3

Linear and Nonlinear Models of Fuel Cell Dynamics

3.1 Introduction

For preliminary fuel cell power system planning, stability analysis, control strategy synthesis, and evaluation, an appropriate dynamic model of a fuel cell system is desired. Since the existing control-oriented models [1–3] do not contain all water components, which are one of the important factors of fuel cell systems [4], it is difficult to design an accurate dynamic fuel cell model based on the existing models. The main motivation for developing dynamic models of PEMFCs is to facilitate the design of control strategies with objectives such as to ensure good load-following performance, to prevent fuel cell stack damage, and to prolong the stack life by controlling the anode and cathode gases pressures. In this chapter, various models of PEMFCs will be described. Using these models of PEMFCs, appropriate controllers of fuel cell systems can be designed as described in Chapter 5.

3.2 Nonlinear Models of PEM Fuel Cell Dynamics

3.2.1 Unified Model of Steady-State and Dynamic Voltage–Current Characteristics

The performance of a fuel cell can be expressed by the polarization curve, which describes the cell voltage–load current (V–I) characteristics of the fuel cell that are highly nonlinear [1–9]. Optimization of fuel cell operating points, design of the power-conditioning units, design of simulators for fuel cell stack systems, and design of system controllers depend on such characteristics [10]. Therefore, the modeling V–I characteristics of fuel cells is important.

It is observed that the known steady-state V–I characteristics computed from the formulated electrochemical modeling are divided into two components: one of which is named as the steady component including the
thermodynamic potential and the ohmic overvoltage; the other is named as the transient component consisting of the activation and concentration overvoltages. Then, the former is fitted by a low-order least-squares polynomial and the latter is described by a high-order least-squares polynomial. The coefficients in the polynomials can be estimated by using the least-squares technique. The sum of these two components can be used to accurately model the steady-state \( V-I \) characteristics of PEM fuel cells. Furthermore, by introducing the first-order time delay to describe the dynamic response of PEM fuel cells, the developed mathematical modeling can also be used to accurately predict the dynamic \( V-I \) characteristics.

For PEM fuel cells, steady-state \( V-I \) characteristics of a fuel cell are determined by \([1, 4, 5]\)

\[
V_{\text{cell}} = E_N - V_a - V_c - V_{\text{ohm}} = V_{\text{st}} - V_{\text{tr}} \tag{3.1}
\]

where

- \( V_{\text{cell}} \) represents the output voltage of the fuel cell
- \( E_N \) represents the reversible voltage of the fuel cell (also named as the thermodynamic potential)
- \( V_a \) represents the voltage drop due to the activation of the anode and cathode (also named as the activation overvoltage)
- \( V_c \) denotes the voltage drop resulting from the reduction in concentration of the reactants gases or from the transport of mass of oxygen and hydrogen (also named as the concentration overvoltage)
- \( V_{\text{ohm}} \) denotes the ohmic voltage drop resulting from the resistance of the conduction of protons through the solid electrolyte and of the electrons through its path (also named as the ohmic overvoltage)
- \( V_{\text{st}} = E_N - V_{\text{ohm}} \) is the steady component of the cell voltage
- \( V_{\text{tr}} = V_a + V_c \) is the transient component of the cell voltage

The unified mathematical model of the steady-state and dynamic voltage–current characteristics of fuel cells is

\[
v_{\text{cell}}(t) = \sum_{k=0}^{2} p_k (I_{\text{cell}} - I_{\text{st}})^k - \sum_{k=0}^{5} q_k (I_{\text{cell}} - I_{\text{tr}})^k

- \left[ \sum_{k=0}^{5} q_k (I_{\text{cell}} - T_{\text{tr}})^k - (I_{\text{cell}} - I_{\text{tr}})^k \right] (1 - e^{-t/\tau_{\text{cell}}}) \tag{3.2}
\]

where

\[
V_{\text{st}}(I_{\text{cell}}) = \sum_{k=0}^{2} p_k (I_{\text{cell}} - I_{\text{st}})^k
\]
Linear and Nonlinear Models of Fuel Cell Dynamics

\[
I_{st} = \sum_{m=0}^{N_{st}-1} \frac{I_{cellm}}{N_{st}}
\]

\[
V_{tr}(I_{cell}) = \sum_{k=0}^{5} q_k (I_{cell} - I_{tr})^k
\]

\[
I_{tr} = \sum_{m=0}^{N_{tr}-1} \frac{I_{cellm}}{N_{tr}}
\]

where \(I_{cell}\) is the cell current, \(p_k\) the coefficients determined by using the least-squares technique, \(I_{cellm}\) the known discrete current values, and \(N_{st}\) is the number of the given discrete current data for the steady component \((N_{st} \geq 3)\).

Where \(q_k\) are the coefficients determined by using the least-squares technique, and \(N_{tr}\) is the number of the given discrete current data for the transient component \((N_{tr} \geq 6)\).

### 3.2.2 Simulation Results

The Ballard Mark V PEM fuel cell is used to test the proposed model. Tables 3.1 and 3.2 show the computed coefficients in the steady and transient components polynomials, respectively. These coefficients are computed by using the least-squares technique, based on the data from the formulated electrochemical modeling and the parameters of the Ballard Mark V PEM fuel cell listed in Table 3.3 (Figures 3.1 and 3.2).

### 3.2.3 Nonlinear Model of PEM Fuel Cells for Control Applications

A PEM fuel cell consists of a polymer electrolyte membrane sandwiched between two electrodes (anode and cathode) in Figure 3.3. In the electrolyte,

**TABLE 3.1**

<table>
<thead>
<tr>
<th>(k)</th>
<th>0</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(p_k)</td>
<td>0.110149E+01</td>
<td>-0.297366E-02</td>
<td>-0.183457E-04</td>
</tr>
</tbody>
</table>

**TABLE 3.2**

<table>
<thead>
<tr>
<th>(k)</th>
<th>0</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(q_k)</td>
<td>0.516228E+00</td>
<td>0.298822E-02</td>
<td>0.265448E-04</td>
</tr>
<tr>
<td>(k)</td>
<td>3</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>(q_k)</td>
<td>-0.323092E-05</td>
<td>-0.603896E-07</td>
<td>0.349527E-08</td>
</tr>
</tbody>
</table>
only ions can pass by, and electrons are not allowed to go through. So, the flow of electrons needs a path like an external circuit from the anode to the cathode to produce electricity because of the potential difference between the anode and cathode. The overall electrochemical reactions for a PEM fuel cell fed with hydrogen-containing anode gas and oxygen-containing cathode gas are as follows:

\[
\text{Overall reaction: } 2H_2 + O_2 \rightarrow 2H_2O
\]

The overall electrochemical reactions for a PEM fuel cell fed with hydrogen-containing anode gas and oxygen-containing cathode gas are as follows:

\[
\text{Anode reaction: } 2H_2 \rightarrow 4H^+ + 4e^-
\]

\[
\text{Cathode reaction: } O_2 + 4H^+ + 4e^- \rightarrow 2H_2O
\]

### TABLE 3.3

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value and Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>Cell number: 35</td>
</tr>
<tr>
<td>V&lt;sub&gt;o&lt;/sub&gt;</td>
<td>Open-cell voltage: 1.032 V</td>
</tr>
<tr>
<td>R</td>
<td>Universal gas constant (J/mol K): 8.314 J/mol K</td>
</tr>
<tr>
<td>T</td>
<td>Temperature of the fuel cell (K): 353 K</td>
</tr>
<tr>
<td>F</td>
<td>Faraday constant (C/mol): 96,485 C/mol</td>
</tr>
<tr>
<td>α</td>
<td>Charge transfer coefficient: 0.5</td>
</tr>
<tr>
<td>M</td>
<td>Constant in the mass transfer voltage: 2/11 \times 10^{-5} V</td>
</tr>
<tr>
<td>N</td>
<td>Constant in the mass transfer voltage: 8 \times 10^{-3} cm&lt;sup&gt;2&lt;/sup&gt;/mA</td>
</tr>
<tr>
<td>R&lt;sub&gt;ohm&lt;/sub&gt;</td>
<td>2.45 \times 10^{-4} Ω cm&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>A&lt;sub&gt;fc&lt;/sub&gt;</td>
<td>Fuel cell active area: 232 cm&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>I&lt;sub&gt;0&lt;/sub&gt;</td>
<td>Exchange current density (A/cm&lt;sup&gt;2&lt;/sup&gt;)</td>
</tr>
<tr>
<td>I&lt;sub&gt;n&lt;/sub&gt;</td>
<td>Internal current density (A/cm&lt;sup&gt;2&lt;/sup&gt;)</td>
</tr>
</tbody>
</table>


### FIGURE 3.1

Computed and given steady-state \(V-I\) characteristics for the Ballard Mark V PEM fuel cell (dotted curve—computed values and solid curve—the given data).
Anode: \(2H_2 \leftrightarrow 4H^+ + 4e^-\)
Cathode: \(O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O\)
Overall reaction: \(2H_2 + O_2 \leftrightarrow 2H_2O + \text{electricity} + \text{heat}\)

In practice, a 5-kW fuel cell stack, such as a Ballard MK5-E PEMFC stack, uses a pressurized hydrogen tank at 10 atm and oxygen taken from

**FIGURE 3.2**
Polarization \(V-I\) curve (Ballard Mark V PEMFC at 70°C).

**FIGURE 3.3**
Schematic of fuel cell operation.
atmospheric air [11,12]. In case of using a reformer, on the anode side, a fuel processor called a reformer that generates hydrogen through reforming methane or other fuels such as natural gas, can be used instead of the pressurized hydrogen tank.

A pressure regulator and purging of the hydrogen component are also required. On the cathode side, an air supply system containing a compressor, an air filter, and an air flow controller are required to maintain the oxygen partial pressure [2,4,7,13]. On both sides, a humidifier is needed to prevent dehydration of the fuel cell membrane [2,4,7]. In addition, a heat exchanger, a water tank, a water separator, and a pump may be needed for water and heat management in the fuel cell systems [2,4,7].

To produce a higher voltage, multiple cells have to be connected in series. Typically, a single cell produces voltage between 0 and 1 V based on the polarization $I-V$ curve, which expresses the relationship between the stack voltage and the load current [2,4,7]. Figure 3.4 shows that their relationship is nonlinear and mainly depends on current density, cell temperature, reactant partial pressure, and membrane humidity [2,4,7].

The output stack voltage $V_{st}$ [4] is defined as a function of the stack current, reactant partial pressures, fuel cell temperature, and membrane humidity:

$$V_{st} = E - V_{activation} - V_{ohmic} - V_{concentration}$$ (3.3)
In the above equation
\[ E = N_o \left[ V_o + \frac{R \cdot T}{2F} \ln \left( \frac{P_{H_2} \sqrt{P_{O_2}}}{P_{H_2O_c}} \right) \right] \]

is the thermodynamic potential of the cell or reversible voltage based on Nernst equation [4], \( V_{activation} \) the voltage loss due to the rate of reactions on the surface of the electrodes, \( V_{ohmic} \) the ohmic voltage drop from the resistances of proton flow in the electrolyte, and \( V_{concentration} \) is the voltage loss from the reduction in concentration gases or the transport of mass of oxygen and hydrogen. Their equations are given as follows:

\[ V_{activation} = N_o \cdot \frac{R \cdot T}{2aF} \cdot \ln \left( \frac{I_{fc} + I_n}{I_o} \right) \]  \hspace{1cm} (3.4) \\
\[ V_{ohmic} = N_o \cdot I_{fc} \cdot R_{ohm} \]  \hspace{1cm} (3.5) \\
\[ V_{concentration} = N_o \cdot m \exp(n \cdot I_{fc}) \]  \hspace{1cm} (3.6) \\

In Equation 3.3, \( P_{H_2}, P_{O_2} \), and partial pressure of water vapor \( (P_{H_2O_c}) \) are the partial pressures of hydrogen, oxygen, and water, respectively. Subscript \( c \) means the water partial pressure, which is vented from the cathode side.

### 3.3 State-Space Dynamic Model of PEMFCs

To derive a simplified nonlinear dynamic PEMFC model, the following assumptions are made:

- Owing to slower dynamics of the stack temperature, the average stack temperature is assumed to be constant.
- The relative humidity can be well controlled to a little over 100%, and thereby, the liquid water always forms the stack. This liquid water is perfectly managed by the water tank and water separator and the water-flooding effects can be controlled.
- A continuous supply of reactants is fed to the fuel cell to allow operation at a sufficiently high flow rate.
• The mole fractions of inlet reactants are assumed to be constant in order to build the simplified dynamic PEMFC model. In other words, pure hydrogen (99.99%) is fed to the anode, and the air that is uniformly mixed with nitrogen and oxygen by a ratio of, say, 21:79, is supplied to the cathode.

• The full state has to be measured to utilize feedback linearization [14].

The ideal gas law and the mole conservation rule are employed. Each partial pressure of hydrogen, the water from the anode, and the oxygen, nitrogen, and water from the cathode are defined as state variables of the PEMFC. The relationship between inlet gases and outgases is described in Figure 3.5 [15].

The partial-pressure derivatives are given by the following equations. Anode mole conservation:

\[
\frac{dP_{H_2}}{dt} = \frac{R*T}{V_A} (H_{2in} - H_{2used} - H_{2out})
\]

(3.7)

Cathode mole conservation:

\[
\frac{dP_{O_2}}{dt} = \frac{R*T}{V_c} (O_{2in} - O_{2used} - O_{2out})
\]

\[
\frac{dP_{N_2}}{dt} = \frac{R*T}{V_c} (N_{2in} - N_{2out})
\]

(3.8)

\[
\frac{dP_{H_2O}}{dt} = \frac{R*T}{V_c} (H_{2O_{cin}} + H_{2O_{cproduced}} - H_{2O_{cout}} + H_{2O_{mbr}} - H_{2O_{mbr}} - H_{2O_{l,cout}})
\]

FIGURE 3.5
Gas flows of PEMFCs.
where \( H_{2\text{in}} \), \( O_{2\text{in}} \), \( N_{2\text{in}} \), \( H_2O_{\text{air}} \) and \( H_2O_{\text{cin}} \) are the inlet flow rates of hydrogen, oxygen, nitrogen, the anode-side water, and the cathode-side water, respectively. In addition, \( H_{2\text{out}} \), \( O_{2\text{out}} \), \( N_{2\text{out}} \), \( H_2O_{\text{out}} \) and \( H_2O_{\text{out}} \) are the outlet flow rates of each gas. \( H_{2\text{used}} \), \( O_{2\text{used}} \) and \( H_2O_{\text{produced}} \) are the usage and the production of the gases, respectively. In general, the membrane water inlet flow rate \( H_2O_{\text{mbr}} \) across the membrane is a function of the stack current and the membrane water content \( \lambda_m \). By assuming that \( \lambda_m = 14 \) \([7,16]\), \( H_2O_{\text{mbr}} \) is defined as a function of the current density only, and \( H_2O_{\text{mbr}} = 1.2684 (N \cdot A_{fc} \cdot I_{fc})/F \) \([7,16]\), where \( A_{fc} \) (cm\(^2\)) is the fuel cell active area, \( N \) the number of the fuel cells, and \( I_{fc} \) is the fuel cell current density. Furthermore, in order to describe a more accurate dynamic model, the back-diffusion of water from the cathode to the anode can be defined with \( H_2O_{v, \text{back}} = \gamma \cdot H_2O_{v,\text{mbr}} \) \([2]\). The back-diffusion coefficient \( \beta \) is measured as to be \( 6 \times 10^{-6} \text{ cm}^2/\text{s} \) with the water content being \( \lambda_m = 14 \) \([2]\). The flow rates of liquid water leaving the anode and cathode are given by \( H_2O_{l,\text{out}} \) and \( H_2O_{l,\text{out}} \) which are dependent on the saturation state of each gas \([7]\). To estimate the liquid water, the maximum mass of vapor has to be calculated from the vapor saturation pressure as follows:

\[
m_{v, \text{max}} = \frac{p_{vs} V_{aorc}}{R_{v} T_{st}}
\]

The saturation pressure \( p_{vs} \) is calculated from an equation presented in Reference 17

\[
\log_{10}(p_{vs}) = -1.69 \times 10^{-10} T^4 + 3.85 \times 10^{-7} T^3 - 3.39 \times 10^{-4} T^2 + 0.143 T - 20.92
\]

where the saturation pressure \( p_{vs} \) is in kPa and temperature \( T \) is in Kelvin. If the mass of water calculated in Equations 3.7 and 3.8 is greater than the maximum mass of vapor in Equation 3.9, the liquid water formation occurs simultaneously. The mass of liquid water and vapor is calculated as follows \([7]\):

Logic 1:

if \( m_{v,\text{a}} \ or \ c \leq m_{v,\text{max}} \ or \ c \) → \( m_{v,\text{a}} \ or \ c = m_{v,\text{a}} \ or \ c \)

if \( m_{v,\text{a}} \ or \ c > m_{v,\text{max}} \ or \ c \) → \( m_{v,\text{a}} \ or \ c = m_{v,\text{max}} \ or \ c \)

\( m_{v,\text{a}} \ or \ c = m_{v,\text{a}} \ or \ c - m_{v,\text{max}} \ or \ c \)

Thereby, \( \beta \) \( a \ or c \) can be used to estimate the liquid water formation in Equation 3.11. According to logic 1, if \( m_{v,\text{a}} \ or \ c \leq m_{v,\text{max}} \ or \ c \) then \( \beta \) \( a \ or c = 0 \); otherwise, \( \beta \) \( a \ or c = 1 \), and therefore \( H_2O_{l,\text{aout}} \) and \( H_2O_{l,\text{cout}} \) are defined by

\[
H_2O_{l,\text{aout}} = \beta_{a \ or c} \cdot \frac{(p_{H2O_{v,\text{aorc}}}/(R_{v} T_{st})) - (p_{vs} V_{aorc})/(R_{v} T_{st})}{M_{H2O}}
\]

(3.11)
where $M_{H_2O}$ is the water molar mass, 18.02 g/mol. All units of flow rates, usages, and the production of gases are defined in mol/s. However, because the liquid water is considered based on our assumption that each relative humidity stays over 100%, $\beta_a$ or $\beta_c$ will be 1, which means that $P_{H_2O_{a,c}} > P_{vs}$ during the simulation. $V_a$ and $V_c$ are the anode and cathode volumes, respectively, and their units are $m^3$. According to the basic electrochemical relationships, the usage and production of the gases are functions of the cell current density $I_{fc}$ [4], as follows:

$$H_{2used} = 2O_{2used} = H_2O_{produced} = \frac{N \cdot A_{fc} \cdot I_{fc}}{2F}$$  \quad (3.12)

For simplicity, let us define

$$\frac{N \cdot A_{fc}}{2F} = C_1 \quad \text{and} \quad \frac{N \cdot A_{fc}}{F} = C_2$$

Thus, in Equations 3.7 and 3.8, $H_2O_{mbr}$ and $H_2O_{vback}$ can be simplified with $C_1$ and $C_2$. With the measured inlet flow rates and the stack current, the outlet flow rates are given by the summation of the anode and cathode inlet flow rates, that is, $Anode_{in}$ and $Cath_{in}$, minus the usage and production of gases as well as the pressure fraction proposed by El-Sharkh et al. [13]. The $Anode_{in}$ is defined by $H_{2in} + H_2O_{ain}$, and the $Cath_{in}$ is defined by $O_{2in} + N_{2in} + H_2O_{cin}$. The outlet flow rates on the anode side are

$$H_2o_{out} = (H_{2in} - C_1 \cdot I_{fc})F_{H_2}$$

$$H_2O_{out} = (H_2O_{ain} - C_2 \cdot I_{fc} + \gamma \cdot C_2 \cdot I_{fc})F_{H_2O_a}$$  \quad (3.13)

and the outlet flow rates on the cathode side are

$$O_{2out} = \left( O_{2in} - \frac{C_1}{2} I_{fc} \right)F_{O_2}$$

$$N_{2out} = N_{2in} \cdot F_{N_2}$$

$$H_2O_{cout} = (H_2O_{cin} + C_1 \cdot I_{fc} + C_2 \cdot I_{fc} - \gamma \cdot C_2 \cdot I_{fc})F_{H_2O_c}$$  \quad (3.14)

where $F_{H_2}$, $F_{H_2O_a}$, $F_{O_2}$, $F_{N_2}$, and $F_{H_2O_c}$ are the pressure fractions of gases inside the fuel cell, given as follows [18]:
To analyze the transient behavior of fuel cells, we take into account the pressure fraction of each gas proposed by Chiu et al. [18]. In Reference 18, only the three pressure fractions $F_{H_2}$, $F_{O_2}$, and $F_{H_2O}$ are considered, but in our study, by considering all pressure fractions of gases, a more accurate dynamic fuel cell model is achieved and a better analysis of the transient behavior of fuel cells is possible than in previous studies [3,7,11,18]. The state equations (3.16) and (3.17) are obtained by substituting Equations 3.13 and 3.14 into Equations 3.7 and 3.8.

The new state equations on the anode side are

$$\frac{dP_{H_2}}{dt} = \frac{R*T}{V_a} \left[ H_{2in} - C_1 \cdot I_{fc} - (H_{2in} - C_1 \cdot I_{fc}) F_{H_2} \right]$$

$$\frac{dP_{H_2O}}{dt} = \frac{R*T}{V_a} \left[ H_{2O_ain} - (H_{2O_ain} - C_2 \cdot I_{fc} + C_2 \cdot I_{fc}) F_{H_2O} - C_2 \cdot I_{fc} + \gamma \cdot C_2 \cdot I_{fc} \right]$$

and the state equations on the cathode side are

$$\frac{dP_{O_2}}{dt} = \frac{R*T}{V_c} \left[ O_{2in} - \frac{C_1}{2} \cdot I_{fc} - \left( O_{2in} - \frac{C_1}{2} \cdot I_{fc} \right) F_{O_2} \right]$$

$$\frac{dP_{N_2}}{dt} = \frac{R*T}{V_c} \left[ N_{2in} - N_{2in} \cdot F_{N_2} \right]$$

$$\frac{dP_{H_2O_c}}{dt} = \frac{R*T}{V_c} \left[ H_{2O_cin} + C_1 \cdot I_{st} - (H_{2O_cin} + C_1 \cdot I_{st} + C_2 \cdot I_{st} - C_2 \cdot I_{st}) F_{H_2O_c} \right.$$

$$+ \left. C_2 \cdot I_{st} - \gamma \cdot C_2 \cdot I_{st} \right]$$

Because the initial mole fractions $Y_{H_2}$, $Y_{O_2}$, and $Y_{N_2}$ are set to be 0.99, 0.21, and 0.79, respectively [3,7,11], the input values $H_{2in}$, $O_{2in}$, and $N_{2in}$ are defined by the mole fractions, which are given as

$$H_{2in} = Y_{H_2} \cdot Anode_{in}$$

$$O_{2in} = Y_{O_2} \cdot Anode_{in}$$

$$N_{2in} = Y_{N_2} \cdot Cath_{in}$$
The water inlet flow rates on the anode and the cathode are expressed in terms of the relative humidity, saturation pressure, and total pressure on each side, as follows [2]:

\[
\begin{align*}
H_2O_{an} &= \frac{\varphi_a P_{vs}}{P_A - \varphi_a P_{vs}} \cdot \text{Anode}_{in} \\
H_2O_{cn} &= \frac{\varphi_c P_{vs}}{P_C - \varphi_c P_{vs}} \cdot \text{Cath}_{in}
\end{align*}
\]

where \(\varphi_a\) and \(\varphi_c\) are the relative humidity on the anode and the cathode sides, respectively; \(P_a = P_{H_2} + P_{H_2O}\) is the summation of partial pressures of the anode; and \(P_c = P_{O_2} + P_{N_2} + P_{H_2O}\) is the summation of partial pressures of the cathode. \(P_{vs}\) is the saturation pressure, which can be found in the thermodynamics tables [19]. The relative humidity \(\varphi_a\) and \(\varphi_c\) are defined from the water injection input \(u_{a,h}\) for the anode, and \(u_{c,h}\) for the cathode. Furthermore, \(\text{Anode}_{in}\) and \(\text{Cath}_{in}\) are defined as the products of the input control variables \(u_a\) and \(u_c\) and the conversion factors \(k_a\) and \(k_c\) [11,18] on each side, which are translated from standard liters per minute (SLPM) to mol/s. In other words:

\[
\begin{align*}
\text{Anode}_{in} &= u_a \cdot k_a \\
\text{Cath}_{in} &= u_c \cdot k_c
\end{align*}
\]

where the conversion factors \(k_a\) and \(k_c\) are 0.065 mol/s, respectively. The hydrogen and the air stoichiometric ratios are assumed to be constant to keep the reactants flowing through the stack [19]. Hence, both of these reactants are able to be fed to the fuel cell continuously, and the fuel cell control system can be mainly dependent on the input control variables \(u_a\) and \(u_c\). First, the anode gas pressure \(P_a = P_{H_2} + P_{H_2O}\) and the cathode gas pressure \(P_c = P_{N_2} + P_{O_2} + P_{H_2O}\) will be controlled by \(u_a\) and \(u_c\), respectively, to avoid an unwanted pressure fluctuation and prevent MEA damage; thus, it can lead to prolong the fuel cell stack life [15]. In terms of control for the relative humidity on both sides, the first-order time-delay water injection inputs \(u_{a,h}\) and \(u_{c,h}\) will be applied because the water injection system has a very slow time constant \(\tau_d\) of about 70 s [20]. Thus, in our dynamics model of PEMFC, the first-order time-delay model for the water injection is considered and the state equation from the relationship between the water injection input and relative humidity is derived as follows:

\[
\begin{align*}
\varphi_a &= \frac{1}{1 + \tau_d s} u_{a,h} \\
\varphi_c &= \frac{1}{1 + \tau_d s} u_{c,h}
\end{align*}
\]

where \(\varphi\) is the relative humidity. As seen in Equation 3.19, because each water input is a function of humidity, the water injection inputs also affect
the pressure controls. So, we can establish a dynamic model of PEMFCs and the details of the control design will be described in Chapter 4.

3.4 Electrochemical Circuit Model of PEM Fuel Cells

3.4.1 Equivalent Circuit

Another important modeling method of PEM fuel cells is to use equivalent electrical circuits. The benefit of this kind of models is that the analysis, simulation, or study of PEM fuel cells can be simplified by using equivalent electrical circuits to replace PEM fuel cells. In this section, we will introduce a typical electrical circuit as proposed in Reference 21.

A mathematical approach is presented for building a dynamic model for a PEM fuel cell stack. The following assumptions are made [2,4,8,18,22]:

- One-dimensional treatment.
- Ideal and uniformly distributed gases.
- Constant pressures in the fuel cell gas flow channels.
- The fuel is humidified and the oxidant is humidified air. Assume that the effective anode water vapor pressure is 50% of the saturated vapor pressure while the effective cathode water pressure is 100%.
- The fuel cell works under 100°C and the reaction product is in the liquid phase.
- Thermodynamic properties are evaluated at the average stack temperature, temperature variations across the stack are neglected, and the overall specific heat capacity of the stack is assumed to be a constant.
- Parameters for individual cells can be lumped together to represent a fuel cell stack.

A schematic diagram of a PEM fuel cell and its internal voltage drops are shown in Figure 3.6. For details of the workings of PEM fuel cell, the reader is referred to References 18, 22, and 23.

After the effective partial pressures of H\(_2\) and O\(_2\) are studied, and the instantaneous change in the effective partial pressures of hydrogen and oxygen is also considered through the ideal gas equations as given in Reference 24, the fuel cell output voltage can be written as follows:

\[
V_{\text{out}} = E - V_c - V_{\text{act1}} - V_{\text{ohm}}
\]  

(3.22)
where

\[ E \] is the reversible potential of each cell (in volts)
\[ V_c \] is the voltage across the capacitor

\[ V_{act} = V_{act1} + V_{act2} \]

where \( V_{act1} = \eta_0 + a(T - 29) \) is the voltage drop affected only by the fuel cell internal temperature, while \( V_{act2} = bT \ln(I) \) is both current and temperature dependent

\[ V_{ohm} \] is the overall ohmic voltage drop

According to the above voltage output equation, the equivalent circuit shown in Figure 3.7 is obtained.

In the above circuit, \( C \) is the equivalent capacitor due to the double-layer charging effect.

### 3.4.2 Simulation Results

To validate the models built in Simulink and PSPICE, real input and output data shown in Figures 3.8 and 3.9 were measured on the 500-W SR-12 Avista...
Labs PEM fuel cell. The Chroma 63 112 programmable electronic load was used as a current load. Current signals were measured by LEM LA100-P current transducers; the output voltage was measured by an LEM LV25-P voltage transducer and the temperature was measured by a k-type thermocouple together with an analog connector. The current, voltage, and temperature data were all acquired by a 12-b Advantech data-acquisition card in a PC.
3.5 Linear Model of PEM Fuel Cell Dynamics

We restrict our attention to models of PEMFC dynamic behavior, and so, we will not focus on models of their static behavior, such as those described in References 25–27. Of course, the static equations are obtainable as a limiting case from the dynamic equations, and the differences between the modeling performances of those derived from static equations can be compared, as in Reference 28. These steady-state models are able to solely simulate the cells’ steady-state behavior, and cannot be used for describing and for model-based feedback control of transient conditions that are important for some specific applications. This is the case, especially, for vehicle applications, given the rapid changes of mechanical and electrical quantities.

Furthermore, our focus is on the fuel cell stack itself and thus, we will not be describing the behavior of the balance of plant (systems), which include the hydrogen and air supplies, the thermal management unit, humidifiers, etc.

Since the PEMFC’s dynamic behavior is inherently nonlinear, any linear model of those dynamics is only an approximation of the original nonlinear equations. The different linear-approximating models studied thus far include the following.

FIGURE 3.9
V–I characteristics of SR-12 and models.
3.5.1 Chiu’s et al. Model

This was one of the earliest-proposed linear models of PEMFC dynamic behavior [18]. It is based on a set of nonlinear dynamic equations as the starting point. In order to linearize these equations, a small-perturbation method was used to model the fuel cell dynamics around particular operating points as an approximating linear system. Such a model is useful for transient response analysis and for control design by linear system techniques subject to the constraint of small perturbations.

The output voltage of the PEMFC is defined as in Reference 4, which gives the stack voltage equation as

$$E = N \left( E_0 + \frac{R^*T}{2F} \ln \frac{P_{H_2}(P_{O_2}/P_{std})^{1/2}}{P_{H_2O}} \right) - L$$  \hspace{1cm} (3.23)

where $E$, $N$, $E_0$, $T$, and $L$ denote the stack output voltage, number of cells in the stack, cell open-circuit voltage at standard pressure, operating temperature, and voltage losses, respectively. In addition, $P_{H_2}$, $P_{O_2}$, and $P_{H_2O}$ represent the partial pressure of each gas inside the cell. Also, $R$ is the universal gas constant, $F$ Faraday’s constant, and $P_{std}$ is the standard pressure. Note the implicit assumption in the equation that all the cells in a stack are identical.

The PEMFC’s voltage losses $L$ consist of the following:

- Activation losses—due to the slowness of the reactions taking place in the cell, which can be minimized by maximizing the catalyst contact area for reactions
- Internal current losses—due to the leakage of electrons passing through the membrane to the cathode side instead of being collected to be utilized, which has a significant effect on the open-circuit voltage
- Resistive losses—caused by current flow through the resistance of the whole electrical circuit including the membrane and various interconnections, with the biggest contributor being the membrane; effective water management to keep it hydrated reduces its ohmic loss
- Mass transport or concentration losses—caused by gas concentration changes at the surface of the electrodes

Hence, the voltage losses $L$ can be expressed as

$$L = (i + i_n)r + a \ln \left( \frac{i + i_n}{i_o} \right) - b \ln \left( 1 - \frac{i + i_n}{i_l} \right)$$  \hspace{1cm} (3.24)
where $i$ is the output current density, $i_n$ the internal current density related to internal current losses, $i_e$ the exchange current density related to activation losses, $i_l$ the limiting current density related to concentration losses, $r$ the area-specific resistance related to resistive losses, and $a$ and $b$ are constants.

### 3.5.1.1 Fuel Cell Small-Signal Model

From Equations 3.23 and 3.24, we can see that there are some nonlinear terms in the equations. In order to linearize the cell voltage equation, we use a small-perturbation method to model the fuel cell dynamics around particular operating points as an approximately linear system. Then, we can easily obtain the dynamic response of the cell’s output voltage at these operating points for small input variable perturbations.

#### 3.5.1.1.1 State Equations

First, we define the partial pressures of hydrogen, oxygen, and water (on the cathode side) as the three state variables of the system. Since the water management is a factor to affect the performance, we have to use humidifiers on both the anode and cathode side to control the humidity inside the cell. The consideration of water on the cathode side is more complicated than on the anode side because it includes not only the water supplied from the humidifiers, but also the by-product of the reaction. Figure 3.10 illustrates the various gas/vapor flows in and out of the cell.

On the basis of an ideal gas law $P^*V = n^*R^*T$, the partial pressure of each gas is proportional to the amount of the gas in the cell, which is equal to the gas inlet flow rate minus gas consumption and gas outlet flow rate. Thus, the state equations are

$$\frac{dP_H^2}{dt} = \frac{R^*T}{V_a}(H_{2in} - H_{2used} - H_{2out}) \tag{3.25}$$

**FIGURE 3.10**
Illustration of gas flows of the PEMFC.
\[
\frac{dP_{O_2}}{dt} = \frac{R^*T}{V_c} (O_{2in} - O_{2used} - O_{2out}) \tag{3.26}
\]

\[
\frac{dP_{H_2O_c}}{dt} = \frac{R^*T}{V_c} (H_2O_{cin} + H_2O_{produced} - H_2O_{cout}) \tag{3.27}
\]

where \(H_{2in}, O_{2in}, \) and \(H_2O_{cin}\) are inlet flow rates of hydrogen, oxygen, and water of cathode, respectively; \(H_{2out}, O_{2out}, \) and \(H_2O_{cout}\) are outlet flow rates of each gas. Furthermore, \(H_{2used}, O_{2used}, \) and \(H_2O_{produced}\) represent usage and production of the gases, which are related to output current \(I\) by

\[
H_{2used} = 2O_{2used} = H_2O_{produced} = 2K_r I = 2K_r A_c i \tag{3.28}
\]

where \(K_r = N/4F, A_c\) is the cell active area, and \(i\) is the cell current density.

Since we can measure the inlet flow rates and output current, we can define the outlet flow rates by the equations

\[
H_{2out} = (Anode_{in} - 2K_r A_c i) F_{H_2} \tag{3.29}
\]

\[
O_{2out} = (Cath_{in} - K_r A_c i) F_{O_2} \tag{3.30}
\]

\[
H_2O_{cout} = (Cath_{in} + 2K_r A_c i) F_{H_2O_c} \tag{3.31}
\]

where \(Anode_{in}\) and \(Cath_{in}\) are the summations of anode inlet flows and cathode inlet flows, respectively, as defined by \(Anode_{in} = H_{2in} + H_2O_{cin}\) and \(Cath_{in} = N_{2in} + O_{2in} + H_2O_{cin}\), while \(F_{H_2}, F_{O_2}, \) and \(F_{H_2O_c}\) are the pressure fractions of each gas inside the fuel cell. At this juncture, we point out the subtle but significant difference between the proposed model and the original U.S. Department of Energy (DoE) model [29] for defining the pressure fractions.

For the original DoE model,

\[
F_{H_2} = \frac{P_{H_2}}{P_{op}} \tag{3.32}
\]

\[
F_{O_2} = \frac{P_{O_2}}{P_{op}} \tag{3.33}
\]

\[
F_{H_2O_c} = \frac{P_{H_2O_c}}{P_{op}} \tag{3.34}
\]
but for the model proposed by Chiu et al. [18]

\[ F_{H_2} = \frac{P_{H_2}}{P_{H_2} + P_{H_2O_2}} \]  (3.35)

\[ F_{O_2} = \frac{P_{O_2}}{P_{N_2} + P_{O_2} + P_{H_2O_2}} \]  (3.36)

\[ F_{H_2O_2} = \frac{P_{H_2O_2}}{P_{N_2} + P_{O_2} + P_{H_2O_2}} \]  (3.37)

In the original DoE model, it is assumed that the cell anode and cathode pressures remain constant and equal at \( P_{opr} \) which is the steady-state operating pressure. But because we are using the model to analyze the transient behavior of fuel cells, we have to account for the perturbation of each gas pressure as soon as we change some conditions. Thus, we use the summation of the gas partial pressures in Equations 3.35 through 3.37 instead of assuming a constant operating pressure.

In order to get the state-equation matrices, we substitute Equations 3.28 through 3.37 into Equations 3.25 through 3.27, and then differentiate both sides.

For example, we substitute Equations 3.29 and 3.32 into Equation 3.25, which becomes

\[ \frac{dP_{H_2}}{dt} = \frac{R^*T}{V_A} \left[ H_{2in} - 2K_r A_c \Delta i - (Anode_{in} - 2K_r A_c i) \frac{P_{H_2}}{P_{opr}} \right] \]

Then, performing linearization (first-order approximation) about the given steady-state operating point yields

\[ \frac{d\Delta P_{H_2}}{dt} = \frac{R^*T}{V_A} \left[ -\left( \frac{H_{2in}}{Y_{H_2}} - 2K_r A_c i \right) \frac{1}{P_{opr}} \Delta P_{H_2} + \left( 1 - \frac{P_{H_2}}{Y_{H_2}} \frac{P_{opr}}{P_{opr}} \right) \Delta H_{2in} \right. \\
\left. - 2K_r A_c \frac{P_{opr} - P_{H_2}}{P_{opr}} \Delta i \right] \]  (3.38)

where \( \Delta P_{H_2} \), \( \Delta H_{2in} \), and \( \Delta i \) are the perturbations of each variable, and \( Y_{H_2} \) is the molar fraction of \( H_2 \) at the anode inlet defined by \( H_{2in}/Anode_{in} \). Moreover, the state and input variables in the equation need to be replaced by their steady-state values at the chosen operating point.
Following this example, we obtained the remaining equations for the DoE and Chiu et al. models as

1. Original DoE model

\[
\frac{d\Delta P_{O_2}}{dt} = \frac{R^*T}{V_c} \left[ -(\text{Cath}_{in} - K_r A_c i) \frac{1}{P_{op}} \Delta P_{O_2} - K_r A_c \frac{P_{op} - P_{O_2}}{P_{op}} \Delta i + \left( 1 - \frac{P_{O_2}}{(Y_{O_2} + Y_{H_2O_c})P_{op}} \right) \Delta O_{2in} \right] \\
- \frac{P_{O_2}}{(Y_{O_2} + Y_{H_2O_c})P_{op}} \Delta H_{2O_{cin}} \right] 
\]

(3.39)

\[
\frac{d\Delta P_{H_2O_c}}{dt} = \frac{R^*T}{V_c} \left[ -(\text{Cath}_{in} + 2K_r A_c i) \frac{1}{P_{op}} \Delta P_{H_2O_c} - \frac{P_{H_2O_c}}{(Y_{O_2} + Y_{H_2O_c})P_{op}} \Delta O_{2in} \right] \\
+ \left( 1 - \frac{P_{H_2O_c}}{(Y_{O_2} + Y_{H_2O_c})P_{op}} \right) \Delta H_{2O_{cin}} + 2K_r A_c \frac{P_{op} - P_{H_2O_c}}{P_{op}} \Delta i \right] 
\]

(3.40)

where \( Y_{O_2} \) is the mole fraction of \( O_2 \) at the cathode inlet defined by \( O_{2in}/\text{Cath}_{in} \), and \( Y_{H_2O_c} \) is the mole fraction of water at the cathode inlet defined by \( H_2O_{cin}/\text{Cath}_{in} \) so that \( \text{Cath}_{in} = \frac{O_{2in} + H_2O_{cin}}{Y_{O_2} + Y_{H_2O_c}} \).

2. Chiu et al. model

\[
\frac{d\Delta P_{H_2}}{dt} = \frac{R^*T}{V_A} \left[ -(\text{Anode}_{in} - 2K_r A_c i) \frac{P_{H_2O_c}}{(P_{H_2} + P_{H_2O_c})^2} \Delta P_{H_2} \right] \\
+ \left( 1 - \frac{P_{H_2}}{Y_{H_2}(P_{H_2} + P_{H_2O_c})} \right) \Delta H_{2in} - 2K_r A_c \frac{P_{H_2O_c}}{P_{H_2} + P_{H_2O_c}} \Delta i \right] 
\]

(3.41)

\[
\frac{d\Delta P_{O_2}}{dt} = \frac{R^*T}{V_C} \left[ -(\text{Cath}_{in} - K_r A_c i) \frac{P_{N_2} + P_{H_2O_c}}{P_{cat}^2} \Delta P_{O_2} + (\text{Cath}_{in} - K_r A_c i) \frac{P_{O_2}}{P_{cat}^2} \Delta P_{H_2O_c} \right] \\
+ \left( 1 - \frac{P_{O_2}}{(Y_{O_2} + Y_{H_2O_c})P_{cat}} \right) \Delta O_{2in} - \frac{P_{O_2}}{(Y_{O_2} + Y_{H_2O_c})P_{cat}} \Delta H_{2O_{cin}} \\
- K_r A_c \frac{P_{N_2} + P_{H_2O_c}}{P_{cat}} \Delta i \right] 
\]

(3.42)
\[
\frac{d\Delta P_{H_2O}}{dt} = \frac{R^*T}{V_c} \left[ (\text{Cath}_{\text{in}} + 2K_r A_c i) \frac{P_{H_2O}}{P_{\text{cathode}}^2} \Delta P_{O_2} \right. \\
\left. - (\text{Cath}_{\text{in}} + 2K_r A_c i) \frac{P_{N_2} + P_{O_2}}{P_{\text{cathode}}^2} \Delta P_{H_2O} - \frac{P_{H_2O}}{(Y_{O_2} + Y_{H_2O}) P_{\text{cathode}}} \Delta O_{2\text{in}} \right. \\
\left. + \left( 1 - \frac{P_{H_2O}}{(Y_{O_2} + Y_{H_2O}) P_{\text{cathode}}} \right) \Delta H_{2O_{\text{cin}}} + 2K_r A_c \frac{P_{N_2} + P_{O_2}}{P_{\text{cathode}}} \Delta i \right] (3.43)
\]

where \(P_{H_2O}\) is the partial pressure of water vapor in the anode, \(P_{N_2}\) the partial pressure of the nitrogen in the cathode, and \(P_{\text{cathode}} = P_{N_2} + P_{O_2} + P_{H_2O}\).

For the fuel cell output, we substitute Equation 3.24 into Equation 3.23 and differentiate both sides. Then, we obtain a linear equation for the perturbation of the stack output voltage \(\Delta E\) in response to the system state changes due to input perturbations at particular operating points as

\[
\Delta E = N \left[ \frac{R^*T}{2F} \frac{1}{P_{H_2}} \Delta P_{H_2} + \frac{R^*T}{4F} \frac{1}{P_{O_2}} \Delta P_{O_2} - \frac{R^*T}{2F} \frac{1}{P_{H_2O}} \Delta P_{H_2O} \right. \\
\left. - \left( r + \frac{a}{i + i_n} + \frac{b}{i_r - i - i_n} \right) \Delta i \right] \]

(3.44)

3.5.1.1.2 Linear State-Space Model

From Equations 3.38 through 3.44, we can form a linear small-signal state-space model of the hydrogen PEMFC described by

\[
\Delta \dot{x} = A \Delta x + B \Delta u
\]

\[
\Delta y = C \Delta x + D \Delta u
\]

\[
\Delta x = [\Delta P_{H_2} \Delta P_{O_2} \Delta P_{H_2O}]^T
\]

\[
\Delta u = [\Delta H_{2\text{in}} \Delta O_{2\text{in}} \Delta H_{2O_{\text{cin}}} \Delta i]^T
\]

\[
\Delta y = \Delta E
\]

where the three system states in \(\Delta x\) are the perturbations of the partial pressures of hydrogen, oxygen, and water vapor inside the cells, and the four inputs in \(\Delta u\) are the perturbations of the inlet flow rates of hydrogen, oxygen,
and water vapor, and also the output current density, while the system output $\Delta y$ is the perturbation of the fuel cell stack voltage.

For the DoE model, the matrices $A, B, C,$ and $D$ are

$$A = R^*T$$

$$B = R^*T$$

$$C = N \frac{R^*T}{2F} \left[ \begin{array}{c} \frac{1}{V_a} - \frac{P_{H_2}}{V_a Y_{H_2} P_{op}} \\ 0 \\ \frac{1}{V_c} - \frac{P_{O_2}}{V_c (Y_{O_2} + Y_{H_2O}) P_{op}} \\ 0 \\ \frac{1}{V_c} - \frac{P_{H_2O}}{V_c (Y_{O_2} + Y_{H_2O}) P_{op}} \end{array} \right]$$

$$D = N \left[ \begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{array} \right]$$

For the Chiu et al. model, the matrices $A, B, C,$ and $D$ are

$$A = R^*T$$

$$B = R^*T$$

$$C = N \frac{R^*T}{2F} \left[ \begin{array}{c} \frac{1}{V_a} - \frac{P_{H_2}}{V_a (P_{H_2} + P_{H_2O})^2} \\ 0 \\ \frac{P_{O_2}}{V_c (Y_{O_2} + Y_{H_2O}) P_{op}} \\ 0 \\ \frac{P_{H_2O}}{V_c (Y_{O_2} + Y_{H_2O}) P_{op}} \end{array} \right]$$

$$D = N \left[ \begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \end{array} \right]$$
3.5.1.2 Correspondence of Simulation and Test Results

MATLAB® was used to perform simulations of PEMFC dynamic response based on the small-signal linear state-space models described above. The values of the fuel cell models’ main parameters, corresponding to a PEMFC stack (composed of four cells) that was tested at the DoE National Energy Technology Lab in Morgantown, WV, are listed in Table 3.4. From auxiliary tests, it was also estimated that the coefficient of $\Delta i$ in Equation 3.44, yielding the instantaneous voltage change for a unit perturbation in current density, equaled 30.762 $\mu\Omega$ m². Furthermore, the state variables’ steady-state values at the chosen operating point of 40 A load current were calculated from the input and output steady-state values, and then substituted into the matrices $A$, $B$, $C$, and $D$.

The following figures compare the responses between the test fuel cell stack, the original DoE model, and the Chiu et al. model. They are of the output voltage response to a step change of the load current with the input flow rates held constant. For the first test case with results shown in Figure 3.11, the stack was operating at a steady-state condition with $H_2\text{in} = 3664$ mL/min, $N_2\text{in} + O_2\text{in} = 11,548$ mL/min (assumed to be equally distributed

\[ B = R^T \begin{bmatrix} \frac{1}{V_a} & 0 & 0 & -2K_A \frac{P_{H_2O}}{V_a (P_{H_2} + P_{H_2O})} \\ 0 & \frac{1}{V_c} & -\frac{P_{O_2}}{V_c (Y_{O_2} + Y_{H_2O}) P_{\text{cathode}}} & -K_A \frac{P_{N_2} + P_{O_2}}{V_c P_{\text{cathode}}} \\ 0 & \frac{1}{V_c} & \frac{P_{H_2O}}{V_c (Y_{O_2} + Y_{H_2O}) P_{\text{cathode}}} & 2K_A \frac{P_{N_2} + P_{O_2}}{V_c P_{\text{cathode}}} \end{bmatrix} \]

\[ C = N \frac{R^* T}{2F} \begin{bmatrix} \frac{1}{P_{H_2}} & \frac{1}{2P_{O_2}} & -\frac{1}{P_{H_2O}} \end{bmatrix} \]

\[ D = N \begin{bmatrix} 0 & 0 & 0 & -\left( \frac{r}{i + i_n} + \frac{b}{i_l - i - i_n} \right) \end{bmatrix} \]

(3.46)

\[ \text{TABLE 3.4} \]

<table>
<thead>
<tr>
<th>Fuel Cell Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell active area $A_c = 136.7$ cm²</td>
</tr>
<tr>
<td>Volume of anode $V_a = 6.495$ cm³</td>
</tr>
<tr>
<td>Volume of cathode $V_c = 12.96$ cm³</td>
</tr>
<tr>
<td>Number of cells $N = 4$</td>
</tr>
<tr>
<td>Operating pressure (for the original DoE model) $P_{op} = 101$ kPa</td>
</tr>
</tbody>
</table>
between four cells), $T = 338.5 \, \text{K}$, and load current of 40 A, when the load current was abruptly increased to 50 A at the 5th second. The measured stack output voltage (with data-acquisition rate of 0.2 samples/s) shows a rapid decrease followed by a steady-state that appears to be a constant accompanied by some “noise.” Simulations of this load current perturbation from the 40 A operating value were then performed using the DoE and the Chiu et al. small-signal dynamic models described by Equations 3.45 and 3.46, respectively. As shown in Figure 3.11, the Chiu et al. model predicts the transient response starting from the output voltage operating value of 2.813 V (the voltage drop at the instant of current change being given by $30.762 \Delta i$) and also the steady-state response of the measured output voltage better than the DoE model. Note that the discrepancy in steady-state values is mainly due to the nonlinear functions found in the exact output voltage of Equation 3.23, i.e., the linear models used are only a fair approximation of the stack’s exact behavior due to the fairly large perturbation involved in this test, as to be expected.

**Operating condition:**

- $H_{2\text{in}} = 3664 \, \text{mL/min}$
- $N_{2\text{in}} + O_{2\text{in}} = 11,548 \, \text{mL/min}$
- $T$ (operating or cell temperature) = 338.5 K

**Perturbation:**

- $I$ at 40 A then stepped up to 50 A at 5th second

---

**FIGURE 3.11**
Comparison of simulated and test results.
For the second test case with results shown in Figure 3.12, the stack was operating at a steady-state condition with $H_{2in} = 3000$ mL/min, $N_{2in} + O_{2in} = 10,000$ mL/min (assumed to be equally distributed between four cells), $T = 338.5$ K, and load current of 40 A, when the load current was abruptly increased to 42 A at 0.1 s. The measured stack output voltage (with data-acquisition rate of 100 samples/s) shows a rapid decrease followed by a gradual increase accompanied by some “noise.” Simulations of this (smaller) load current perturbation from the 40 A operating value were then performed again using the DoE and the Chiu et al. small-signal dynamic models. As shown in Figure 3.12, the Chiu et al. model again predicts the transient response and the steady-state response of the output voltage better than the DoE model. However, their difference has been reduced as has the difference between them and the measured response, which was expected because of the smaller perturbation from the chosen operating point.

**FIGURE 3.12**
Another comparison of simulated and test results.

<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test</td>
<td>Proposed</td>
</tr>
</tbody>
</table>

Operating condition: $H_{2in} = 3000$ mL/min  
$N_{2in} + O_{2in} = 10,000$ mL/min  
$T$ (operating or cell temperature) = 338.5 K

Perturbation: $I$ at 40 A then stepped up to 42 A at 0.1th second
Note that the test response showing the output voltage slowly increasing over time after the initial drop was also observed consistently at various operating conditions after a load increase; this was more noticeable for smaller perturbations (when a finer voltage scale was used) than for larger perturbations. But the phenomenon does not appear to represent an undershoot and subsequent recovery as they pertain to a linear dynamic system. It may be that the membrane conductivity changes as its level of hydration increases after a load change leading to the gradual increase in cell voltage. This will need to be addressed in future research.

3.5.2 Page’s et al. Model

A different approach from Page et al. [30] was adopted toward obtaining a linear model of PEMFC dynamics in [13]. This approach is based on acquisition of test data from a single cell or a multiple-cell stack, followed by a least-squares estimation of the parameters (component values) for the proposed equivalent circuit model (Figure 3.13). But this is an input–output model where the equivalent circuit internal variables do not actually correspond to actual physical quantities.

3.5.3 University of South Alabama’s Model

A partially linearized model of PEMFC dynamics is applied, where the partial pressures of hydrogen, oxygen, and water in the fuel cell were each modeled as having first-order dynamics [13,31]. But the PEMFC output voltage still nonlinearly depends on these partial pressures in their model.

3.5.4 Other Models

Reference 32 also adopts a small-signal approach toward modeling the dynamics of PEMFCs, but chooses to ignore the dynamics of all variables except temperature, as being the dominant (slowest evolving) system variable. In any case, this approach does not lead to a strictly linear model of PEMFC dynamics.

FIGURE 3.13
Page’s et al. equivalent circuit model.
In Reference 33, the dynamic model presented (essentially amounting to a single equivalent capacitance) was not validated with respect to transient responses from actual PEMFCs, although the steady-state values predicted by the model were compared to the polarization curves of actual PEMFCs.

### 3.6 Parametric Sensitivity of PEMFC Output Response

There is significant motivation to identify which fuel cell parameters have greater impact on the cell’s steady-state and transient responses so as to facilitate improved simulations and designs (internal modifications as opposed to external controller designs) of such cells. A sensitivity analysis was described in Reference 34 using a PEMFC electrochemical model and data from a 500 W PEMFC stack manufactured by BCS Technology [35]. The goal was to identify the relative importance of each parameter to the FC model simulation’s accuracy. To investigate this, the parametric sensitivity of the FC electrochemical model was calculated using a multiparametric sensitivity analysis approach. To represent the FC stack electrochemical behavior, a first-order (one capacitor) electrical circuit was used to model the FC dynamic behavior. But the main focus was on FC steady-state response and evaluating the parameters effects on the stack polarization curve. To evaluate accuracy of the model’s dynamic response, since the charge double-layer effect is responsible for a delay in the FC voltage change after a change in its current, the parameter used to describe this behavior is an equivalent capacitance; so, its effect on the model’s step response (representing a real-world current interruption test) was studied. This capacitance does not influence the stack polarization curve because each point on this curve is obtained after the voltage has reached its steady-state value. As expected, the results of the transient response analysis were similar to that of a basic RC circuit.

The remainder of this section describes the results obtained in References 36 and 37 from a sensitivity analysis performed on an input–output transfer function (which is a linear systems concept) that is derived from the linear small-signal model of PEM fuel cell dynamics previously described in Section 3.6.1 [18]. These provide a greater insight into the issue of which physical parameters have the greater impacts on fuel cell dynamic response. The transfer function being investigated represents the fuel cell’s output voltage response (system output) to a perturbation of the load current (system input), which is equivalent to its output impedance. It is well known that this impedance has long been studied, usually through AC measurements termed impedance spectroscopy, as a means to characterize a cell’s physical processes, electrical properties, and transient response [38–40]. But in this book, we describe a slightly different use of PEMFC output impedance.
Sensitivity is mathematically defined as the partial derivative of a function with respect to one of its parameters divided by the ratio of the function to that parameter. Here, it gauges the effect of a unit change in a given fuel cell parameter on the cell’s input–output transfer function (for small load current changes). The sensitivity of the PEMFC’s dynamic response can be evaluated for the following parameters: cell active area, parameter associated with cell activation losses (the slope of Tafel line), parameter associated with cell concentration losses, cell-limiting current density (corresponding to concentration losses), cell internal current density (corresponding to internal current losses), cell exchange current density (corresponding to activation losses), number of cells in the stack, cell area-specific resistance (corresponding to resistive losses), stack operating temperature (actually an operating condition parameter), cell anode volume, and cell cathode volume. Several plots will be presented below to illustrate and compare these sensitivity functions.

### 3.6.1 Fuel Cell Dynamic Response and Sensitivity Analysis

Now, note that the fuel cell’s output impedance represents its output voltage response to a perturbation of the load current, which is the system transfer function of main practical interest. This impedance function can be obtained from Equation 3.46 as

$$
G_{Vi}(s) = C(sI_3 - A)^{-1}B_4 + D_4
$$

where $s$ represents complex frequency, $I_3$ the $3 \times 3$ identity matrix, $B_4$ and $D_4$ represent the fourth columns of $B$ and $D$, respectively, and $m_{ij}$ refers to the element in the $i$th row and $j$th column of the corresponding matrix $M$.

### 3.6.1.1 Sensitivity Function

A sensitivity analysis can be performed on the PEMFC output impedance. This analysis quantitatively characterizes the effect that each particular parameter and operating point variable of the fuel cell has on that impedance. Such information can then be used for prescribing design changes to a fuel cell system in order to improve its dynamic behavior.

The sensitivity function is defined here as the ratio of the partial derivative of the transfer function (3.47) with respect to a particular parameter to the transfer function divided by that parameter, i.e.,

$$
S_\theta = \frac{\partial G_{Vi}}{\partial \theta} \left/ \frac{G_{Vi}}{\theta} \right.
$$

(3.48)
where $\theta$ represents any parameter or operating point variable of the fuel cell. It shows how sensitive the system is to different parameters and variables as a function of frequency.

As examples, we present the sensitivity functions for $G_V(s)$ with respect to $H_{2\text{in}}$ and for $G_V(s)$ with respect to $V_a$, which were among the simplest of the derived functions, as

$$S_{H_{2\text{in}}} = \frac{\text{Num}_{H_{2\text{in}}}(s)}{\text{Den}_{H_{2\text{in}}}(s)}$$

$$\text{Num}_{H_{2\text{in}}}(s) = 2^*A_c^*H_{2\text{in}}^*K_1^2*K_2^*P_{\text{anode}}^*P_{H_2O_2}^2*R^*T^*Y_{H_2}$$

$$\text{Den}_{H_{2\text{in}}}(s) = F^*P_{H_2}^5*(H_{2\text{in}}^*K_1^*P_{H_2O_2}^*I^*K_1^*K_2^*P_{H_2O_2}^*Y_{H_2}$$

$$+ P_{\text{anode}}^2*s*Y_{H_2})^2*[−4*I(2^*A_c^*K_1^*K_2^*P_{\text{anode}}^*P_{H_2O_2}^*R^*T^*Y_{H_2})$$

$$/(F^*P_{H_2}^5*(H_{2\text{in}}^*K_1^*P_{H_2O_2}^*I^*K_1^*K_2^*P_{H_2O_2}^*Y_{H_2} + P_{\text{anode}}^2*s*Y_{H_2}))$$

$$+(A_c^*K_2^*K_3^*P_{\text{cath}}^*(P_{H_2O_2} + P_{N_2}^*)R^*T^*Y_{O_2}^*(-(P_{\text{cath}}^*s*Y_{O_2})$$

$$- K_3^*(P_{N_2} - P_{O_2}^*)(O_{2\text{in}} + I^*K_2^*Y_{O_2}))$$

$$/(F^*P_{O_2}^5*(2^*P_{\text{cath}}^4*s^2*Y_{O_2} + K_3^*P_{\text{cath}}^2*s*Y_{O_2}^*(2^*O_{2\text{in}}^*(P_{H_2O_2}$$

$$+ 2^*P_{N_2} + P_{O_2}^*) - I^*K_2^*(P_{H_2O_2} - P_{N_2} - 2^*P_{O_2})^*Y_{O_2})$$

$$+K_3^2*P_{N_2}^*(P_{\text{cath}}^*)^2(2^*O_{2\text{in}}^* + I^*K_2^*O_{2\text{in}}^*Y_{O_2} + K_2^*Y_{O_2}))$$

$$+(I^*A_c^*K_2^*K_3^*P_{\text{cath}}^*(P_{N_2} + P_{O_2}^*)R^*T^*Y_{O_2}^*(4^*I^*P_{\text{cath}}^*s*Y_{O_2}$$

$$+ K_3^3*(P_{H_2O_2} + 2^*P_{N_2}^*)^2(2^*I^*O_{2\text{in}} + K_2^*Y_{O_2}))$$

$$/(F^*P_{H_2O_2}^5*(2^*P_{\text{cath}}^4*s^2*Y_{O_2} + K_3^*P_{\text{cath}}^2*s*Y_{O_2}^*(2^*O_{2\text{in}}^*(P_{H_2O_2}$$

$$+ 2^*P_{N_2} + P_{O_2}^*) - I^*K_2^*(P_{H_2O_2} - P_{N_2} - 2^*P_{O_2})^*Y_{O_2})$$

$$+K_3^2*P_{N_2}^*(P_{\text{cath}}^*)^2(2^*O_{2\text{in}}^* + I^*K_2^*O_{2\text{in}}^*Y_{O_2} + K_2^*Y_{O_2}))$$

and

$$S_{V_a} = \frac{\text{Num}_{V_a}(s)}{\text{Den}_{V_a}(s)}$$

$$\text{Num}_{V_a}(s) = -2^*A_c^*K^2^*P_{\text{anode}}^3^*P_{H_2O_2}^*R^2^*s^*T^2^*V_a$$
\[ \text{Den}_{VA}(s) = F*P_{H_2}*(F_{in}*P_{H_2O}*R*T - I*K_2*P_{H_2O}*R*T + P_{anode}^2*s*V_a)^2*[4*L} \\
+ (A_c*K_2*K_3*P_{cath}*(P_{H_2O} + P_{N_2})*R*(A_{in}*K_3*(P_{N_2} - P_{O_2})} \\
+ I*K_2*K_3*(P_{N_2} - P_{O_2}) + P_{cathode}^2*s)*T) \\
/(F*P_{O_2}*(2*A_{in}^2*K_3^2*P_{N_2}*(P_{cath} + K_2^2*K_3^2*P_{N_2}*(P_{cath})} \\
- I*K_2*K_3*P_{cath}^2*(P_{H_2O} - P_{N_2} - 2*P_{O_2})*s + 2*P_{cath}^4*s^2} \\
+ A_{in}^2*K_3^2*(P_{N_2} + P_{O_2})*R*(2*A_{in}^2*K_3^2*(P_{H_2O} + 2*P_{N_2})} \\
- I*K_2*K_3*(P_{H_2O} + 2*P_{N_2}) + 4*P_{cath}^2*s)*T) \\
/(F*P_{H_2O}*(2*A_{in}^2*K_3^2*P_{N_2}*(P_{cath} + K_2^2*K_3^2*P_{N_2}*(P_{cath})} \\
- I*K_2*K_3*P_{cath}^2*(P_{H_2O} - P_{N_2} - 2*P_{O_2})*s + 2*P_{cath}^4*s^2} \\
+ A_{in}^2*K_3^2*(P_{N_2} + P_{O_2})*R*(2*A_{in}^2*K_3^2*(P_{H_2O} + 2*P_{N_2} + P_{O_2})*s))))} \\
+ (2*A_{in}^2*K_2^2*P_{anode}^2*P_{H_2O}^2*R^2*T^2)/(F*P_{H_2}*(F_{in}*P_{H_2O})*R*T} \\
- I*K_2*P_{H_2O}^2*R*T + P_{anode}^2*s*V_a))}} (3.54)

where

\[ K_1 = \frac{(R^*T)}{V_a}, \quad K_2 = 2*Kr, \quad K_3 = \frac{(R^*T)}{V_c}, \quad P_{anode} = P_{H_2} + P_{H_2O}, \]

\[ P_{cath} = P_{O_2} + P_{N_2} + P_{H_2O}, \quad F_{in} = \frac{H_{2in}}{Y_{H_2}}, \quad A_{in} = \frac{O_{2in}}{Y_{O_2}} \] (3.55)

### 3.6.1.2 Sensitivity Function Plots

The various sensitivity functions for the PEMFC’s output impedance were evaluated using MATLAB and then plotted. Since the calculated sensitivity functions are complicated expressions and the parameters and input variables are many, only a few representative plots are presented here.

The baseline parameter and input values that were used are given in Table 3.5. These correspond to a PEMFC stack at the DoE’s National Energy Technology Laboratory, Morgantown, WV that underwent testing in 2003. This stack had four cells and ran on air (rather than pure oxygen).

These sensitivity function plots for the DoE National Energy Technology Laboratory (NETL) model were derived for the anode and cathode volume,
cell’s active area, output current density, cell’s temperature, inlet flow of hydrogen, inlet flow of air, and voltage loss constants, based on the NETL fuel cell’s parameter values and one set of operating conditions.

We first present the output impedance sensitivity plot with respect to the fuel cell’s anode volume (Figure 3.14). From the plot, we can notice that the overall impedance function is more sensitive to changes in the anode volume at frequencies around 1 rad/s.

We next present the output impedance sensitivity plot with respect to the fuel cell’s cathode volume (Figure 3.15). From the plot, we can notice that the overall impedance function is more sensitive to changes in the cathode volume at frequencies around 1 rad/s.

We next present the output impedance sensitivity plot with respect to the fuel cell’s active area (Figure 3.16). From the plot, we can notice that the overall impedance function is more sensitive to changes in the cell’s active area at low frequencies.

### TABLE 3.5
Fuel Cell Parameter and Input Values for Sensitivity Analysis

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Value or Input</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>Number of cells in the stack</td>
<td>4</td>
</tr>
<tr>
<td>T</td>
<td>Stack operating temperature</td>
<td>338.6 K</td>
</tr>
<tr>
<td>H_{an}</td>
<td>Anode inlet flow rate of hydrogen</td>
<td>3000 mL/min</td>
</tr>
<tr>
<td>Air_{in}</td>
<td>Cathode inlet flow rate of air</td>
<td>10,000 mL/min</td>
</tr>
<tr>
<td>I</td>
<td>Cell output current</td>
<td>40.25 A</td>
</tr>
<tr>
<td>A_c</td>
<td>Cell active area</td>
<td>136.7 cm²</td>
</tr>
<tr>
<td>i</td>
<td>Cell output current density</td>
<td>2926 A/m²</td>
</tr>
<tr>
<td>V_s</td>
<td>Volume of the cell anode channels</td>
<td>6.495 cm³</td>
</tr>
<tr>
<td>V_c</td>
<td>Volume of the cell cathode channels</td>
<td>12.96 cm³</td>
</tr>
<tr>
<td>L</td>
<td>Sum of cell voltage losses</td>
<td>−36 μV/cell (for a 2.2 A change)</td>
</tr>
<tr>
<td>a</td>
<td>Constant associated with cell activation losses</td>
<td>0.06 V</td>
</tr>
<tr>
<td>b</td>
<td>Constant associated with cell concentration losses</td>
<td>0.05 V</td>
</tr>
<tr>
<td>i_n</td>
<td>Cell internal current density corresponding to internal current losses</td>
<td>20 A/m²</td>
</tr>
<tr>
<td>i_o</td>
<td>Cell exchange current density corresponding to activation losses</td>
<td>9000 A/m²</td>
</tr>
<tr>
<td>i_l</td>
<td>Cell-limiting current density corresponding to concentration losses</td>
<td>3 μΩ m²</td>
</tr>
<tr>
<td>Y_{H₂}</td>
<td>Molar fraction of H₂ at the anode inlet</td>
<td>0.9</td>
</tr>
<tr>
<td>Y_{O₂}</td>
<td>Molar fraction of O₂ at the cathode inlet</td>
<td>0.189 (= 0.9*0.21)</td>
</tr>
</tbody>
</table>
We next present the output impedance sensitivity plot with respect to the fuel cell's output current density (Figure 3.17). From the plot, we can notice that the overall impedance function is more sensitive to changes in the cell's output current density at frequencies above 10 rad/s.

We next present the output impedance sensitivity plot with respect to the inlet flow rate of hydrogen (Figure 3.18). From the plot, we can notice that the overall impedance function is more sensitive to changes in the flow rate of hydrogen at a frequency range below 10 rad/s.

We next present the output impedance sensitivity plot with respect to the inlet flow rate of air (Figure 3.19). From the plot, we can notice that the overall impedance function is more sensitive to changes in the flow rate of oxygen at frequencies below about 1 rad/s.

We next present the output impedance sensitivity plot with respect to the fuel cell's temperature (Figure 3.20). From the plot, we can notice that the overall impedance function is more sensitive to changes in temperature at frequencies around 0.1 rad/s.

We next present the output impedance sensitivity plot with respect to the voltage losses constant $a$ (Figure 3.21). From the plot, we can notice that the overall impedance function is more sensitive to changes in the voltage losses constant $a$ at frequencies above 10 rad/s.
FIGURE 3.15
Output impedance sensitivity plot with respect to cell cathode volume.

FIGURE 3.16
Output impedance sensitivity plot with respect to cell’s active area.
FIGURE 3.17
Output impedance sensitivity plot with respect to output current density.

FIGURE 3.18
Output impedance sensitivity plot with respect to the hydrogen inlet flow.
FIGURE 3.19
Output impedance sensitivity plot with respect to the air inlet flow.

FIGURE 3.20
Output impedance sensitivity plot with respect to the cell temperature.
We next present the output impedance sensitivity plot with respect to the voltage losses constant \( b \) (Figure 3.22). From the plot, we can notice that the overall impedance function is more sensitive to changes in the voltage losses constant \( b \) at frequencies above 10 rad/s.

We next present the output impedance sensitivity plot with respect to the internal and fuel crossover current density constant \( i_n \) (Figure 3.23). From the plot, we can notice that the overall impedance function is more sensitive to changes in the internal current density at frequencies above 10 rad/s.

We next present the output impedance sensitivity plot with respect to the limiting current density constant \( i_l \) (Figure 3.24). From the plot, we can notice that the overall impedance function is more sensitive to changes in the limiting current density at frequencies above 10 rad/s.

We next present the output impedance sensitivity plot with respect to the specific area resistance \( r \) (Figure 3.25). From the plot, we can notice that the overall impedance function is more sensitive to changes in the specific area resistance \( r \) at frequencies above 10 rad/s.

Comparing the plots of the output impedance’s sensitivities with respect to the cell’s anode volume and to its cathode volume in Figures 3.14 and 3.15, respectively, note that the plots are somewhat similar to each other. However, the magnitude of the function for cathode volume is greater at the higher
### FIGURE 3.22
Output impedance sensitivity plot with respect to the voltage losses constant $b$.

### FIGURE 3.23
Output impedance sensitivity plot with respect to the internal current density constant $i_n$. 
FIGURE 3.24
Output impedance sensitivity plot with respect to the limiting current density constant \( i_l \).

FIGURE 3.25
Output impedance sensitivity plot with respect to the specific area resistance \( r \).
frequencies above 1 rad/s than the corresponding function for anode volume, and vice versa for frequencies below 1 rad/s. Hence, we infer that the high-frequency component of the cell’s dynamic response is more sensitive to changes in its cathode volume than to its anode volume under typically expected operating conditions. Considering the impedance sensitivity function with respect to the fuel cell’s active area as graphed by Figure 3.16, we can see that the overall impedance function is also more sensitive to changes in the fuel cell’s active area at lower frequencies than at frequencies higher than about 1 rad/s. The impedance sensitivity functions with respect to the inlet flow rates of hydrogen and air are shown in Figures 3.18 and 3.19, respectively. From these plots, we can see that the impedance is more sensitive to changes in the flow rate of hydrogen at a frequency range lower than 0.1 rad/s. On the other hand, for the flow rate of air, the impedance has a higher sensitivity at frequencies below about 1 rad/s.

3.6.2 Summary

In this section, we have described the results obtained from a sensitivity analysis performed on an input–output transfer function that is derived from the linear small-signal model of PEMFC dynamics proposed by Chiu et al. [18]. These results provide greater insight into the important design issue of which fuel cell parameters have greater impacts on the cell’s dynamic response. As one example, it was determined that the fuel cell’s dynamic response at higher frequencies is typically more sensitive to changes in its cathode volume than to its anode volume, which implies that the former is a more significant parameter for influencing the higher-frequency component of transient response than the latter.

3.7 Temperature and Fuel Dependence of an Equivalent Circuit Model of Direct Methanol Fuel Cells’ Dynamic Response

This section will focus on DMFCs. As has been mentioned in Chapter 1, methanol is easier to transport than the hydrogen used by PEMFCs and easier to work with; so, DMFCs are an attractive option for various portable and mobile applications, such as powering military equipment, forklifts, and scooters [41–43]. Moreover, methanol can be produced quite easily from biomass [44].

3.7.1 Importance of Equivalent Circuit Model

As is the case from PEMFCs, it is important to properly characterize an equivalent circuit model of the DMFC’s dynamic behavior, for performing
analysis and optimal design of the power systems based on such sources. Such characterization includes identifying the circuit’s components, their connection, and also the dependence of the component values on variable operating conditions such as temperature and fuel flow rate. The characterized model can then be used in several ways, such as for accurately evaluating and then improving how the DMFC interacts with other components of the complete power system (such as ultracapacitors (UCs) and switch-mode power converters), e.g., the effects of DC–AC converter ripple current on the lifespan of the fuel cell. Another way is for adjusting, either statically or dynamically, and in either an open-loop or closed-loop fashion, the temperature and/or fuel flow to obtain a more optimal dynamic performance of DMFCs in applications with fast, frequent, and/or significant load changes.

In the following sections, we will describe two such equivalent circuits, as well as the experimental dynamic response data we obtained that determined the particular circuit we would use for our study. Thereafter, we present the procedure used to estimate the component values of that equivalent circuit model and discuss the ensuing results, followed by several conclusions.

### 3.7.2 Equivalent Circuit Models of DMFC Dynamic Response

Several equivalent circuit models have been proposed to model the dynamic response of H₂-fueled PEMFCs as has been described in the previous sections of this chapter. Moreover, some of these models have been fit to, and its component values estimated from, measured frequency-domain (AC impedance) data with varying degrees of agreement [45,46]. On the other hand, only a couple of equivalent circuits have been proposed specifically to model the dynamic response of DMFCs. Other kinds of models, such as those presented in References 47–49, while important in their own right, are usually not as useful as circuit-type models to electrical engineers and control system engineers when they perform diagnostics, design, or analysis, e.g., to determine the amount of AC (ripple) current being drawn from the fuel cell by a given switch-mode DC–AC converter, which affects the cell’s lifespan.

The circuit model described in Reference 50 for DMFCs is a first-order model (see Figure 3.26) that has the following components: a source $E$ for the open-circuit voltage, which depends on the methanol and oxygen feed...
concentrations; a resistance $R_a$ representing the combined activation and mass-transport losses; a capacitance $C$ for the double-layer capacitance of the electrodes; and a resistance $R_{\text{ohmic}}$ representing the ohmic loss. In addition, second-order equivalent circuit models were proposed in References 51 and 52 (see Figures 3.27 and 3.28, respectively). Note that the model described in Reference 51 is identical to that in Reference 52, except for the additional resistor representing the cell’s ohmic resistance. The other components described in Reference 52 to model the DMFC anode impedance are an inductance $L$ to represent inductive behavior (phase delay) that can be explained using kinetic theory [53] for the reaction mechanism for methanol electro-oxidation involving intermediate adsorbates, a behavior confirmed by others such as in Reference 49; a resistance $R_o$ that serves to modify the phase delay according to the reaction scheme; a resistance $R_{\infty}$ that is associated with the part of the current response occurring without change in adsorbate coverage; and a capacitance $C_d$ that is believed to be associated with the redistribution of charge at the anode (it depended on parameters such as current density) instead of double-layer capacitances of the DMFC anode and cathode, since double-layer capacitance values for similar electrodes have been reported to be an order of magnitude lower than values calculated for this $C_d$. This circuit models well the frequency-domain impedance spectra of a DMFC.

FIGURE 3.27
Second-order equivalent circuit model of DMFC dynamic response, described in Reference 54.

FIGURE 3.28
Second-order equivalent circuit model of DMFC dynamic response, described in Reference 55.
operating with fuel flow at several times the stoichiometric rate, so excluding mass-transport limitations [52].

The model described in Reference 51, based on the model in Reference 52, includes an ohmic resistance $R_{\text{ohmic}}$ and a capacitance $C$ similar to $C_d$ in Reference 52; both of these values are supposedly constant. On the basis of impedance spectra measured with the cell output voltage at various levels from 0.5 V to 0.1 V, Wang et al. [51] also proposed nonlinear functions of current for the values of the parameters $R_{ct}$, $R_L$, and $L$, which are similar to $R_\infty$, $R_o$, and $L$, respectively, in Reference 52.

### 3.7.3 Testing of DMFC to Ascertain Equivalent Circuit Model Parameters

As described in Reference 54, testing of DMFCs can be performed to ascertain the equivalent circuit model parameters describing their dynamic response. Only a summary of the procedures followed therein for DMFC testing and for parameter identification is now provided, as is its conclusions.

A series of experiments were conducted at different combinations of temperature and fuel flow rate using the experimentation setup diagrammed in Figure 3.29. Tests were performed with temperature of the DMFC controlled to 30°C, 50°C, and 70°C on separate occasions with the aid of a thermocouple and electric heating elements embedded in the DMFC end plates, allowing for closed-loop control by the fuel cell test station (FCTS) software. The fuel flow rate was also varied, at each temperature setting, using the same software interface to be 0.2, 0.4, and then 0.6 mL/min on separate tests; however, the flow rate of air was fixed at 1 L/min. Tests were conducted first with fuel having a concentration of 1 mol/L, and then with fuel having a concentration of 0.5 mol/L.

The tests consisted of applying a fixed load resistance (16.8 Ω) to the terminals of the fuel cell, thus drawing a current of about 40 mA while the FCTS software recorded the voltage values at these terminals at a 1 Hz rate. The test data were first of the voltage values across the DMFC terminals after the load resistance was connected to the fuel cell; this part of the fuel cell response will be referred to as the “load-on” response. After an interval of 5 min, the load resistance was disconnected to produce an open circuit across the terminals, but the values for DMFC terminal voltage continued being recorded for another 5 min; this portion of the test will be referred to as the “load-off” response. This load-on, load-off test was repeated several times in order to ensure repeatability and also with the intent to average out the effect of random phenomena, such as electrical noise.

Note that, as compared to circuit modeling using electrochemical impedance spectra data, which is a frequency-domain approach, this test procedure does not require an expensive AC impedance (frequency response) analyzer. Instead, only time-domain data are collected. Moreover, that the choice of test conditions (temperature, fuel flow) was aimed at obtaining responses over a fairly wide range of possible operating conditions. Finally, the choice
of concentrations of 1 and 0.5 mol/L, was mainly determined for the ease of obtaining those values, given the limited precision of the volume measurements that could be made.

Figure 3.30 is illustrative of the measured load-on, load-off responses at the various operating conditions, although it was noted that the test data obtained at the 1 mol/L, 70°C, and 0.4 mL/min condition had somewhat greater variability (reduced repeatability) than the data at other test conditions (the $R^2$ values comparing the data sets at a given condition to each other, all being greater than 0.95, where $R^2$ has its usual definition as the ratio of the sum of squares of the regression to the total sum of squares), which

![Comparison of averaged data (with error bars) of load-on/load-off response of DMFC output voltage for an input of 1 mol/L concentration methanol at 0.4 mL/min, 50°C, to its least-squares estimate.](image)

**Figure 3.30**
Comparison of averaged data (with error bars) of load-on/load-off response of DMFC output voltage for an input of 1 mol/L concentration methanol at 0.4 mL/min, 50°C, to its least-squares estimate.
may explain certain results described in the next section; this was very likely due to random effects, and was not especially grievous (the $R^2$ values comparing the three data sets at this one-test condition to each other being 0.89, 0.98, and 0.84). It was observed from these responses of the fuel cell output voltage that the load-on response typically had an undershoot—meaning the response’s minimum value is less than its steady-state value. This type of response requires a mathematical function with at least two exponential terms to describe, which a first-order circuit cannot produce—its response, by definition, is a single exponential function of time [55]. Furthermore, small overshoots of a few millivolts—overshoot meaning the response’s maximum value is greater than its steady-state value—were observed from the 0.5 mol/L tests at 70°C. It is uncertain, at this time, which of the several difference(s) between these tests and those in Reference 50 result(s) in load-on responses with undershoots documented in Reference 54 but (first-order) responses without undershoots in Reference 50. But these observed undershoots meant that Singh et al. [54] focused on the second-order equivalent circuit model of Figure 3.27 for their study.

It is well known that second-order circuits can yield a transient response that is either overdamped (sum of two real exponential responses) or underdamped (sum of two complex exponential responses, resulting in an exponentially damped sinusoidal response). From the data collected by Singh et al. [54], it was clear that the load-off responses belonged to the overdamped category while the load-on responses belonged to the underdamped category; so, the corresponding capacitor voltage can be expressed as shown below

\[ v_c(t) = a e^{bt} + c e^{dt} \]  

(3.56)

\[ v_l(t) = \chi e^{-at} \cos(\omega t + \delta) + \Delta v \]  

(3.57)

where $v_c(t)$ is the capacitor voltage as indicated in Figure 3.27, $t$ time, $\Delta v$ the voltage to which $C$ is charged to during the load-on response, and the rest are constants that need to be determined from each test response. For both cases, the output voltage can be readily related to the capacitor voltage $v_c(t)$ by Kirchoff’s voltage law, and so the load-on response is given by

\[ v_r(t) = E - (a e^{bt} + c e^{dt}) - (v_c(t) R_t) R_{ohmic} \]  

(3.58)

and the load-off response is given by

\[ v_r(t) = E - (\chi e^{-at} \cos(\omega t + \delta) + \Delta v) \]  

(3.59)

However, the crux of the problem is centered on estimating the parameters $a, b, c, d$ or $\alpha, \omega, \chi, \delta$ embedded in the capacitor voltage expression, since the
voltage $E$ and resistance $R_{\text{ohmic}}$ can be readily obtained. Therefore, this guided their analysis, as described next, to relate the model component values to the parameters $a, b, c, d$ of Equation 3.56 or $\alpha, \omega, \chi, \delta$ of Equation 3.57.

### 3.7.4 Model Component Value Estimation

First, the (either load-on or load-off) responses were averaged and then approximated by nonlinear least-squares curve fitting using the MATLAB Curve Fitting Toolbox to determine the four response parameters, either $a, b, c, d$ of (3.56) or $\alpha, \omega, \chi, \delta$ of (3.57). Twenty-five iterations of each fitting were performed with different initial guesses of the parameter values to greatly increase the likelihood of obtaining the globally optimal solution. After selecting the best outcome of these iterations, it was found that all of the 1 mol/L load-on curves were fitted with $R^2 > 0.990$ with the exception of the 70°C, 0.4 mL/min case where the best fit yielded $R^2 = 0.961$. In addition, all of the 0.5 mol/L load-on curves were fitted with $R^2 > 0.987$. Moreover, all of the 1 mol/L load-off curves were fitted with $R^2 > 0.997$ with the exception of the 70°C, 0.4 mL/min case where the best fit yielded $R^2 = 0.990$. All of the 0.5 mol/L load-off curves were fitted with $R^2 > 0.997$.

Next, the values for the passive elements of the model were derived. Before analyzing this model, it was checked and verified that the model would work as expected. In particular, at steady-state, the capacitor acts as an open circuit and the inductor $L$ acts as a short circuit, allowing all the current to flow through it. Then, when the $R_{\text{load}}$ resistor is either connected or disconnected from the terminals of the fuel cell, the current through the inductor, and also the voltage drop across the capacitor, cannot change instantaneously.

To find the values for the capacitance, inductance, and resistances in the circuit of Figure 3.27, Laplace-domain circuit analysis was performed with the appropriate initial inductor current and initial capacitor voltage. For the load-off response, this analysis yielded an expression for the capacitor voltage that was of the form

$$V_c(s) = \frac{A_1s + A_0}{s^2 + J_1s + J_0}$$

(3.60)

where $A_1, A_0, J_1, J_0$ are functions of $R_{ct}, R_L, L, C$, and/or $E$. Whereas for the load-on response, the circuit analysis yielded an expression for the capacitor voltage that was of the form

$$V_c(s) = \frac{-B_1s + B_0}{s^2 + K_1s + K_0} + \frac{B_1}{s}$$

(3.61)

where $B_1, B_0, K_1, K_0$ are functions of $R_{ct}, R_L, L, C$, and/or $E$. Also, note that the Laplace transform of Equation 3.56 yields
\[ V_i(s) = \frac{(a + c)s - (ad + bc)}{s^2 - (b + d)s + bd} \]  
(3.62)

which is comparable to Equation 3.60, whereas the Laplace transform of Equation 3.57 yields

\[ V_i(s) = \frac{\chi \cos(\delta) s + \chi[\alpha \cos(\delta) - \alpha \sin(\delta)]}{s^2 + 2\alpha s + (\alpha^2 + \omega^2)} + \frac{\Delta v}{s} \]  
(3.63)

which is comparable to Equation 3.61. For the load-on responses, \( R_{\text{ohmic}} \) was easily calculated from the initial instantaneous drop in \( v_o(t) \), since \( v_c(t) \) cannot change instantaneously from its initial zero value, while matching expressions (3.61) through (3.63) resulted in four equations that nonlinearly depend on the to-be-determined \( R_{ct} \), \( R_L \), \( L \), and \( C \). They also depend on the known value of \( E \), which is the open-circuit voltage and also the initial value of the load-on response, and on the known value of \( \Delta v \), which is the difference between the initial and final (steady-state) values of the load-on, and ideally also the load-off, responses. These component values were then estimated by the nonlinear least-squares approach, making use of the MATLAB Optimization Toolbox, and the results obtained are shown in Tables 3.6 and 3.7. Note that the estimations resulted in the sum of squared errors (SSE) being less than \( 2.63 \times 10^{-4} \) and \( 2.86 \times 10^{-5} \) for each of the nine 1 mol/L and nine 0.5 mol/L operating conditions, respectively.

For the load-off response, \( R_{\text{ohmic}} \) could not be calculated, whereas matching expressions (3.60) and (3.62) resulted in one equation giving an exact solution for \( R_{ct} \) and three equations that nonlinearly depended on the obtained \( R_{ct} \) and the to-be-determined \( R_L \), \( L \), and \( C \). The values of \( R_L \), \( L \), and \( C \) were then estimated by the nonlinear least-squares approach, making use of the MATLAB Optimization Toolbox again, and the results obtained are shown in Tables 3.8 and 3.9. Note that the estimations resulted in the SSE being less than \( 3.92 \times 10^{-7} \) and \( 3.55 \times 10^{-7} \) for each of the nine 1 mol/L and nine 0.5 mol/L operating conditions, respectively.

### 3.7.5 Estimated Model Component Value Results

#### 3.7.5.1 For 1 mol/L Fuel Concentration

For the load-on response, the estimated resistance \( R_{ct} \) was observed to be essentially independent of the fuel flow rate between 0.2 and 0.6 mL/min, but increasing significantly with temperature between 30°C and 70°C. A mesh plot of the variation of \( R_{ct} \) is shown in Figure 3.31 for visualization purposes. The dependence of \( R_L \) on temperature and fuel flow rate is quite similar to that of \( R_{ct} \) except it showed a large abrupt increase at the 70°C, 0.4 mL/min operating condition; recall that the test data at this condition had somewhat greater variability (reduced repeatability) than the data at other
### TABLE 3.6
Second-Order Equivalent Circuit Model Values

<table>
<thead>
<tr>
<th></th>
<th>$R_{ct}$ (Ω)</th>
<th></th>
<th>$R_L$ (Ω)</th>
<th></th>
<th>$L$ (H)</th>
<th></th>
<th>$C$ (F)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.2 mL/min</td>
<td>0.4 mL/min</td>
<td>0.6 mL/min</td>
<td>0.2 mL/min</td>
<td>0.4 mL/min</td>
<td>0.6 mL/min</td>
<td>0.2 mL/min</td>
</tr>
<tr>
<td>30°C</td>
<td>1.495</td>
<td>1.555</td>
<td>2.502</td>
<td>45.22</td>
<td>52.14</td>
<td>88.73</td>
<td>3.611</td>
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<tr>
<td>50°C</td>
<td>4.676</td>
<td>5.847</td>
<td>7.959</td>
<td>141.2</td>
<td>173.1</td>
<td>308.0</td>
<td>2.534</td>
</tr>
<tr>
<td>70°C</td>
<td>18.39</td>
<td>21.64</td>
<td>15.23</td>
<td>578.2</td>
<td>1006</td>
<td>341.1</td>
<td>1.651</td>
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</table>

<table>
<thead>
<tr>
<th></th>
<th>$R_{ohmic}$ (Ω)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.2 mL/min</td>
<td>0.4 mL/min</td>
<td>0.6 mL/min</td>
<td>0.2 mL/min</td>
<td>0.4 mL/min</td>
<td>0.6 mL/min</td>
<td>0.2 mL/min</td>
<td>0.4 mL/min</td>
<td>0.6 mL/min</td>
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<tr>
<td>30°C</td>
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<tr>
<td>50°C</td>
<td>0.1300</td>
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<td>0.1699</td>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>70°C</td>
<td>0.1220</td>
<td>0.1241</td>
<td>0.1613</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Note:* Component values estimated from DMFC output voltage load-on responses at various temperatures and (1 mol/L concentration) fuel flow rates.
### TABLE 3.7
Second-Order Equivalent Circuit Model Values

<table>
<thead>
<tr>
<th></th>
<th>$R_{ct}$ (Ω)</th>
<th>$R_f$ (Ω)</th>
<th>$L$ (H)</th>
<th>$C$ (F)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.2 mL/min</td>
<td>0.4 mL/min</td>
<td>0.6 mL/min</td>
<td>0.2 mL/min</td>
</tr>
<tr>
<td>30°C</td>
<td>1.020</td>
<td>1.023</td>
<td>1.024</td>
<td>21.14</td>
</tr>
<tr>
<td>50°C</td>
<td>1.006</td>
<td>1.003</td>
<td>1.007</td>
<td>84.44</td>
</tr>
<tr>
<td>70°C</td>
<td>0.9832</td>
<td>0.9664</td>
<td>0.9835</td>
<td>85.80</td>
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</table>

*Note:* Component values estimated from DMFC output voltage load-off responses at various temperatures and (1 mol/L concentration) fuel flow rates.
### TABLE 3.8
Second-Order Equivalent Circuit Model Values

<table>
<thead>
<tr>
<th></th>
<th>$R_{ct}$ ($\Omega$)</th>
<th>$R_L$ ($\Omega$)</th>
<th>$L$ (H)</th>
<th>$C$ (F)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.2 mL/min</td>
<td>0.4 mL/min</td>
<td>0.6 mL/min</td>
<td>0.2 mL/min</td>
</tr>
<tr>
<td>30°C</td>
<td>6.672</td>
<td>23.68</td>
<td>11.08</td>
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<td></td>
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<td>26.27</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>6.653</td>
</tr>
<tr>
<td>50°C</td>
<td>5.276</td>
<td>32.09</td>
<td>33.72</td>
<td>0.3887</td>
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<td></td>
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<td>21.27</td>
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<td></td>
<td>9.329</td>
</tr>
<tr>
<td>70°C</td>
<td>1.705</td>
<td>2.921</td>
<td>6.951</td>
<td>4.117</td>
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<td></td>
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<td></td>
<td></td>
<td>102.8</td>
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<td></td>
<td>19.30</td>
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<table>
<thead>
<tr>
<th></th>
<th>$R_{ohm}$ ($\Omega$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.2 mL/min</td>
</tr>
<tr>
<td>30°C</td>
<td>0.1226</td>
</tr>
<tr>
<td>50°C</td>
<td>0.1553</td>
</tr>
<tr>
<td>70°C</td>
<td>0.1583</td>
</tr>
</tbody>
</table>

**Note:** Component values estimated from DMFC output voltage load-on responses at various temperatures and (0.5 mol/L Concentration) fuel flow rates.
### Table 3.9
Second-Order Equivalent Circuit Model Values

<table>
<thead>
<tr>
<th></th>
<th>$R_{ct}$ (Ω)</th>
<th>$R_L$ (Ω)</th>
<th>$L$ (H)</th>
<th>$C$ (F)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.2 mL/min</td>
<td>0.4 mL/min</td>
<td>0.6 mL/min</td>
<td>0.2 mL/min</td>
</tr>
<tr>
<td>30°C</td>
<td>0.9997</td>
<td>0.9566</td>
<td>0.9606</td>
<td>14.33</td>
</tr>
<tr>
<td></td>
<td>0.9976</td>
<td>1.001</td>
<td>0.9999</td>
<td>98.99</td>
</tr>
<tr>
<td>70°C</td>
<td>0.9831</td>
<td>0.9770</td>
<td>0.9396</td>
<td>99.09</td>
</tr>
</tbody>
</table>

**Note:** Component values estimated from DMFC output voltage load-off responses at various temperatures and (0.5 mol/L Concentration) fuel flow rates.
test conditions, so that this increase may be slightly suspect. Interestingly, $L$ did not show much variation (in absolute terms) over the studied ranges of temperature and fuel flow rate. On the other hand, the estimates of $C$ varied widely in value and without a discernible trend with respect to temperature or fuel flow rate.

For the load-off response, the estimated resistance $R_{ct}$ was observed to be essentially unchanged over the tested ranges of temperature and fuel flow rate. Whereas $R_L$ increased rather abruptly with temperature between 30°C and 50°C and then leveled off up to 70°C, but was relatively independent of fuel flow rate. On the other hand, $C$ was observed to be essentially independent of fuel flow conditions but had an inverse dependency on temperature. $L$ also increased with temperature between 30°C and 50°C, but was relatively independent of fuel flow rate at these two temperatures; while at 70°C, its values at both 0.2 and 0.6 mL/min decreased from their values at 50°C, but its value at 0.4 mL/min instead increased from the value at 50°C. Since it was noted that the test data at this 70°C, 0.4 mL/min condition had somewhat greater variability (reduced repeatability) than the other test data, this inconsistent behavior (dissimilar from the 0.2 and 0.6 mL/min values) is again slightly suspect, and needs to be confirmed in future studies.

### 3.7.5.2 For 0.5 mol/L Fuel Concentration

For the load-on response when using fuel of lower concentration, the resistances $R_{ct}$ and $R_{ohmic}$ were essentially independent of the fuel flow rate between 0.2 and 0.6 mL/min, and of the temperature between 30°C and

![FIGURE 3.31](https://example.com/figure331.png)

Dependence of resistance $R_{ct}$ values, estimated from load-on step responses, on temperature and (1 mol/L concentration) fuel flow rate.
70°C, although $R_{ct}$ varied somewhat more than $R_{ohmic}$. Furthermore, the $R_{ohmic}$ values were very much consistent with those obtained from the 1 mol/L tests, as expected. The $L$ values varied slightly more than the $C$ values (in absolute and percentage terms) over the studied ranges of temperature and fuel flow rate, although both were without a discernible trend with respect to temperature or fuel flow rate. Compared to the 1 mol/L results, the $L$ values had increased by an order of magnitude, while the $C$ values had decreased by at least one order of magnitude; so, these were significantly affected by the fuel concentration.

For the load-off response, the resistance $R_{ct}$ was essentially independent over the tested ranges of temperature and fuel flow rate, and also very much consistent with those obtained from the 1 mol/L tests. Whereas $R_{ct}$ increased rather abruptly with temperature between 30°C and 50°C and then leveled off up to 70°C; however, it was relatively independent of fuel flow rate at 50°C and 70°C, just like the 1 mol/L case. On the other hand, $C$ was essentially independent of fuel flow conditions at 50°C and 70°C, but had an inverse dependency on temperature (see Figure 3.32), just like the 1 mol/L cases. The $L$ values also increased with temperature between 30°C and 50°C to become somewhat independent of fuel flow rate at 50°C, although curiously its values for the 30°C 0.4 mL/min and 30°C 0.6 mL/min cases were 2 orders of magnitude lower than for the other cases, of which values were in line with the $L$ values for the 1 mol/L condition.

Finally, in broadly comparing the component values for the 1 mol/L cases to the 0.5 mol/L cases, it was noted that the higher fuel concentration resulted in greater variability of those values. This comparison was between

![FIGURE 3.32](https://example.com/figure3.32.png)

Dependence of capacitance $C$ values, estimated from load-off step responses, on temperature and (0.5 mol/L concentration) fuel flow rate.
the values for the various temperature and fuel flow rate conditions, as well as between the values for the load-on and load-off responses.

### 3.7.6 Further Discussion

Muller et al. [52], presented values of $C = 0.135 \text{ F/cm}^2$, $R_\text{ct} = 1.705 \Omega \text{ cm}^2$, $R_L = 0.863 \Omega \text{ cm}^2$, and $L = 0.716 \text{ H/cm}^2$ for their proposed second-order model (Figure 3.28), obtained under load, and estimated using frequency-domain (AC impedance) data and technique. For a 25 cm$^2$ active area membrane as in Reference 54, these would correspond to values of $C = 3.375 \text{ F}$, $R_\text{ct} = 68.2 \text{ m\Omega}$, $R_L = 34.5 \text{ m\Omega}$, and $L = 179 \text{ H}$. Comparison of these values to the corresponding estimates in Tables 3.6 and 3.8 (under load) yielded average percentage errors of $\{12, 819\%, 880, 315\%, -85\%, -335,790\%\}$ and $\{20, 118\%, 3, 699\%, 122\%, 156\%\}$, respectively, for $R_\text{ct}$, $R_L$, $L$, and $C$. The likely explanation for the large discrepancies is that the operating conditions in Reference 52 differed significantly in a few key respects from the operating conditions used in Reference 54; in particular, the lowest current density in the tests by Muller et al. was 100 mA/cm$^2$, although it is not completely clear from Reference 52 which set of data (and operating conditions) corresponded to their estimates as given above, while the tests described by Singh et al. [54] were at a current density of about 2 mA/cm$^2$. These parameters’ dependence on current was described in Reference 51.

On the other hand, let us now consider the output impedances corresponding to the obtained parameter estimates. The output impedance of the studied second-order equivalent circuit model (Figure 3.27) is expressed as

$$Z = R_\text{ohmic} + \frac{R_L s + R_\text{ct} R_L}{R_\text{ct} L C s^2 + (L + R_\text{ct} R_L) s + (R_\text{ct} + R_L)}$$

(3.64)

The Nyquist plots using the estimates presented in Tables 3.6 and 3.7 are shown in Figure 3.33, while the Nyquist plots using the estimates presented in Tables 3.8 and 3.9 are shown in Figure 3.34. These plots compare well to the DMFC impedance plots shown in Reference 49, which have similar shapes, and $\text{Re}(Z)$ values ranging from 0 to 5 $\Omega$ and $\text{Im}(Z)$ values ranging from $-2.5$ to 1 $\Omega$. These similarities provide a measure of support for the validity of the method proposed by Singh et al. [54] and the resulting model component estimates.

### 3.7.7 Conclusions

This section has described the equivalent circuit modeling of DMFC dynamics from measured temporal (time-domain) responses during step changes in load current at various temperature and fuel flow-rate operating conditions as proposed by Singh et al. [54]. The simulated responses of the assumed
FIGURE 3.33
Nyquist plots of second-order equivalent circuit model's output impedance using component values estimated from (a) load-one step responses and (b) load-off step responses; 1 mol/L concentration fuel.
FIGURE 3.34
Nyquist plots of second-order equivalent circuit model’s output impedance using component values estimated from (a) load-on step responses and (b) load-off step responses; 0.5 mol/L concentration fuel.
second-order circuit model, a first-order model being determined to be less accurate for reproducing the observed response undershoots and overshoots, with its estimated component values yielded excellent fits with the experimental data for the 30–70°C temperature range and the 0.2–0.6 mL/min fuel flow range under study. The results provide all the information that is obtained by an AC impedance measurement, without requiring an impedance (frequency response) analyzer, and also determines the contribution of each component to the overall impedance. One can use these modeling results in ways such as: (1) diagnostically—to determine which parts of a fuel cell are degrading or have degraded and (2) prospectively—to guide changes to the fuel cell’s design and fabrication (such as the MEA’s various components) that would improve its output impedance, dynamic behavior, etc. Perhaps, even more importantly, this equivalent circuit model can be used to evaluate and then improve upon how the DMFC interacts with other components of the complete power system (such as UCs and switch-mode power converters), e.g., the effects of DC–AC converter ripple current on the lifespan of the fuel cell, similar to Reference 45 for H₂-fueled PEMFCs.

It was further determined in Reference 54 that the model’s capacitor, inductor, and resistor values are quite sensitive to temperature but relatively insensitive to fuel flow rates—more so for load-off than for load-on responses—for the same fuel concentration. Moreover, each component’s dependencies on temperature and fuel flow rate differ from those of the other components. Such dependencies could mean that in practice, they should be adjusted either statically or dynamically, and in either an open-loop or closed-loop fashion, to obtain a more optimal performance of DMFCs in applications with fast, frequent, and/or significant load changes. In addition, different fuel concentrations resulted in greater variability of the parameter values during the load-on responses as compared to the load-off responses, which is expected since the former correspond to when current is flowing and thus fuel being consumed to produce that current.

Nomenclature

\[ E_0 \]  
Cell open-circuit potential at standard pressure

\[ N \]  
Number of cells in the stack

\[ E \]  
Fuel cell (stack) output voltage

\[ L \]  
Sum of cell voltage losses

\[ i \]  
Cell output current density

\[ i_n \]  
Cell internal current density corresponding to internal current losses

\[ i_o \]  
Cell exchange current density corresponding to activation losses
Cell-limiting current density corresponding to concentration losses
Cell area-specific resistance corresponding to resistive losses
Constant associated with cell activation losses (slope of Tafel line)
Constant associated with cell concentration losses
Stack operating temperature
Partial pressure of hydrogen inside the cell anode
Partial pressure of oxygen inside the cell cathode
Partial pressure of water vapor inside the cell anode
Partial pressure of water vapor inside the cell cathode
Summation of partial pressures inside the cell cathode
Universal gas constant (8.3144 J/mol K)
Faraday’s constant (96,439 C/mol)
Standard pressure (101,325 Pa)
An assumed constant cell operating pressure
Anode inlet molar flow rates of hydrogen and water vapor
Cathode inlet molar flow rates of oxygen, nitrogen, and water vapor
Anode outlet molar flow rates of hydrogen and water vapor
Cathode outlet molar flow rates of oxygen, nitrogen, and water vapor
Molar usage and production rates of hydrogen, oxygen, and water vapor (in the cathode)
Cell output current
Cell active area
Volume of the cell anode channels
Volume of the cell cathode channels
Pressure fractions of hydrogen, oxygen, and water vapor (in the cathode) inside the fuel cell
Molar fraction of $H_2$ at the anode inlet
Molar fraction of $O_2$ at the cathode inlet
Molar fraction of water vapor at the cathode inlet
Perturbations of the partial pressures of hydrogen, oxygen, and water vapor (in the cathode) inside the fuel cell
ΔH_{2in}, ΔO_{2in}, ΔH_2O_{cln}  Perturbations of the inlet flow rates of hydrogen, oxygen, and water vapor (to the cathode)

Δi  Perturbation of the output current density

ΔE  Perturbation of the fuel cell stack output voltage

References


