An non-uniformity voltage model for proton exchange membrane fuel cell

Kelei Li, Yankun Li, Jiawei Liu and Ai Guo

1 CRRC Qingdao Sifang Co., Ltd, Qingdao, 266111, China.
2 School of Electrical Engineering, Southwest Jiaotong University, Chengdu, 610031, China.

E-mail: daben2011@foxmail.com

Abstract. The fuel cell used in transportation has environmental protection, high efficiency and no line traction power system which can greatly reduce line construction investment. That makes it a huge potential. The voltage uniformity is one of the most important factors affecting the operation life of proton exchange membrane fuel cell (PEMFC). On the basis of principle and classical model of the PEMFC, single cell voltage is calculated and the location coefficients are introduced so as to establish a non-uniformity voltage model. These coefficients are estimated with the experimental datum at stack current 50 A. The model is validated respectively with datum at 60 A and 100 A. The results show that the model reflects the basic characteristics of voltage non-uniformity and provides the beneficial reference for fuel cell control and single cell voltage detection.

1. Introduction

PEMFC is a new generation device gradually used and recognized in the transport sector with the advantages of no pollution, high efficiency and fast start up [1-3]. In the field of rail transportation, fuel cell has built-in power system without the line traction power system and greatly reduces line construction investment with the tremendous development potential. But some bottleneck problems are also needed to solve such as cost and life in fuel cell commercialization [4-6].

Fuel cell model is classified as mechanism model and simplified model. Their characteristics and performances are studied. With some rational assumptions, the mechanistic model is obtained by mass conservation, energy conservation law, ideal gas equation, heat equation, mass transfer, electrochemical equation and internal cell characteristics. Due to the complex process of the fuel cell, the simplified model ignoring certain factors is put forward to reflect some essential characteristics of the fuel cell.

Mechanism model is on the basis of strict physical relationship. Its form is complex and sometimes some key parameters are difficult to get. Thus this modeling approach has been curbed and reduces its effectiveness and feasibility. Actual phenomenon and the experimental datum are used to describe the system experience model. In order to avoid the complex relationships between physical quantities, simplify the model and improve the feasibility, experimental model has been widely applied. In membrane electrode model, the most classic fuel cell performance model is set up under the steady-state condition of MK-IV PEMFC by Amphlett J C et al. [7] The model can predict the degree of polarization in different working conditions. Mann R F et al. [8] consider the anodic polarization phenomenon and get electricity output characteristic model by introducing membrane resistance...
The coefficient as calculating the ohmic overvoltage. Based on the single cell performance empirical formula, Lee J H et al. [9] divides stack into several units and obtains stack power by adding each unit power. It is a more complete experience model to predict PEMFC voltage characteristics. Li Qi et al. [10] are proposed for engineering analysis about PEMFC experimental model. The key parameters are identified by particle swarm optimization algorithm of the model. Chen Huicui et al. [11] study the dynamic variable loading voltage response process through an equivalent circuit model. Su Zhou et al. [12] add the gas diffusion layers and the membrane electrode assembly dynamic model to the existing model in order to study the membrane water content. In addition, control theories and methods are gradually applied to the fuel cell modeling. These models are more complex and difficult for control strategy.

The important factors affecting the PEMFC operation life include operating conditions, stack temperature, reaction gas distribution, gas excessive coefficient, pressure, frequent start-stop and dynamic loading. The stack consists of many series single fuel cell. Its life depends on the performance of the worst single cell. The individual voltage uniformity is an important factor affecting stack life and used to measure the single voltage difference. The evaluation of fuel cell voltage uniformity has four methods, such as single cell voltage fluctuation rate, single voltage root-mean-square, single voltage fluctuation amplitude and graphical method [13, 14]. The single cell voltage fluctuation rate is the ratio of the standard deviation to the mean cell voltage, called a relative standard deviation. The single cell voltage root-mean-square is the absolute standard deviation. The single cell voltage fluctuation amplitude is difference between the maximum voltage and the minimum voltage. Graphical method is a figure of single cell voltage distribution which can directly reflect cell voltage uniformity.

Individual voltage uniformity is not involved in existing fuel cell models. Based on classic model proposed by Amphlett J C [7] and Lee J H[9], this paper establishes the fuel cell stack model reflecting the individual voltage uniformity. The stack voltage model is verified by 14.4 kW PEMFC test platform. Position coefficients are estimated with the experimental datum at stack current 50 A. The model is validated respectively with datum at 60 A and 100 A. The results show that the model reflects the basic characteristics of voltage non-uniformity and provides the beneficial reference for fuel cell control and single cell voltage detection.

2. PEMFC working principle

The single structure of PEMFC is mainly composed of bipolar plate, diffusion layer, catalyst layer and electrolyte membrane as shown in figure 1. Air (oxygen) and hydrogen respectively enter into cathode and anode of the cell.

![Figure 1. The single structure of PEMFC](image)

The electrolyte membrane separates cathode and anode into two parts. The hydrogen reduces the activation energy and dissociates into hydrogen ions and electrons under the catalyst:

\[ H_2 \rightarrow 2H^+ + 2e^- \] (1)
Hydrogen ions move toward cathode through the proton exchange membrane. The electrons move to cathode through the external circuit. In the role of catalyst, oxygen molecules, electrons and hydrogen ions produce water. The reduction reaction is:

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$$

(2)

The overall reaction is an electrochemical reaction of hydrogen and oxygen producing water:

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

(3)

3. Voltage model of PEMFC

Open circuit voltage $E$ is calculated according to the Faraday constant and the energy balance between the reaction gas and products[15]:

$$E = 1.229 - 0.85 \times 10^{-7}(T_f - T_{atm}) + 4.3085 \times 10^{-4}T_f[\ln(p_{H_2}) + \frac{1}{2}\ln(p_{O_2})]$$

(4)

where $T_f$ is fuel cell temperature, $T_{atm}$ is ambient temperature, $p_{H_2}$ is hydrogen pressure and $p_{O_2}$ is oxygen pressure. When the current passes through the fuel cell, a series of physical and chemical changes occur in the process. There is resistance during each process. In order to make the reaction continuously, it is necessary to consume energy to overcome their resistance, so the voltage will be lost. Depending on the cause of the generated loss, it can be divided into three parts: the activation loss, ohmic loss and concentration loss. Activation loss is the energy loss caused by electron transfer at anode and cathode. Activation overpotential occurs in anode and cathode plates of the fuel cell. However, the hydrogen oxidation reaction is very fast at the anode, but the oxygen reduction reaction at the cathode is very slow. Therefore, voltage drop generated by the activation loss is controlled by the cathodic reaction condition. Activation over potential $v_{act}$ is [16]:

$$v_{act} = v_0 + v_a(1 - e^{-ci})$$

(5)

where $i$ is the current density, $v_0$ is the voltage drop under zero current density, $v_a$ and $c_i$ are constants affected by oxygen partial pressure and temperature.

Ohmic loss is caused by the resistances of proton transmission and electric transmission. The current density is proportional to the voltage drop, namely:

$$v_{ohm} = i \cdot R_{ohm}$$

(6)

where $R_{ohm}$ is the internal resistance. Resistance mainly depends on the humidity and temperature of the fuel cell membrane. The ohmic resistance is a function of the membrane conductivity $\sigma_m$:

$$R_{ohm} = \frac{t_m}{\sigma_m}$$

(7)

where $t_m$ is the thickness of the proton exchange membrane. Concentration loss is due to the change of the reactant concentration. At high current densities these losses appear as a rapid voltage drop. An approximate equation of voltage drop caused by the concentration loss is [17]:

$$v_{conc} = i \left( c_2 \frac{i}{i_{max}} \right)^{c_3}$$

(8)

where $c_2$, $c_3$ and $i_{max}$ are constants depending on the temperature and partial pressure of the reactants determined by experiment, $i_{max}$ is the current density caused by a steep voltage drop.

By combining formula (4)-(8), the terminal voltage $v_{fc}$ of fuel cells can be written as:

$$v_{fc} = E - v_{act} - v_{ohm} - v_{conc}$$

(9)
The block diagram is classical PEMFC model shown in figure 2(a) from formula (9). Inputs are stack current, stack temperature, anode and cathode pressure. These amounts will calculate open-circuit voltage, activation loss, ohmic loss and concentration loss by the formula (4)–(8). The space position of monomer is different in the stack. The pressure and temperature of the anode and cathode of monomer can’t be same, so that the voltage of monomer is not equal. Position coefficient is introduced in order to reflect their non-uniformity, whose block diagram is shown in figure 2(b).

The voltage non-uniformity model is established in MATLAB/Simulink software. The thickness of proton exchange membrane is 125 μm and stack active area is 300 cm$^2$. By the law of partial pressure, the oxygen partial pressure is 21% of the cathode pressure. Air humidity exceeds 95% before entering the stack. Because stack reaction product is water, the humidity of proton exchange membrane is inferred 100%.

![Figure 2. PEMFC model](image)

4. Experimental verification

4.1. Experiment platform

The experiment platform is established as shown in figure 3 with Ballard's FCvelocity®-9SSL 14.4 kW liquid-cooled stack. Stack is constituted by 75 cells. The rated current is 300 A and the rated voltage is 48 V. The hydrogen enters into the PEMFC anode from the hydrogen storage tank with 13 Mpa high-pressure through the reducing valve, mass flow controller and humidifier. The open degree of the backpressure valve is adjusted at the anode outlet to meet pressure difference between the cathode and anode at the stack inlet. Compressed air enters into the high pressure gas bomb, then passes through mass flow adjustor and humidifier. Perma Pure FC-125 and FC-300 series humidifiers are used for hydrogen and air respectively. The way is gas-liquid humidifying. The terminal of stack connects electronic load to extract a specified stack current. For data acquisition and control, ZTYC’s USB7635BD data acquisition card is applied to connect LabVIEW software. In the system, temperature, pressure, flow rate, current, stack voltage, cell voltage can be real-time monitored.
4.2. Experimental verification
The experiment condition is under constant temperature and isopiestic pressure. Firstly, experiment platform runs for half an hour to ensure the stack activity released in full. The temperature at stack outlet of cooling liquid meets expected value. The experimental conditions are set as shown in Table 1.

| Ambient temperature(℃) | Air inlet pressure(kPa) | Hydrogen inlet pressure(kPa) | Cooling liquid inlet temperature(℃) |
|------------------------|------------------------|-----------------------------|-----------------------------------|
| 27.81                  | 178.42                 | 192.72                      | 58                                |

The relationship between the excess coefficient of fuel and air and the extraction current is shown in Table 2 according to the parameters of Ballard’s technical manual[18].

| Current(A) | Fuel excessive coefficient | Air excessive coefficient |
|------------|----------------------------|--------------------------|
| 15         | 6.3                        | 5.1                      |
| 30         | 3.4                        | 2.4                      |
| 60         | 2.2                        | 1.8                      |
| 120        | 1.9                        | 1.8                      |
| 180        | 1.6                        | 1.8                      |

Stack current is gradually loaded from 20A to 160A with step 10A. Every time current changes, stack has been in a steady state. The steady-state voltage values of 75 cells are tested at different current, and average cell voltage is as shown in Figure 4. With the stack current increasing, average single voltage decreases gradually. When the stack current is 30A~140A range, cell model voltage mean value matches with experimental preferably. When the stack current is 10A, 160A, errors were 4.015% and -1.101%. It indicates that the model can reflect the experimental stack cell mean voltage.
5. Results and discussion

Individual voltage uniformity is not involved in existing fuel cell models. Position coefficient responds the degree of deviating from the average cell and can be represented as the cell voltage divided by the average cell voltage, namely:

$$\alpha_{pi} = \frac{V_i}{\bar{V}} \quad i = 1, \ldots, N$$

where $\alpha_{pi}$ is the position coefficient, $V_i$ is the single cell voltage, $\bar{V}$ is the stack single average voltage and $N$ is the stack monomer number. The position coefficient is shown in figure 5 with experimental data at 50 A.

Based on the model, the comparison curves of the voltage model and the experimental results are shown in figure 6 and 7. In figure 6, the experimental values is higher than model values when the current is 60 A. However, in figure 7 the model value is higher than the experimental value at 100 A. Their trends are basically same. The experimental value is slightly higher than the model value in figure 6, but the model value is higher than the experimental value in figure 7. The model is fitted well with the experimental data in cell No. 1-55 and differs slightly in the cell No. 56-75.

Fuel cell voltage fluctuation rate $C_v$ satisfies:

$$C_v = \frac{\sqrt{\frac{\sum_{j=1}^{N} (V_j - \bar{V})^2}{N}}} \cdot 100$$

(10)
The fluctuation rates of 60A and 100A are calculated according to equation (11), as shown in Table 3.

Model voltage fluctuation rate is the same, because the location coefficient is only got by 50A numerical calculation. Current will affect the position coefficient. Since the model does not consider its impact, fluctuation rate of model and experiment has a large difference.

Table 3. Voltage fluctuation rate

| Stack current(A) | Model  | Test  |
|------------------|--------|-------|
| 60               | 0.1823 | 0.1309|
| 100              | 0.1823 | 0.2882|

6. Conclusion

Monomer voltage non-uniformity is an important performance index for PEMFC. This paper firstly introduces the working principle of fuel cell and voltage model. The position coefficient is introduced based on the classical model to represent monomer voltage. The position coefficient is calculated with experimental data at 50 A. The model is validated at 60 A and 100 A. The model and experimental values can well reflect the stack cell voltage imbalance at 60 A. At 100A, the model values coincide with the experimental values when the cell numbers are 1-55. The model and experimental values differ at No. 56-75. The model voltage fluctuation rate is same, because the position coefficient is only got by experimental data at 50 A. There is no consideration of the impact on the current. Thus there is a big fluctuation rate difference between model and experiment. In addition, the current impact on location coefficient is the next step to research project.

Appendices

Table A1.

| Symbol | Meaning                        | Unit   |
|--------|--------------------------------|--------|
| $T_f$  | fuel cell temperature          | K      |
| $T_{atm}$ | ambient temperature          | K      |
| $p_{H_2}$ | hydrogen pressure         | Pa     |
| $p_{O_2}$ | oxygen pressure          | Pa     |
| $i$    | current density               | A/cm$^2$ |
| $v_0$  | voltage drop under zero current density | V |
| $R_{ohm}$ | internal resistance       | $\Omega \cdot cm^2$ |
| $t_m$  | thickness of the PEM         | $\mu m$ |
| $i_{max}$ | current density caused by steep voltage drop | A/cm$^2$ |
| $\alpha_{p,j}$ | position coefficient   | constant |
| $V_i$  | single cell voltage          | V      |
| $\bar{V}$ | stack single average voltage | V      |
| $N$    | stack monomer number         | constant |

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