Supplementary Materials

PEMFC notion

PEMFC is a static electro-chemical device that is capable of developing electrical energy efficiently through internal membrane reactions. The main parts of the cell are two catalyst-coated-electrodes (one is called anode and the other is cathode) separated by a solid polymer electrolyte. The construction of the cell membrane is depicted in Figure 1. The hydrogen fuel is supplied through the anode channels reaching the catalytic layer to initiate the reaction. Then the hydrogen protons migrate across the membrane to meet oxygen atoms fed through cathode channels.
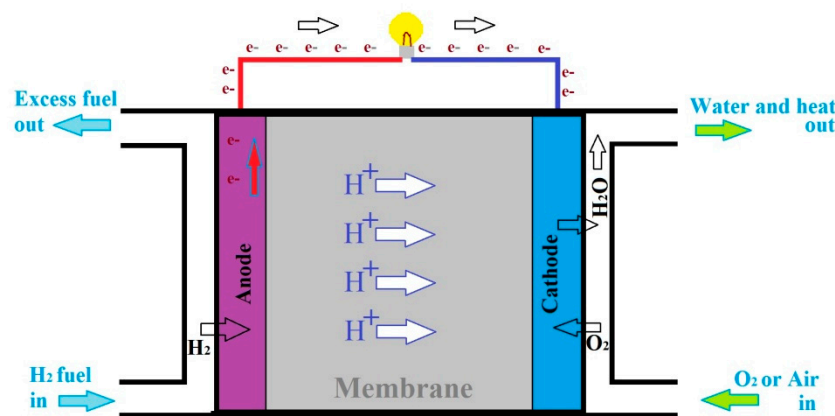

Figure S1. PEMFC layout

The entire chemical reaction takes place in the PEMFC membrane can be expressed by:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O + Energy \tag{S1}$$

From equation (S1) the term energy refers to the output-electricity produced by the cell by electrons extracted from hydrogen atoms at the anode side crossing the external electric circuit (supplying a load) to reach finally the cathode side to equalize the chemical reaction as in Figure S1 [2, 4].

PEMFC quasi-empirical model

The most commonly recognized formulation in PEMFC modeling studies has been developed by Amphlett et al. found in ref. [3]. This model formulation is utilized in this study taking into account the enhancements that followed [1,18, 28]. In which the output voltage at the terminals of the PEMFC (V_{FC}) is expressed by the following equation:

$$V_{FC} = N_{Cells} * (E_{Nernst} - V_{Act} - V_{Ohmic} - V_{Conc}) \tag{S2}$$

where N_{Cells} is the number of a PEMFC stack cells, E_{Nernst} represents the PEMFC theoretical voltage or may called reversible voltage given by equation (S3), while the terms V_{Act} (the cell activation loss due to reaction initiation at anode and cathode electrodes), V_{Ohmic} (the cell ohmic loss due to resistance of polymer electrolyte membrane met by migrant protons) and V_{Conc} (the mass transfer loss, also called concentration loss that takes place due to over crowd of hydrogen and oxygen migrants in the membrane), respectively express the entire potential losses internally occurs through the cell membrane.

The PEMFC theoretical potential E_{Nernst} is given by:

$$E_{Nernst} = 1.229 - 0.85 \times 10^{-3}(T - 298.15) \tag{S3}$$

$$+4.3085 \times 10^{-5} \times T \times ln\left(\frac{p_{H_2}^1 p_{O_2}^{0.5}}{p_{H_2O}}\right)$$

where T expresses the operating temperature of the PEMFC in Kelvin, while the symbols p_{H_2} and p_{O_2} represents the hydrogen and oxygen partial pressures inside the cell membrane respectively in atm computed by equations (S4, S5); p_{H_2O} represents the water saturation pressure across the cell membrane in atm which can be computed by equation (S6) [3, 5, 14].

$$p_{H_2} = 0.5(RH_a \times p_{H_2O})\left[\left(\frac{RH_a * p_{H_2O}}{p_a} e^{\frac{1.635\left(I_{FC}/A\right)}{T^{1.334}}}\right)^{-1} - 1\right] \tag{S4}$$

$$p_{O_2} = (RH_c \times p_{H_2O})\left[\left(\frac{RH_c * p_{H_2O}}{p_c} e^{\frac{4.192\left(I_{FC}/A\right)}{T^{1.334}}}\right)^{-1} - 1\right] \tag{S5}$$

$$p_{H_2O} = 2.95 \times 10^{-2}(T - 273.15) - 9.18 \times 10^{-5}(T - 273.15)^2 \tag{S6}$$

$$+1.44 \times 10^{-7}(T - 273.15)^3 - 2.18$$

where I_{FC} represents the PEMFC output current in $Amperes$; RH_a and RH_c express the vapor relative humidity across the membrane electrodes, respectively; p_a and p_c refers to the inlet pressures at anode and cathode, respectively in atm; while, A expresses the effective area of cell membrane in cm^2.

As mentioned above the initiation of the cell chemical reaction is expressed by the term called the activation loss V_{Act}, calculated by:

$$V_{Act} = -(\xi_1 + \xi_2 \times T + \xi_3 \times T \times \ln(C_{O_2}) + \xi_4 \times T \times \ln(I_{FC})) \tag{S7}$$

Where $\xi_1, \xi_2, \xi_3, \xi_4$ are unknown parameters of the model that will be estimated in the following sections on bases of experimental data for a certain type of PEMFCs. The term C_{O_2} refers to the electrodes oxygen concentration in mol/cm^3, which is given by equation (S8) [27, 28].

$$C_{O_2} = \frac{p_{O_2}}{5.08 \times 10^6 \times e^{-498/T}} \tag{S8}$$

The ohmic voltage loss V_{Ohmic} depends on two parts: First, The cell membrane resistance R_m that is a variable part relies on the hydration level of the membrane medium. Second part is the interface connection resistance R_c that is fixed part appears between the electrodes and the load external circuit, all in Ohm and can be computed by:

$$V_{Ohmic} = I_{FC}(R_m + R_c) \tag{S9}$$

where
$$R_m = \frac{\rho_m l}{A} \tag{S10}$$

While l represents the cell membrane thickness in cm, and ρ_m is the specific resistance of the cell membrane ($\Omega.cm$) that can be given by equation (S11).

$$\rho_m = \frac{181.6 \times \left[1 + 0.03\left(\frac{I_{FC}}{A}\right) + 0.062\left(\frac{T}{303}\right)^2 \left(\frac{I_{FC}}{A}\right)^{2.5}\right]}{\left[\Psi - 0.634 - 3\left(\frac{I_{FC}}{A}\right)\right] e^{\frac{4.18(T-303)}{T}}} \tag{S11}$$

From the above formula it is obvious that ρ_m relies on the membrane hydration level parameter Ψ which is an adjustable factor with changeable values in the range of (10-24), in addition to the cell temperature and membrane current density $\left(\frac{I_{FC}}{A}\right)$.

The mass transfer/concentration loss V_{Conc} is computed using equation (S12), which depends on the reactant migrants' density through the membrane represented by the current density i_d (mA/cm^2) drawn by the external electric circuit from the cell [8, 24].

$$V_{Conc} = -B.\ln\left(1 - \frac{i_d}{i_L}\right) \tag{S12}$$

Where B is an unknown coefficient in $Volt$ needs to be estimated. An increase in the current in the external circuit leads to an equivalent increase in the density of transmembrane-reactive migrants. Reaching a certain value of membrane migrants saturation causes concentration loss to jump to crucial values. This is why the terminal voltage decays at higher current densities. This is illustrated by the polarization curve of the PEMFC in Figure S2. From experimental measurements, the maximum

permissible current density i_L in mA/cm^2 is determined experimentally that should not be exceeded to ensure efficient operation of the PEMFC [21].
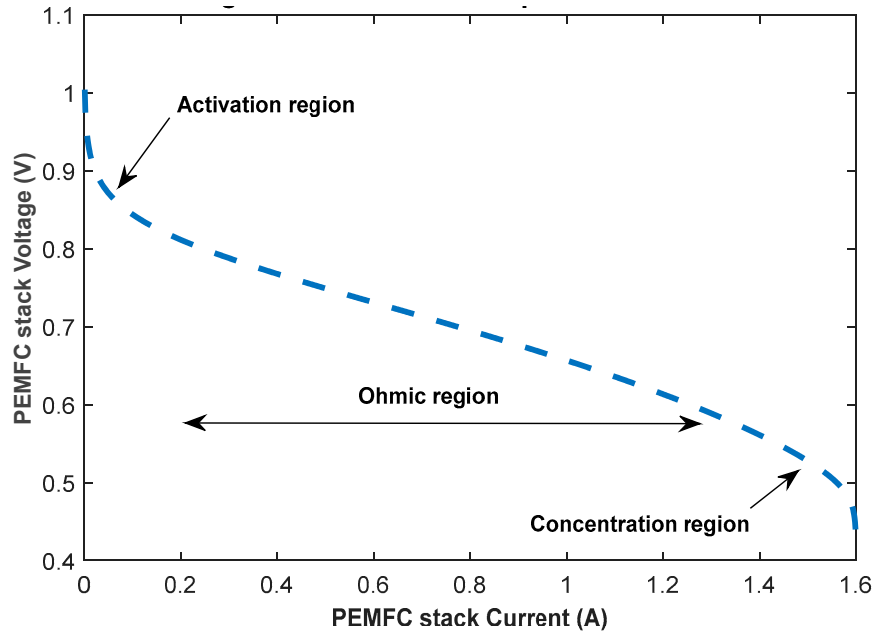

Figure S2. PEMFC Polarization (or characteristic) curve.

Therefore, the mathematical equations (S2-S12) describe the phenomena of the PEMFC representing its quasi-empirical model. It is obvious that there are unknown parameters ($\xi_1. \xi_2. \xi_3. \xi_4. \Psi. R_c. and\ B$) needs to be optimally estimated to complete the modeling process and obtain the accurate characteristic curve of a certain PEMFC device.