r_{cell} are constant, and that functions $V = \Psi(i)$ (the external load's characteristic) and $\eta(i_r, \ldots)$ are given, the time "constant" τ depends essentially on i and i_r:

$$\tau(i, i_r) = \frac{C}{\left(r_{cell} + \frac{\mathrm{d}\Psi}{\mathrm{d}i}\Big|_i\right)^{-1} + \left(\frac{\mathrm{d}\eta}{\mathrm{d}i_r}\Big|_{i_r}\right)^{-1}} \quad (4)$$

Considering the basic expression of the voltage of a fuel cell (2), and looking at figure 4, it is evident that the instantaneous characteristic at a given steady-state point stays at higher voltages than the polarization curve when moving to higher values of current density, and, conversely, at lower voltages for lower values of current density; in other words, a step change in the external resistance always results in some overshoot. Under these assumptions, a perfect step change in power output can in theory be obtained if the controller manages to steer the fuel cell properly.

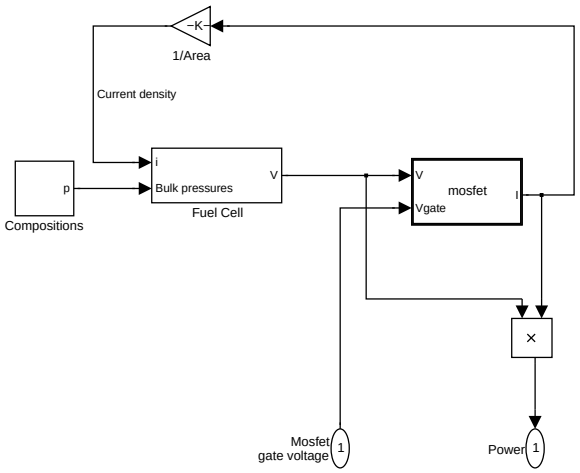

Figure 5: The structure of the fuel cell-MOSFET system in Simulink. The control input is the MOSFET's gate voltage, while the output is the power produced by the cell.

PID CONTROL

Using Skogestad's PID-tuning rules [11], a simple PI controller was devised to operate a fuel cell so that its power output would match the power necessary for an appropriately-scaled standard driving cycle. The control system operates by manipulating the gate voltage of a MOSFET transistor, which acts like a "valve" for the cell's power output. Measuring the error in watts, and using the parameters of a IRF1404 MOSFET by International Rectifier Inc., the parameters of the controller were found to be $k = 0.191$ and $\tau_I = 0.4\,\mathrm{s}$.

Several driving cycles were implemented, and in figure 6 the results for the European Urban Driving Cycle (ECE 15) are shown. It can be seen that the cell is definitely slower at following the reference signal at low power values, which correspond to high voltages and low activation overvoltages. This is consistent with the formula for time constants (4) that was found previously.

It should be remarked that this synthesis has not yet accounted for disturbances, since a satisfactory model for the main disturbance in the process, CO poisoning, is not yet available; it would therefore be

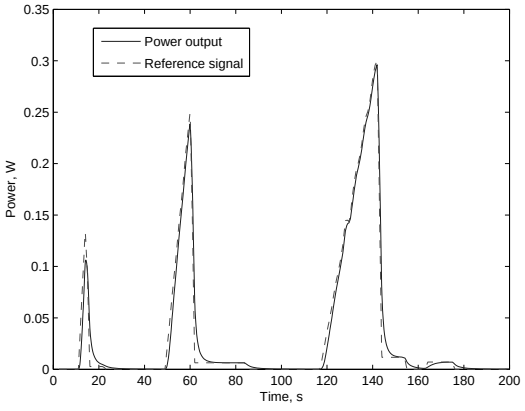

Figure 6: Simulation of a feedback-controlled fuel cell trying to deliver the power required by the ECE 15 standard driving cycle.

possible to make the cell model follow the reference almost perfectly if the proportionality constant in the controller were set to $k = \infty$. Of course this would just be a simulation trick. A more thorough synthesis will be possible when the effect of disturbances will have been estimated.

IMPEDANCE MEASUREMENTS

Given the model developed above, it is important to obtain values for its parameters. Impedance measurements are a good way to achieve this, allowing visual assessment as well as more precise techniques as nonlinear regression to estimate, among other things, the internal resistance, the overvoltages and the capacitances of both cathode and anode.

Using measurements obtained directly by logging data from transients when changing the load in a certain way is not always a good idea, since these measurements are often clouded by other transients, such as temperature variations at the reaction sites due to the different reaction rate; this is especially true for PBI fuel cells.

Impedance tests are performed by keeping the fuel cell in a known condition of voltage, temperature, partial pressures in the inlet gases, and eventually other relevant state variables, and measuring its impedance at various frequencies. The impedance values can then be plotted in a Bode diagram or, more commonly, in a Nyquist diagram[3].

Model layout

In order to estimate the model parameters, it was necessary to reformulate the model in a way that would present the user a function $Z = f(\mathbf{X}, \Theta)$, where Z is the impedance (in general a complex number), $\mathbf{X}$ is the vector of states, and Θ is the vector of parameters. The model was reimplemented in C++, and an interface function to allow its use in OCTAVE was written[4].

This time, the model was a steady-state model, but included also the anode in the description of the fuel cell. Since most impedance measurements show a "tail" at the highest frequencies, an inductance has been added in series with the fuel cell, and can be considered a parameter of the model. The model scheme is shown in figure 7.

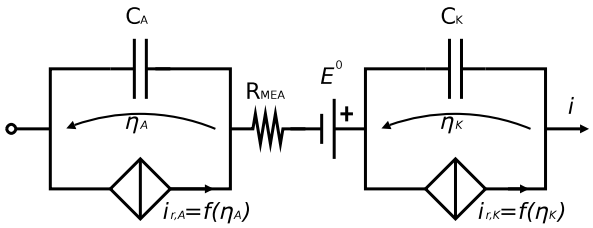

Figure 7: Diagram of the fuel-cell model used for impedance simulations.

Given this model, it is possible to develop the following formula for the impedance of the fuel cell:

$$\begin{aligned} \mathrm{Re}(Z) &= R_{cell} + \frac{R_a}{1+\omega^2 R_a^2 C_a^2} + \frac{R_c}{1+\omega^2 R_c^2 C_c^2} \\ \mathrm{Im}(Z) &= \omega L_{ext} - \frac{\omega R_a^2 C_a}{1+\omega^2 R_a^2 C_a^2} - \frac{\omega R_c^2 C_c}{1+\omega^2 R_c^2 C_c^2} \end{aligned}$$

where we have set, for ease of notation, $R_{\{a,c\}} = \eta_{\{a,c\}}/i_{r,\{a,c\}}$.

The compiled function showed excellent performance, calculating up to 4,000 values of impedance per second on a 2.4 GHz computer. Some values calculated by the function are shown in figure 8.

Assuming these equations are valid, an impedance plot can used to easily estimate some properties just by eye inspection. For instance, it is obvious that, for $\omega \to 0$, $\mathrm{Im}(Z) = 0$ and $\mathrm{Re}(Z) = R_{cell} + R_a + R_c$. When, instead, $\omega \to \infty$, $\mathrm{Re}(Z) = R_{cell}$. Fuel cells often show a similar pattern in impedance plots, with a large semicircle that represents the cathode, and a smaller one to represent the anode. The diameter of these semicircles is respectively R_c and R_a. Since we have defined these quantities to be the overvoltage divided by the reaction current at cathode and anode, and since the overvoltage has a very nonlinear dependence on the reaction current, it follows that these semicircles will vary greatly with the fuel cell's voltage. The presence of a crossover current will also be very influent, as it will cause overvoltage to be present even if there is no current moving through the outer circuit. In this latter case of open-circuit condition, the impedance plot degenerates into a vertical line (or, equivalently, a circle of infinite radius), with equations:

[3] It is common, for such Nyquist diagrams, to use an inverted ordinate axis.

[4] Writing a similar interface function to MATLAB is also possible.

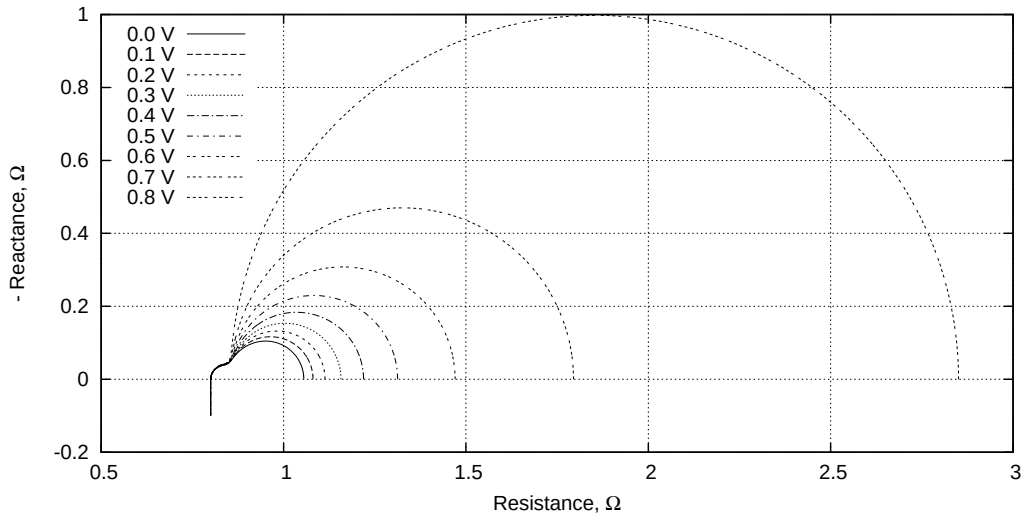

Figure 8: Nyquist plot of the impedance of a fuel cell at various voltages; the operating conditions and parameters are $p_{H_2} = 75\,\mathrm{kPa}$, $p_{O_2} = 21\,\mathrm{kPa}$, $C_a = 100\,\mathrm{F/m^2}$, $C_c = 500\,\mathrm{F/m^2}$, $T = 150\,^\circ C$, $L_{ext} = 1\,\mu\mathrm{H}$, crossover current $i_C = 300\mathrm{A/m^2}$.

$$\mathrm{Re}(Z) = R_{cell} \quad (5)$$

$$\mathrm{Im}(Z) = \omega L_{ext} - \frac{1}{\omega C_a} - \frac{1}{\omega C_c} \quad (6)$$

It should be noted that *Warburg impedance*, caused by diffusion phenomena, cannot be simulated by the model, since it was assumed for simplicity that the diffusion transient was infinitely fast. In experimental results, the Warburg impedance usually appears in the form of a small "tail" in the Nyquist plot in the lower range of frequencies, and more clearly so at high currents.

Finally, it can be demonstrated, by calculating the derivative, that the summit of the semicircles (assuming they can be isolated with reasonable precision) satisfies the equation:

$$\omega_{summit,\{a,c\}} = \frac{1}{R_{\{a,c\}} C_{\{a,c\}}} \quad (7)$$

RC has the dimensions of time, and is therefore often written τ in he literature.

These observations can be used to estimate the value of some parameters, in order to provide a more precise starting guess for a nonlinear regression algorithm for experimental values, which will be subject of further work.

Nyquist plots are also commonly used in control theory; in that context, the impedance can be viewed as the *transfer function* between current and voltage.

CONCLUSION

By using the characteristic of the circuit connected to a fuel cell as an input to a dynamic model, instead of more common inputs as current or voltage, it was possible to explain the shape of transients observed in a laboratory fuel cell, and to estimate their time constants. A simple PI controller has been synthesised, and it was observed that its performance was dependent on the power output of the fuel cell. In order to estimate the parameters of the dynamic model, the model was reimplemented in parametric form. The reimplemented model currently shows acceptable stability and good performance, and will soon be applied to data analysis.

ACKNOWLEDGEMENTS

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