EVALUATION OF A PEM FUEL CELL MODEL
Outline

- Motivation
- Fuel Cell Modeling Requirements for Control Systems
- PEM Fuel Cell Electrochemical Model
- Parameters and Simulation of Fuel Cell Stack
- Multi-Parametric Sensitivity Analysis
- Evaluation of Relative Sensitivity
- Dynamical Evaluation of PEMFC Stack
- Conclusions
Types of Fuel Cells

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>PEMFC</th>
<th>DMFC</th>
<th>AFC</th>
<th>PAFC</th>
<th>MCFC</th>
<th>SOFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte</td>
<td>Proton Exchange Membrane</td>
<td>Proton Exchange Membrane</td>
<td>Potassium Hydroxide</td>
<td>Phosphoric Acid</td>
<td>Molten Carbonates (Li, K, Na)</td>
<td>Solid Oxide ZrO₂-Y₂O₃</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>50-90</td>
<td>50-130</td>
<td>50-250</td>
<td>180-200</td>
<td>650</td>
<td>750-1050</td>
</tr>
<tr>
<td>Charge Carrier</td>
<td>H⁺</td>
<td>H⁺</td>
<td>OH⁻</td>
<td>H⁺</td>
<td>CO₃²⁻</td>
<td>O²⁻</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Pt</td>
<td>Pt</td>
<td>Pt, Ni</td>
<td>Pt</td>
<td>Ni, LiNi</td>
<td>Ni</td>
</tr>
<tr>
<td>Fuel</td>
<td>H₂ (Pure or Reformed)</td>
<td>CH₃OH</td>
<td>H₂ (Reformed)</td>
<td>H₂ and CO reformed &amp; CH₄</td>
<td>H₂ and CO reformed &amp; CH₄</td>
<td></td>
</tr>
<tr>
<td>Poison</td>
<td>CO&gt;10ppm</td>
<td>Adsorbed intermediates</td>
<td>CO, CO₂</td>
<td>CO&gt;1% H₂S&gt;50ppm</td>
<td>H₂S&gt;0.5ppm</td>
<td>H₂S&gt;1ppm</td>
</tr>
<tr>
<td>Main Applications</td>
<td>Portable, Transportation</td>
<td>Portable, Transportation</td>
<td>Space</td>
<td>Power gener., Co-generation, Transportation</td>
<td>Power gener., Co-generation</td>
<td>Power gener., Co-generation</td>
</tr>
</tbody>
</table>

Main characteristics of PEMFC stacks are:

- they produce water as a residue;
- they have high efficiency when compared to thermal generation;
- they operate at low temperatures which allows a fast start-up and improved dispatchability; and
- they use a solid polymer as the electrolyte, which reduces concerns related to construction, transport and safety.
Power Based Fuel Cell Applications

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>Portable electronics equipment</th>
<th>Cars, boats, and domestic CHP</th>
<th>Distributed power generation, CHP, also buses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power</td>
<td>1</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>Typical applications</td>
<td>Higher energy density than batteries. Faster recharging</td>
<td>Potential for zero emissions, higher efficiency</td>
<td>Higher efficiency, less pollution, quiet</td>
</tr>
</tbody>
</table>

- **AFC**
- **PEMFC**
- **SOFC**
- **MCFC**
- **PAFC**
Fuel Cell Modeling

- Difficulties for accurate PEMFC dynamical model
- Lack of information and familiarity for the modeling parameters.
- Parameters choice affect voltage, power, efficiency and time response.
- Disagreements arise of uncertainties on hard experimental verification and ill-defined parameters.
- Multi-Parametric Sensitivity Analysis (MPSA) is a tool to find the relative importance of the physical and electrochemical processes.
Multi-Parametric Sensitivity Analysis (MPSA) comprises the ranking of parameters importance and assessment of ill-defined parameters that limit the accuracy of modeling.

The goal is to perform a variance decomposition sensitivity analysis of the system in various situations characterized by different nominal values of the parameters, so as to put in evidence how they may affect the system behavior, or which are the grade of redundancy on the uncertainty of some signals.

The procedure includes the following steps:

- Select the parameters to be tested;
- Set the range of each parameter to include expected variations;
- For each parameter generate a large series of independent random values in the design range;
- Run the model using this large series and calculate an objective function;
- Determine the validity range (from acceptable to unacceptable) by comparing the objective function to a given criterion(R);
- Evaluate the distributions of the parameters with the acceptable/non-acceptable results to define relative importance.
The output voltage of a single cell, $V_{FC}$, can be defined as follow:

$$V_{FC} = E_{Nernst} - V_{act} - V_{ohmic} - V_{con}$$

For $n$ cells connected in series, forming a stack, the voltage, $V_s$, can be calculated by:

$$V_s = n \cdot V_{FC}$$

- $E_{Nernst}$ is the thermodynamic potential of each unit cell and it represents its reversible voltage;
- $V_{act}$ is the voltage drop associated with the activation of the anode and of the cathode;
- $V_{ohmic}$ is the ohmic voltage drop, a measure of the voltage drop associated with the conduction of protons and electrons;
- $V_{con}$ represents the voltage drop resulted from the decrease in the concentration of oxygen and hydrogen.

Each individual term is defined by:

\[ E_{Nernst} = 1.229 - 0.85 \times 10^{-3} (T - 298.15) + 4.31 \times 10^{-5} T \left[ \ln(P_{H_2}) + \frac{1}{2} \ln(P_{O_2}) \right] \]

\[ V_{ohmic} = i_{FC} \cdot (R_M + R_C) \]

\[ V_{con} = -B \cdot \ln \left( 1 - \frac{J}{J_{\text{max}}} \right) \]

\[ V_{act} = -\left[ \xi_1 + \xi_2 T + \xi_3 T \cdot \ln(c_{O_2}) + \xi_4 T \cdot \ln(i_{FC}) \right] \]

\[ c_{O_2} = \frac{P_{O_2}}{5.08 \times 10^6 e^{-\left(\frac{498}{T}\right)}} \]
where

- $P_{H2}$ and $P_{O2}$ are the partial pressures (atm) of hydrogen and oxygen, respectively;
- $T$ is the cell absolute temperature (K);
- $i_{FC}$ is the cell operating current (A);
- $c_{O2}$ is the concentration of oxygen in the catalytic interface of the cathode (mol/cm$^3$);
- $\xi_i (i=1...4)$ represent the parametric coefficients for each cell model;
- $R_M$ is the equivalent membrane resistance to proton conduction;
- $R_C$ is the equivalent contact resistance to electron conduction;
- $J_{max}$ is the maximum current density;
- $B (V)$ is a constant dependent of the cell type and its operation state;
- $J$ is the actual cell current density (A/cm$^2$).
The equivalent membrane resistance can be calculated by:

\[ R_M = \frac{\rho_M \cdot \ell}{A} \]

\( \rho_M \) is the membrane specific resistivity (Ω.cm), which can be obtained by

\[
\rho_M = \frac{1}{\left[ \psi - 0.634 - 3 \left( \frac{i_{FC}}{A} \right) \right] \cdot \exp \left[ 4.18 \left( \frac{T - 303}{T} \right) \right]}
\]

\[
181.6 \left[ 1 + 0.03 \frac{i_{FC}}{A} \right] + 0.062 \left( \frac{T}{303} \right)^2 \left( \frac{i_{FC}}{A} \right)^{2.5}
\]
where

- the term $181.6/(\psi - 0.634)$ is the specific resistivity ($\Omega \cdot \text{cm}$) at zero current and at temperature of $30^\circ\text{C}$ (303 K);
- the exponential term in the denominator is the temperature factor correction if the cell is not at $30^\circ\text{C}$.
- The parametric coefficient $\psi$ is considered an adjustable parameter, with a possible minimum value of 14 and a maximum value of 23.

Such nine equations represent the fuel cell stack static behavior.
An electrical circuit can be used to model the FC dynamical behavior:

\[ R_{\text{con}} \]
The dynamical equation is represented by:

$$\frac{dv_d}{dt} = \frac{1}{C} i_{FC} - \frac{1}{\tau} v_d$$

$v_d$ represents the dynamical voltage (associate with $V_{act}$ and $V_{con}$), $C$ is the equivalent electrical capacitance and $\tau$ is the FC electrical time constant (where $R_a$ is an equivalent resistance)

$$\tau = C.R_a = C.(R_{act} + R_{con}) = C.\left(\frac{V_{act} + V_{con}}{i_{FC}}\right)$$

Including the dynamic behavior:

$$V_{FC} = E_{Nernst} - V_{ohmic} - v_d$$

Therefore, the dynamic behavior is incorporated in the model.
Parametric Sensitivity Analysis

- The model needs definition of several parameters.
- Parameters are based on manufacturing data.
- PEMFC operation is difficult to assess accurately because those processes are electrochemical in nature and some design considerations are proprietary.
- A 500 W BCS stack was simulated to investigate the parameter sensitivity.


BCS Technology Co.; Data sheet for a 500 W FC stack; 2001
Simulation of fuel cell stack

The following block diagram shows the overall simulation requirements:

- Parameters: $n, A, \ell, \xi, \psi, J_n, J_{\text{max}}, R_C, B, C$

Diagram:

- Fuel Cell Model:
  - $P_{H2}$
  - $P_{O2}$
  - Parameters:
    - $n, A, \ell, \xi, \psi, J_n, J_{\text{max}}, R_C, B, C$
- Load:
  - $i_{FC}$
  - $T$
  - $V_s$

Connections:
- $T, i_{FC}$
- $i_{FC}$
### Parameter Set for a 500 W BSC Stack

<table>
<thead>
<tr>
<th>Param.</th>
<th>Value</th>
<th>Param.</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td>32</td>
<td>$\xi_1$</td>
<td>-0.948</td>
</tr>
<tr>
<td>$A$</td>
<td>64 cm$^2$</td>
<td>$\xi_2$</td>
<td>$0.00286+0.0002 \ln (A)+ (4.3\times10^{-5}) \ln (cH2)$</td>
</tr>
<tr>
<td>$\ell$</td>
<td>178 mm</td>
<td>$\xi_3$</td>
<td>$7.6\times10^{-5}$</td>
</tr>
<tr>
<td>$T$</td>
<td>333 K</td>
<td>$\xi_4$</td>
<td>$-1.93\times10^{-4}$</td>
</tr>
<tr>
<td>$P_{O2}$</td>
<td>0.2095 atm</td>
<td>$\psi$</td>
<td>23.0</td>
</tr>
<tr>
<td>$P_{H2}$</td>
<td>1 atm</td>
<td>$J_n$</td>
<td>3 mA/cm$^2$</td>
</tr>
<tr>
<td>$R_C$</td>
<td>0.0003 $\Omega$</td>
<td>$J_{max}$</td>
<td>469 mA/cm$^2$</td>
</tr>
<tr>
<td>$B$</td>
<td>0.016 V</td>
<td>$C$</td>
<td>3 F</td>
</tr>
</tbody>
</table>
Simulation of fuel cell stack – cont.

Using the previous parameter set presented the simulated polarization curve, obtained with the electrochemical model is presented and compared to the manufacturer data.

The simulated results present a good agreement with the real data, except at the very beginning and at the very end of the polarization curve.
Multi-Parametric Sensitivity Analysis

- Sensitivity analysis is a tool which may be used to study the behavior of a model and to ascertain how outputs of a given model depend on each or some of its input parameters.
- Statistics may help in defining performance figures, such as:
  - Mean — the average of the data
  - Median — the value of middle observation
  - Mode — the value with greatest frequency
  - Standard Deviation — measure of average deviation
  - Variance — the square of standard deviation
  - Coefficient of variation — standard deviation divided by mean
  - Skewness — measure of symmetry
  - Kurtosis — measure of flatness or peakedness

- However, an index of importance (objective function) must be computed to measure how much a parameter or a component influences the uncertainty in the system must be computed.
Multi Parametric Sensitivity Analysis - Cont.

The procedure of MPSA was based on the reference below. The following steps were employed:

1. Select the parameters to be tested.
2. Set the range of each parameter.
3. For each parameter, generate a series of independent random numbers with a uniform distribution within the defined range.
4. Run the model using the selected series and calculate the objective function for each value of cell current.
5. Determine the relative importance of each parameter for each value of current.
6. Evaluate parametric sensitivity (to define the sensitive and insensitive parameters).

Multi Parametric Sensitivity Analysis – Cont.

- **Objective function**
  \[ f = \sum_{i=1}^{k} [x_0(i) - x_c(i)]^2 \]

- **Relative Importance**
  \[ \delta_i = \frac{f_i}{x_0(i)} \]

where \( f \) is the objective function value, \( x_0(i) \) is the observed value, \( x_c(i) \) is the calculated value and \( k \) is the number of elements contained in the random series (Step 3)

- **500 uniformly distributed values were used to calculate the above figure of merit.**
## Range of Parameters Used for MPSA

<table>
<thead>
<tr>
<th>Param.</th>
<th>Test range</th>
<th>Param.</th>
<th>Test range</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>$64 \pm 5% \text{[cm}^2\text{]}$</td>
<td>$\xi_1$</td>
<td>$-0.948 \pm 10%$</td>
</tr>
<tr>
<td>$\ell$</td>
<td>$178 \pm 5% \text{[\mu m]}$</td>
<td>$\xi_3$</td>
<td>$7.6.10^{-5} \pm 10%$</td>
</tr>
<tr>
<td>$R_C$</td>
<td>$0.0003 \pm 15% \text{[\Omega]}$</td>
<td>$\xi_4$</td>
<td>$-1.93.10^{-4} \pm 10%$</td>
</tr>
<tr>
<td>$B$</td>
<td>$0.016 \pm 15% \text{[V]}$</td>
<td>$\psi$</td>
<td>$15 - 24$</td>
</tr>
<tr>
<td>$J_n$</td>
<td>$3 \pm 25% \text{[mA/cm}^2\text{]}$</td>
<td>$C$</td>
<td>$1 - 5 \text{[F]}$</td>
</tr>
<tr>
<td>$J_{max}$</td>
<td>$469 \pm 10% \text{[mA/cm}^2\text{]}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Relative Importance Results

Cell active area \( (A) \)

Maximum current density \( (J_{\text{max}}) \)

Internal current density \( (J_{n}) \)
Relative Importance Results - Cont.

**Membrane thickness ($\ell$)**

**Contact resistance ($R_c$)**

**Parameter B**
Relative Importance Results - Cont.

Parameter $\xi_1$

Parameter $\xi_2$

Parameter $\xi_3$
Relative Importance Results - Cont.

Parameter $\psi$

![Graph showing the relationship between sensitivity and current, with sensitivity increasing as current increases.](image)
Evaluation of Relative Sensitivity

As higher is the relative importance index, more sensitive is the modeling in respect to the parameter. An inspection on the previous results suggests the following classification:

- Insensitive: $A$, $\ell$, $R_C$
- Sensitive: $J_n$, $B$, $\xi_4$, $\psi$
- Highly sensitive: $J_{\text{max}}$, $\xi_1$, $\xi_3$
Insensitive parameters: the ones related to the cell construction

Parameter $J_n$ only affects the simulation results at low current values

Parameters $B$, $\xi_4$ and $\psi$ also have more influence on the stack voltage for high current values
Evaluation of Relative Sensitivity - Cont.

For the parameter $J_{\text{max}}$ the model results are more affected for high current values. This can be explained by the logarithm term in the correspondent equation. When the current density is close to the maximum value, the logarithm term tend to zero as well the concentration voltage. This, by its turn, changes the resulting stack voltage.

For parameters $\xi_1$ and $\xi_3$ the model results are affected for all current values in a same order. Their electrochemical exact definition is given by R. F. Mann et alii.

Evaluation of Relative Sensitivity – Cont.

\[ \xi_1 = - \frac{\Delta G_a}{2 \cdot F} - \frac{\Delta G_c}{\alpha_c \cdot n \cdot F} \quad \text{and} \quad \xi_3 = \frac{R \cdot (1 - \alpha_c)}{\alpha_c \cdot F} \]

where:

- \( \Delta G_a \): free activation energy for the standard state (J/mol), referred to the anode;
- \( \Delta G_c \): free activation energy for the standard state (J/mol), referred to the cathode;
- \( \alpha_c \): parameter for the anode chemical activity;
- \( F \): Faraday constant;
- \( R \): gases universal constant;
- \( A \): cell active area (cm\(^2\));
- \( c_{H_2} \): hydrogen concentration (mol/cm\(^3\)); and
- \( c_{H_2O} \): water concentration (mol/cm\(^3\)).

All these elements are related to the electrochemical process needed for electrodes activation and they are difficult to determine with great accuracy. The values used in the presented model are based on calculation and measured results.
Influence of the uncertainty due $\xi_1$ and $\xi_3$

- The following stack polarization curve was calculated considering that $\xi_1$ and $\xi_3$ vary in the range of $\pm$ 5% (at random).
- It can be seen the stack voltage changes considerably, making the polarization curve far from similar to the real data.
Dynamical Evaluation of PEMFC Stack

The dynamical behavior of a PEMFC stack is modeled as an equivalent electrical circuit.

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 the equivalent capacitance $C$, whose value, for the PEMFC, is of a few Farads.

This capacitance does not influence the stack polarization curve, because each point of this curve is obtained after the voltage has reached its steady-state value. To evaluate its effect, a current interruption test can be simulated.

In practical electronics circuits, the values of the capacitors are much less than these. Despite of that, these values are representative of the PEMFC dynamical behavior and do not represent real capacitors.

Dynamical Evaluation of PEMFC Stack - Cont.

- The figure shows the effect for a reduction in the stack current, from 15 A to 0 A (open circuit). The curves showed in are from equivalent capacitances values from 0.5 F to 5 F, resulting in a range of 1:10.

- The current reduction occurs after 10 seconds of simulation. The stack voltage presents an instantaneous change (ohmic overpotential), followed by a first order delay, until it reaches its new final steady-state value (open circuit voltage).
Conclusions

In this seminar, an investigation of the influence of the modeling parameters on the dynamical performance of PEMFC simulations was conducted.

To show the effects of some key parameters, an electrochemical model was used to evaluate the stack polarization curve based on the dynamic behavior of a 500 W BCS stack and some data from the literature.

The parameters are analyzed using a Multi-Parametric Sensitivity Analysis (MPSA). As a result, the parameters were classified according to their influence in the model results as: insensitive ($A$, $\ell$ and $R_C$), sensitive ($J_n$, $B$, $\xi_4$ and $\psi$.) and highly sensitive ($J_{\max}$, $\xi_1$ and $\xi_3$).

For the most sensitive parameters ($\xi_1$ and $\xi_3$) it was shown that the polarization curve can present results that are not similar to the real data.

The results do not have a fixed trend but are dispersed along the real curve.
Conclusions - Cont.

- The definition of the values for the fuel cell simulation parameters is not a simple task,
- Once the parameter set is defined, it is only valid for a specific cell or stack. To simulate other fuel cells, almost all the values must be defined again.
- This work evaluated the importance of each parameter in the simulations accuracy.
- A synergy must exist between Electrical Engineers and Chemical Engineers to define the best parameters for a consistent fuel cell stack simulation!!!