Section 1 - Project Description

1.1 Project

Simulation of a Proton Exchange Membrane Fuel cell.

1.2 Description

Development of a Proton Exchange Membrane Fuel cell simulation on Microsoft Excel using empirical relations. The project has two models depending on the data available with the user. The model takes inputs from the user and simulates the operation of the fuel cell that depends on the input constraints.

1.3 Revision History

Date	Comment	Author
16th January 2020	Entire documentation of the 1st version of the model	Gautama Bharadwaj,
		Harikrishnan U,
		Navedya Ojha,
		Venu Bhargav
17th January 2020	Added references, figures and edited document	Gautama Bharadwaj,
		Harikrishnan U

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PEM Fuel Cell Simulation Documentation				

Section 2 - Introduction

2.1 Purpose of the document

This document is intended to serve as the user manual for using the fuel cell simulation. It also technically describes the product including the methodology, mathematical and empirical relations, and the design and implementation constraints.

2.2 Current system

While a few commercial fuel cell simulations are available, there are only a handful number of open-source fuel cell simulations.

2.3 Limitations of the current system

The limitations of the commercial fuel cell simulations are the cost and the limitations to the available open-source simulations are its limited accuracy and dependency on the user inputs.

2.4 Proposed system

Two models of the simulation is proposed. As the simulation depends on the user input, the usage of either of these models depends on the data available to the user.

2.4.1 With polarization curve

This model is used if the user has the data from the polarization curve available. This data is provided in the manufacturer's datasheet for the fuel cell and needs to be extracted by the user. The data extracted from the polarization curve is provided as input to the model.

2.4.2 Without polarization curve

This model is used if the user does not have the polarization curve. This user utilizes empirical relations to determine the operation of the fuel cell and expects a few inputs from the user.

Section 3 - Definitions, acronyms, abbreviations

PEMFC Proton Exchange Membrane Fuel Cell

 E_{nernst} Nernst Voltage (V) T Temperature (K)

Z No of electrons involved in the reaction (2)
F 96485(Faraday's constant) (As/mol)
R_{ohmic} Total resistance of fuel cell (ohms)

 i_{fc} fuel cell current (A)

 ΔG Gibbs free energy (KJ/mol) E_{oc} Open circuit voltage (V)

i₀ Exchange current density (A/cm²) i_L Limiting current density (A/cm²)

A Cell area (cm²)

a Exchange coefficient (--)

P_{H2} Partial pressure of Hydrogen (bar)

Partial pressure of O2 (bar)

P Total pressure at anode and cathode(equal)(refer assumption 2) (bar)

 $α_1$ Pressure ratio(partial pressure of H_2 to Total pressure) βPressure ratio(partial pressure of O_2 to Total pressure) ΦPressure ratio(partial pressure of O_2 to Total pressure)

 E,V_{fc} Fuel cell voltage (V)

E₁ Fuel cell voltage without considering voltage drops(V)

ηact Activation lossesηohm Ohmic losses

ηconc Concentration losses

- E_{nernst}: The Nernst equation is derived from the standard changes in the Gibbs free energy associated with an electrochemical transformation.
- nact: This term stands for Activation losses. This is directly related to the slowness of the reaction at the electrode surface. Essentially this loss component appears only at the beginning and then slowly decreases to a nominal value. It is largely influenced by the value of Eoc.
- nohm: This term stands for Ohmic losses of the fuel cells. It is essentially the resistance offered to the flow of electrons by the fuel cell hardware, electrolyte, etc. It is directly proportional to the current density and hence increases in a linear manner.
- nconc: This term stands for Concentric losses. Also called Mass transport losses, this results from
 the decrease in reactant concentration at the surface of the electrodes as fuel is used. At maximum
 (limiting) current, the concentration at the catalyst surface is practically zero, as the reactants are
 consumed as soon as they are supplied to the surface.

- E: This is the theoretical voltage that can be obtained from the fuel cell. It does not take into account the voltage drops due to resistances(for this model Rohmic).
- Gibbs energy: Gibbs energy gives us the maximum amount of reversible work that can be done by the substance.
- Exchange current density (i₀): Exchange current is the nominal current flow due to the exchange of ions across the electrolyte when it is open-circuited or is at a steady-state with no load connected to it. Exchange current density is basically exchange current for a particular cell area.
- Resistance(R_{ohmic}): This is assumed to be constant throughout the simulation process. This takes into account the different resistances such as Electrolytic, Ohmic, Internal resistances, etc.
- NA: This is the product of N (number of cells) and A (Tafel's slope).
- Tafel's plot: It is a graphical technique used to find out overpotential and the exchange current density. It is plotted separately for the electrodes. An example of Tafel's slope is shown below:

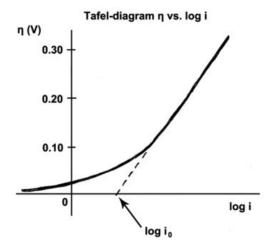


Fig 1: Tafel's slope

Section 4 - With Polarization curve

4.1 Product overview

The model is intended to assist the research community in simulating the operation of a Proton Exchange Membrane Fuel Cell using Polarisation curve as reference.

4.2 Block diagram

Fig 2: Block diagram of model using polarization curve

4.3 Tools/Softwares required

Platform: Windows 7,8,10,Ubuntu Windows: Microsoft Office Excel

Ubuntu: LibreOffice Calc

4.4 Assumptions

1. The polarization curve is available with the user to input the required coordinates.

Reason: There is a set of coordinates that needs to be obtained from the polarisation curve for obtaining the following parameters:

V1: Voltage when 1 Amps of current flows through the fuel cell to the load.

Vnom, Inom: This is essentially obtained the intersection point of Polarisation curve and the Power curve of the fuel cell.

Vmin, Imax: This point indicates the maximum current that the fuel cell can produce and the corresponding voltage when that current is being drawn from the fuel cell.

 \mathbf{E}_{oc} : This is obtained when the Polarisation curve intersects the Voltage axis.

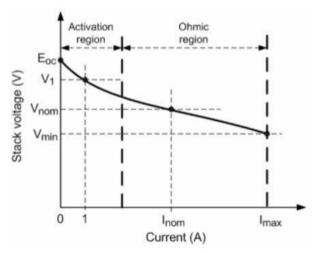


Fig 3: Typical polarization plot

Fig1: Shown above is a typical Polarization curve at the coordinates that need to be obtained from it. The parameters that are obtained using these points are:

- 1. **R**_{ohmic}: Total resistance offered by the fuel cell which includes internal resistance, Ohmic resistance, Electrolytic resistance, etc.
- 2. NA: Product of the number of cells and the Tafel's slope value. For more information about Tafel's slope.

2. Pressure at anode and cathode remains constant.

Reason: Pressure at the cathode and anode plays an important role as it can influence the movement of electrons in the electrolyte and the membrane. A huge pressure difference between Anode and Cathode can lead to the rupturing of the membrane and other physical conditions becoming abnormal. Hence to nullify the deviations that are caused due to the changes in pressures, they are considered to be constant at anode and cathode. Practically, the effect of pressure is more pronounced for cathode and at low current densities.

3. Temperature remains constant throughout the simulation.

Reason: Thermal drifting causes significant changes in the current values especially when the fuel is just put into operation. At higher temperatures, this effect becomes significant and nonlinear. Hence to avoid its interference onto the fuel cell current, the temperature is assumed to be constant.

4. Exchange current density or exchange current itself is assumed to be constant.

Reason: Since the R_{ohmic} is obtained from the polarization curve for a particular region it may not be constant for all the time. This value of resistance can be considered constant as the temperature of operation of the fuel cell is assumed to be constant and fuel effects are not taken into account. As R_{ohmic} becomes constant, the exchange current density also becomes constant.

5. Load current varies from 0 to 1A in steps of 0.05.

Reason: This is a flexible value and for simplification purposes, the fuel cell current has been set to limit at 1A. This can be modified by the user according to his setup.

4.5 Mathematical modeling

Governing equations:

$$\begin{split} E_{_{1}} &= E_{_{0}} + (RT/2F)*(\ \alpha_{_{1}}*\beta^{\wedge}0.5/\Box) + (RTln(p)/2F)^{[5]} \\ V_{fc} &= E - i_{fc}*R_{ohmic}^{\quad \ [5]} \end{split}$$

Enernst gives the ideal open circuit potential of the fuel cell. This indicates the upper limit or maximum performance of the fuel cell.

- $$\begin{split} \bullet \quad & E_{nernst} = 1.229 + (T\text{-}298.15)*(\text{-}44.43/(z*F)) + (R*T*ln(P_{H2}*P_{O2})/(z*F))^{[1]} \\ \bullet \quad & \eta act := R*T*ln(i_{fc}/i_0)/(z*\sigma*F)^{[1]} \end{split}$$
- $\eta ohm = i_{fc} * R_{ohmic}$ [1]
- $\eta \text{conc}=2.11*\exp(-5)*\exp(0.08*i_{f_0})^{[5]}$

4.6 Auxiliary equations

Gibbs energy : $\Delta G = E_{oc} * z * F - 1$ (approximation)^[5]

Exchange current density: $i_0 = ((R/(2*F)*(1/R_{obmic})/A)^{[4]})$

For this particular model, the exchange current is assumed to be constant although practically it varies with a lot of factors such as the fuel flow rate, concentration and pressure of fuels etc.

The exchange current becomes constant because the resistance offered by the fuel cell(Rohmic) is considered constant.

Resistance (Rohmic): $R_{\text{ohmic}} = V_1 - V_{\text{nom}} - NA*ln(I_{\text{nom}}))/I_{\text{nom}} - 1^{[1]}$

This is assumed to be constant throughout the simulation process and is obtained with the help of polarisation curve as explained before(fig1)

This takes into account the different resistances such as Electrolytic, Ohmic, Internal resistances etc.

NA : NA =
$$(V_1 - V_{nom})^* (I_{max} - 1) - (V_1 - V_{min})^* (I_{nom} - 1)) / (LN(I_{nom})^* (I_{max} - 1) - LN(I_{max})^* (I_{max} - 1))^{[1]}$$

This is the product of N(number of cells) and (A)Tafel's slope.

4.7 Methodology

Step 1 : Calculating Rohm and Eoc form the coordinates taken as input from polarisation curve.

$$\begin{split} R_{\text{ohmic}} = & V_1 - V_{\text{nom}} - NA*ln(I_{\text{nom}}))/I_{\text{nom}} - 1^{[1]} \\ NA := & (V_1 - V_{\text{nom}})*(I_{\text{max}} - 1) - (V_1 - V_{\text{min}})*(I_{\text{nom}} - 1))/(LN(I_{\text{nom}})*(I_{\text{max}} - 1) - LN(I_{\text{max}})*(I_{\text{max}} - 1))^{[1]} \end{split}$$

Step 2 : Calculating Nernst Voltage.

$$E_{nernst} = 1.229 + (T-298.15)*(-44.43/(z*F)) + (R*T*ln(P_{H2}*P_{O2})/(z*F))^{[1]}$$

- **Step 3 :** Calculating Gibbs energy $\Delta G = E_{oc} *z*F-1^{[5]}$
- **Step 4 :** Cross verifying(approx) Eoc with the input(checking Gibbs energy range).
- **Step 5 :** Calculating ohmic losses, activation losses and concentration losses.

$$\begin{array}{l} \text{\eta act:=}R*T*ln(i_{fc}/i_{0})/(z*a*F)^{[1]} \\ \text{\eta ohm=}i_{fc}*R_{ohmic}^{\quad \ \ \, [1]} \\ \text{\eta conc=}2.11*exp(-5)*exp(0.08*i_{fc})^{[5]} \end{array}$$

Step 6: Calculating E.

$$E=E_0+(RT/2F)*(\alpha_1*\beta^0.5/\Box)+(RT\ln(p)/2F)^{[5]}$$

Step 7 : Varying i_{fc} from 0 to 1.

Step 8 : Calculating
$$V_{fc}$$
 for each i_{fe} .
$$V_{fc} = E - i_{fc} * R_{ohmic}^{~~[5]}$$

Step 9 : Plotting the polarisation curve for user's reference.

4.8 Design and implementation constraints

1.Exchange current is assumed to be constant which is practically not true as it depends on input parameters such as fuel utilisation, temperature etc.

Exchange current also has a linear relationship with limiting current which can be used to find out the regions of saturation of fuel cell. This model suffers from this drawback as it restricts the user to 1A(default) of load current which can be varied.

Secondly, limiting current is not obtained and it assumed that the exchange current density remains constant and hence effects all the operating regions of fuel cell equally which is practically not true.

2. The effect of fuel flow and its concentration is not taken into account. Practically, Eoc and gibbs energy gets effected by these factors. For this model, Gibbs energy is approximated using Eoc which is true to some extent but the effects of fuel concentration is completely neglected for calculating Gibbs energy(Thermodynamic aspects).

Hence calculating the enthalpies and entropies would enable us to get a better value of Gibbs energy using the thermodynamic relation :

$$\Delta G = \Delta H - T \Delta S^{[2]}$$

3. For this model, the fuel cell current is obtained using an electrical perspective but it is also dependent on the molar flow rate of the fuel. Hence using the relation given below, a better fuel cell current could

be obtained:

Ifc=Z*Molar flow rate*F^[2]

4.Exchange current is also dependent on the fuel utilisation factors which can be incorporated by calculating the utilisation factors.

4.9 User manual

The inputs and outputs are colour coded for user's use.

By default, there are some values that are assigned to each variable. The user can edit /delete these values by clicking on them.

Specific ranges are given to each value and an error message is displayed if the user tries to exceed the same.

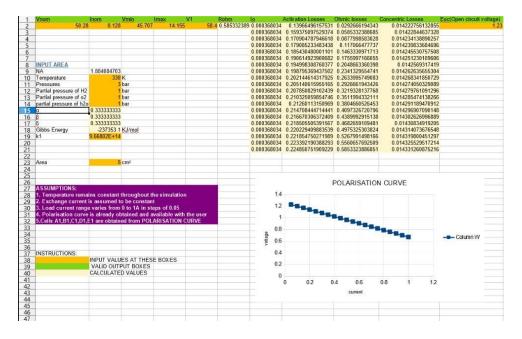


Fig 4: Screenshot of the excel sheet model with Polarisation curve plotted for default values

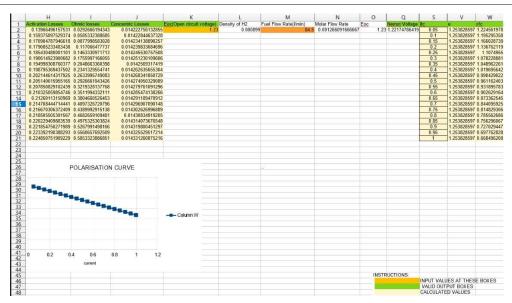


Fig 5 : Screenshot of Output area

Section 5 - Without Polarization curve

5.1 Product overview

This model can be used by a user without having the polarization curve. The model does require certain input parameters that should be known by the user such as temperature of operation, charge transfer coefficient, exchange current, limiting current, internal resistance, partial pressure of H_2 , and partial pressure of H_2 .

5.2 Block diagram

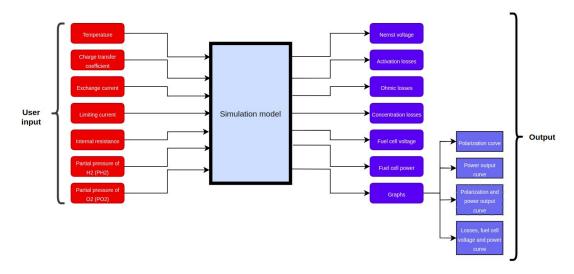


Fig 6: Block diagram of model without polarization plot

5.3 Tools/Softwares

Platform: Windows 7,8,10,Ubuntu Windows: Microsoft Office Excel

Ubuntu: LibreOffice Calc

5.4 Assumptions

The assumptions made for the model are:

- Internal resistance (R_{ohmic}) is taken as constant throughout operation of fuel cell.
- i_1 and i_0 are known by the user.
- Partial pressures (P_{H2} and P_{O2}) are known by the user.

5.5 Mathematical modeling

This model is constructed using pure empirical relations. The inputs that are required from the user are temperature of operation (T), Charge transfer coefficient (α), exchange current (i_0), limiting current (i_L), internal resistance (R_{ohmic}), partial pressure of $H_2(P_{H2})$, and partial pressure of $O_2(P_{O2})$.

Apart from the user inputs, the constants considered for simulation are ideal gas constant (R), Faraday's constant (F), and number of moving electrons (z).

The mathematical modeling is made as follows:

Step 1 : Calculate Nernst voltage using the formula : $E_{nernst} = 1.229 + (T-298.15)*(-44.43/(z*F)) + (R*T*ln(P_{H2}*P_{O2})/(z*F))$ [1]

Step 2 : Calculate the activation losses : η act = $R*T*ln(i/i_0)/(z*a*F)$ [6]

Step 3 : Calculate the ohmic losses : η ohm = $i*R_{ohmic}$ [8]

Step 4 : Calculate the concentration losses : $\eta conc = R*T*ln(i_1/(i_1-i))/(z*F)$ [6]

Step 5 : Calculate the fuel cell voltage : $E = Enernst - \eta act - \eta ohm - \eta conc [1]$

Step 6 : Calculate the power output : P = E*i

Step 7: Plot the polarization curve and power output curve

Step 8 : Obtain nominal values of voltage and current by observation of polarization and power output curve.

The fuel cell current density is increased in steps of 0.05 A/cm² upto the limiting current value. Step 2 to step 6 is iterated for every value of current. Thus for each value of fuel cell current density, the activation losses, ohmic losses, concentration losses, fuel cell voltage, and power output is calculated.

The polarization curve, power output curve, and losses curve are plotted to indicate the variations with fuel cell current density. The graph with polarization and power output curve can be used to determine the nominal values of fuel current density and fuel cell voltage.

In case the user does not know certain input values, the model by default assumes the most likely value of the input parameter. For example, the charge transfer coefficient is assumed to be 0.35 if the user does not know the value as the charge transfer coefficient value is generally between 0.2 and 0.5. []

For the input parameters

Quantity	Value	Units
Ideal gas constant (R)	8.314	J/(mol K)
Faraday's constant (F)	96485	As/mol
Number of moving electrons (z)	2	
Temperature (T)	320	K
Charge transfer coefficient (0)	1	
Exchange current (i ₀)	0.0032	A/cm ²
Limiting current (i _L)	3.2305	A/cm ²
Internal resistance (R _{ohmic})	0.18	Ω cm ²
Partial pressure of H ₂ (P _{H2})	0.375	atm
Partial pressure of O ₂ (P _{O2})	1	atm

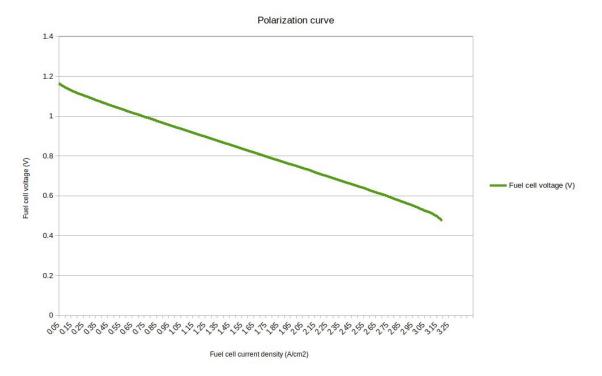


Fig 7: Polarization curve

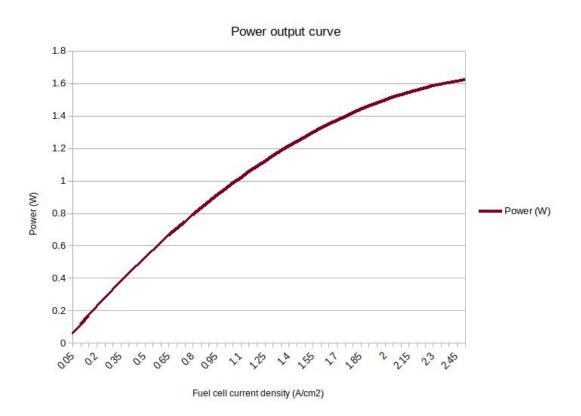


Fig 8: Power output curve

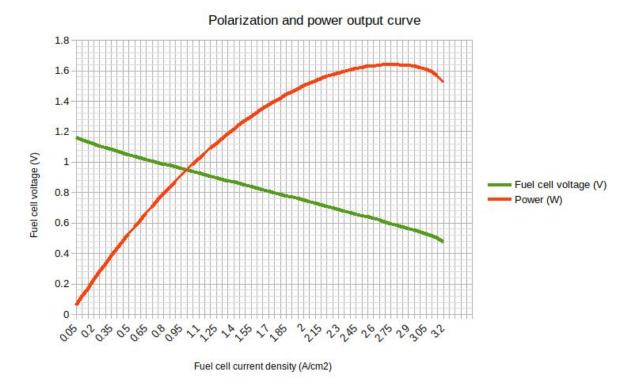


Fig 9: Polarization and power output curve

The meeting point of the polarization curve and power output curve will give us the nominal values of operation of fuel cell.

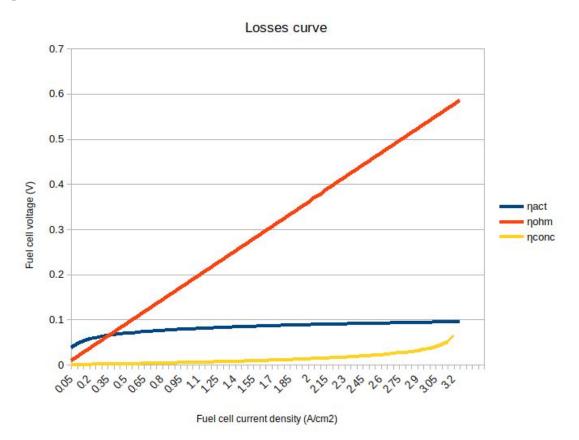


Fig 10: Losses curve

5.6 Design and implementation constraints

The drawbacks of this model are as follows:

- The users are required to know the values of limiting current density and exchange current density.
- The activation losses appear to increase initially and remain constant (as seen in fig.)which does not correspond to the theoretical study as the activation losses are supposed to be maximum at low current densities and reduces as the current density increases.

5.7 User manual

The excel sheet model is shown below. The sheet contains section for input, output, and graphs. It also contains a section that explains the steps and formulae. The following images show the different sections and explains the usage.

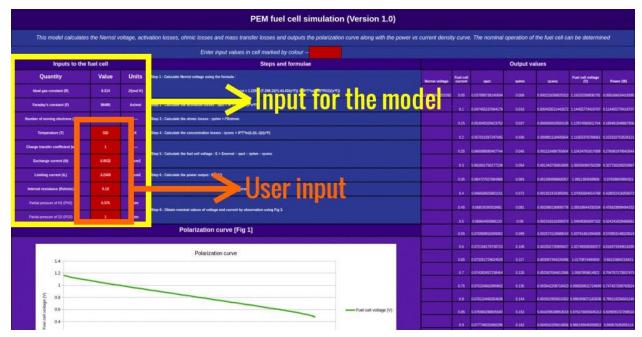


Fig 11: Input section in the model

The user inputs are entered in the cells marked in red. Other cells should not be edited by the user. Once the user enters the values in cells marked in red, the output values automatically get updated. The output values are displayed in the section as shown below.

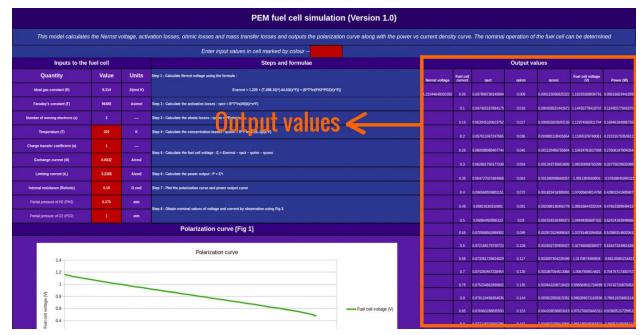


Fig 12: Output section in the model

The output values consists of the Nernst voltage [which remains constant], activation losses (η act), ohmic losses (η ohm), concentration losses (η conc), fuel cell voltage (E), and power (P).

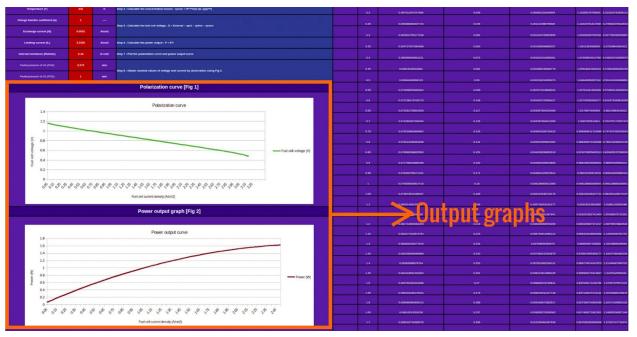


Fig 13: Graphs displayed



Fig 14: Graphs displayed

The output graphs are displayed in the model as shown above.

Section 6 - Without Polarization curve

6.1 Product overview

This model can be used by a user without having the polarization curve. The model does require certain input parameters that should be known by the user such as the temperature of operation, internal resistance, the pressure at the cathode and anode and the fuel flow rate.

6.2 Block diagram

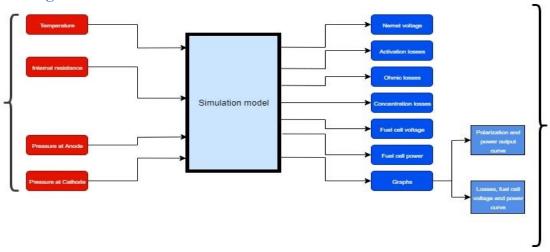


Fig 6: Block diagram of model without polarization plot

6.3 Tools/Softwares

Platform: Windows 7,8,10,Ubuntu Windows: Microsoft Office Excel

Ubuntu: LibreOffice Calc

6.4 Assumptions

- The following assumptions are made in order to build the model on an excel sheet:-
- The nominal voltage ratio K_c is taken as 1. $(E_{oc} = E_n)$
- The thickness of diffusion layer $\delta = 100 \mu m$. [10]
- 'D' Diffusion Coefficient = 10^{-2} cm²/s. [10]
- Area Specific Resistance (ASR) R_{ohm} is known to the user and is constant (The effect of membrane water concentration is not considered).
- $I_L = K*I_0 \text{in this relation } K = 10^3. [11]$

- The temperature for operation is below 100°C.
- The load current density (I_{E_c}) is varied until $4A/cm^2$.
- Ideal and Uniform gas Distribution. [1]
- The fuel flow rate is kept constant throughout the operation.
- The value of α is not limited between 0 and 1

6.5 Mathematical modeling

This model is constructed using pure empirical relations. The inputs that are required from the user are the temperature of operation in Kelvin (T), the internal resistance (R_{ohmic}), the pressure of fuel at the anode, and the pressure of air at the cathode.

Apart from the user inputs, the constants considered for simulation are ideal gas constant (R), Faraday's constant (F), and number of moving electrons (z).

The mathematical modeling is made as follows:

Step 1: $P_{H2} = P_{anode} * (1 - Uf_{H2})$, here P_{anode} is the pressure of the fuel at the anode and Uf_{H2} is the utilization factor of H_2 [9]

Also,

 $P_{O2} = P_{cathode}$, $P_{cathode}$ is the pressure of air entering the cathode. [9]

<u>Utilization factor</u> is given as:

$$Uf_{H2} = (60000*R*T*I_{fc})/(z*V_{fuel}*F*x\%)$$
 [1]

 I_{fc} is the fuel cell current (in A/cm²) which is drawn by the load and V_{fuel} is the fuel flow rate (in Lpm). In this model x% is taken as 0.9995 (99.95% of H_2 {purity}). [1]

Step 2 : Calculate Nernst voltage using the formula :

$$E_{nernst} = 1.229 + (T-298.15)*(-44.43/(z*F)) + (R*T*ln(P_{H2}*P_{O2})/(z*F)) [1]$$

Step 3 : Calculate the activation losses : η act = $R*T*ln(i/i_0)/(z*q*F)$ [6]

Step 4: Calculate the ohmic losses: η ohm = $i*R_{ohmic}$ [8]

Step 5 : Calculate the concentration losses : $\eta conc = R*T*ln(i_1/(i_1-i))/(z*F)$ [6]

Step 6 : Calculate the fuel cell voltage : $E = Enernst - \eta act - \eta ohm - \eta conc [1]$

Step 7 : Calculate the power output : P = E*i

Step 8: Plot the polarization curve and power output curve

Step 9: Obtain nominal values of voltage and current by observation of polarization and power output curve.

The fuel cell current density is increased in steps of 0.25 A/cm² up to 4 A/cm². Step 1 to step 7 is iterated for every value of current. Thus for each value of fuel cell current density, the activation losses, ohmic losses, concentration losses, fuel cell voltage, and power output is calculated.

The polarization curve, power output curve, and losses curve are plotted to indicate the variations with fuel cell current density. The graph with polarization and power output curve can be used to determine the nominal values of fuel current density and fuel cell voltage.

For the input parameters

Quantity	Value	Units
Ideal gas constant (R)	8.314	J/(mol K)
Faraday's constant (F)	96485	As/mol
Number of moving electrons (z)	2	
Temperature (T)	338	K
Internal Resistance	0.18	Ω
Pressure at Anode	1	Bar
Pressure at Cathode	1	Bar
Fuel Flow Rate	84.5	Lpm

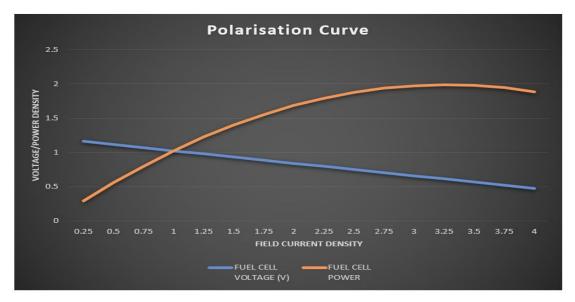


Fig 9: Polarization and power output curve

The meeting point of the polarization curve and power output curve will give us the nominal values of operation of the fuel cell.

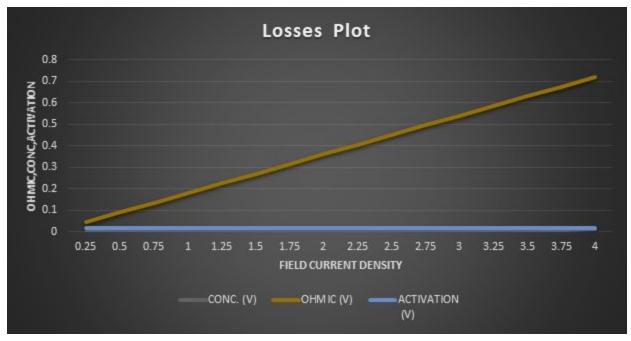


Fig 10: Losses curve

6.6 Design and implementation constraints

The drawbacks of this model are as follows:

In this model the criteria of ' α ' – charge transfer coefficient is not in ideal range(0-1). This is generally 0.5 for a reaction in which the constituents are H_2 and O_2 with platinum electrode (Pt). Another relation may be used to accurately determine the value of α . Along the same lines an empirical relation to determine exchange current density can also be obtained.

The effect of membrane water concentration on internal resistance can also be determined and need not be taken as an input from the user in future models.

6.7 User manual

The excel sheet model is shown below. The sheet contains a section for input, output, and graphs. It also contains a section that explains the steps and formulae. The following images show the different sections and explain the usage.

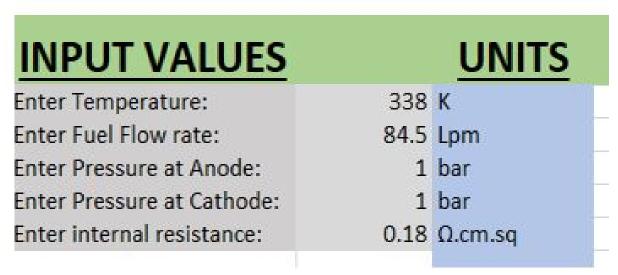


Fig 11: Input section in the model

The user inputs are entered in the cells marked in red. Other cells should not be edited by the user. Once the user enters the values in cells marked in red, the output values automatically get updated. The output values are displayed in the section as shown below.

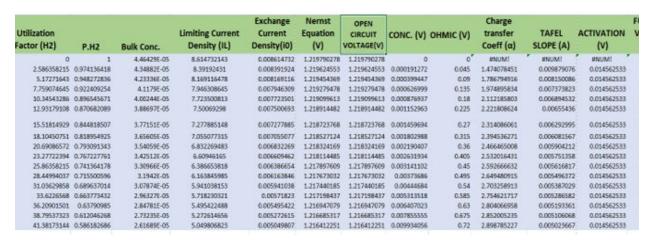


Fig 12: Output section in the model

The output values consist of the Nernst voltage, activation losses (η act), ohmic losses (η ohm), concentration losses (η conc), fuel cell voltage (E), and power (P).

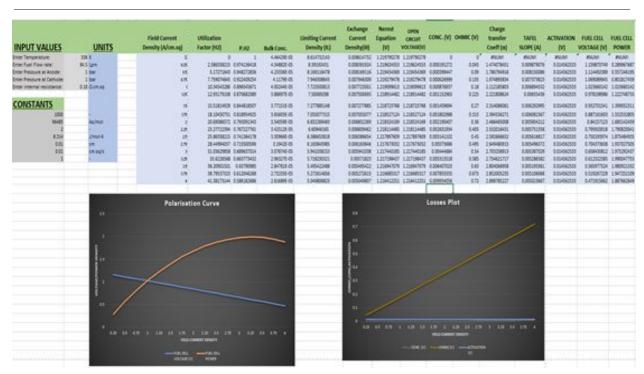


Fig 13: Graphs displayed

Section 7 - References

Sl.no	Title	Author
1	Development of a generic fuel cell model: application to a fuel cell vehicle simulation	Souleman Njoya Motapon*, Olivier Tremblay and Louis-A. Dessaint
2	Fuel cell handbook	US Department of Energy
3	Fuel Parameter and Quality Constraints for Fuel Cell Distributed Generators	Phanikrishna Gomatom, Student Member, IEEE, and Ward Jewell, Fellow, IEEE
4	Apparent ion-exchange current densities at valinomycin-based potassium ion-selective PVC membranes obtained with an ac-impedance method	Sheng-Luo Xie ** and k. Cammann Department of Analytical Chemistry, Anorganisch-Chemisches Institut, Technische Universitiit Munchen
5	Excel sheet assessment.xls Excel sheet model by University of Strathclyde	University of Strathclyde
6	Designing and building fuel cells	Colleen Spiegel
7	Modelling and validation of Proton exchange membrane fuel cell (PEMFC)	A K M Mohiuddi, N Basran, and A A Khan
8	How to Predict Fuel Cell Performance https://www.fuelcellstore.com/blog-section/how-to-predict-fuel-cell-performance	Colleen Spiegel
9	CACHE Modules on Energy in the Curriculum	Michael D. Gross
10	Fuel Cell Mass Transport	M. Oliver
11	Determination of an optimum performance Of PEMFC based on its limiting current density	Ayoub Kazim