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A semi-empirical voltage degradation model for a low-pressure proton exchange membrane fuel cell stack under bus city driving cycles

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Abstract

A voltage degradation model for the low-pressure proton exchange membrane fuel cell (PEMFC) stack used in a fuel cell bus is presented: (1) the oxygen concentration term was derived from the PEMFC output voltage equation, and the concept of oxygen concentration resistance coefficient was introduced; (2) a 5 kW low-pressure PEMFC stack was used in this study. Two similar tests were carried out before and after the stack operating in the driving cycle for 640 h. First, the ohmic losses under different temperatures were measured using the current interrupt method and formulized with linear fitting method. Then, the oxygen concentration term was studied by the experiments with different air stoichiometric ratios while keeping the other operating parameters unchanged. The oxygen concentration resistance coefficient was obtained from the difference of voltages for the PEMFC stack in different air stoichiometric ratios using the genetic optimization algorithm. Then, the activation loss was obtained based on the PEMFC output voltage, the ohmic loss, and the concentration loss. The degradation model of the stack was built finally by comparing the two test results; (3) the correlation of the model to the actual experimental data is good; (4) the overvoltage of the stack with aging was analyzed using this model. The analysis showed that the activation overvoltage dominated the stack loss with about 80% of the total losses, followed by the ohmic loss. The concentration loss almost does not change with aging in the driving cycle condition; (5) the comparison of the simulation with the actual data from the PEMFC bus running for 30,000 km indicated that after 36,000 km the rated power of the PEMFC bus must be reduced.

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Keywords: PEMFC stack; Voltage degradation model; Concentration resistance coefficient; Ohmic loss; Activation loss

1. Introduction

As the vehicle emission regulations become more and more strict, electrical vehicles have become the focus of people's attention. Proton exchange membrane fuel cell (PEMFC) is one of the most promising power sources for electric vehicles. PEMFC stack is the core of the PEMFC vehicle. The performance and the lifetime of the fuel cell system and the fuel cell vehicle are strongly influenced by the degradation of the PEMFC stack. Therefore, it is necessary to establish a voltage degradation model of the PEMFC stack. There are two type of models [1], one is the mechanism model, and the other is the empirical model. The mechanism model is established based on

0378-7753/\$ – see front matter © 2006 Elsevier B.V. All rights reserved. doi:10.1016/j.jpowsour.2006.10.061 some proper assumptions. It consists of the mass transfer functions, the thermal transport functions, and the electrochemical reaction functions. Mechanism model is complex though it can discover the inner mechanism of the fuel cell stack. It is more suitable for studying the inner phenomena of fuel cell stacks. The empirical model described with meaningful coefficients is usually based on the fuel cell voltage-ampere experimental data without considering the fuel cell inner structure. The empirical model is much simpler and more suitable for the system analysis. Different empirical models have been developed [2-14]. The model developed by Amphlett et al. [6-9] uses a combination of mechanistic and empirical modeling techniques, and every coefficient has its meaning. Based on the Amphlett's model, Mann et al. took into the reactant humidity in their study [11]. A more sophisticated model has been developed by Pukerushpan et al. which incorporates the reaction gases humidity and the concentration overvoltage into the Amphlett's model [12,13].

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Nomenclature

- $c_{O_2,interface}$ oxygen concentration at the cathode membrane/gas interface (mol cm^{-3}) oxygen concentration resistance coefficient $C_{\rm r}$
- $(atm mA^{-1} cm^2)$ Ε thermodynamic potential (V)
- current density, $(mA cm^{-2})$
- i
- internal and fuel crossover equivalent current denin sity (mA cm $^{-2}$)
- I stack output current (A)
- п cell number in series
- $p_{\text{anode, channel}}$ the total pressure in the anode gas channel (atm)
- the cathode operating pressure (atm) $p_{\rm ca}$
- $p_{\rm H_2,interface}$ hydrogen partial pressure in the reactive interface (atm)
- $p_{\rm H_2O,anode}$ the partial pressure of water vapor in the flow channels
- $p_{O_2,interface}$ oxygen partial pressure in the reactive interface (atm)
- $p_{O_2,anode}$ oxygen partial pressure in the bipolar channel (atm)
- $p_{O_2,channel,\lambda_1}, p_{O_2,channel,\lambda_2}$ the oxygen partial pressure in the bipolar channel under stoichiometric ratio λ_1 and λ_2 (atm)

$$p_{\text{anode,H}_2O}^{\text{sat}}$$
 water saturated pressure in the anode (atm)

 p_{ca,H_2O}^{sat} the water saturation partial pressure in cathode (atm)

R stack internal resistance (Ω)

- stack operating time under the driving cycle test t (h)
- T fuel cell operating temperature (K)
- Vfuel cell output voltage (V)
- Vact activation overvoltage (V)
- $V_{\rm con}$ concentration overvoltage (V)
- ohmic overvoltage (V) Vohm
- Vstack stack output voltage (V)
- ΔV the voltage difference of the PEMFC output voltage under the air stoichiometric ratio λ_1 and λ_2 (V)

Greek letters

- fuel cell stack efficiency n
- $\xi_1, \xi_2, \xi_3, \xi_4, \zeta_1, \zeta_2, \zeta_4$ empirical coefficients for calculation of activation overvoltage
- empirical coefficients for calculation of concen- ζ_3, ψ tration overvoltage

The PEMFC performance becomes worse as the stack ages. All the above models deal little with degradation. A few empirical models can handle the voltage degradation but were used for the system analysis, i.e., Fowler et al. have incorporated the voltage degradation into their model based on the Amphlett's model [14]. In this paper, we report a PEMFC stack model used for both the fuel cell bus hybrid system and the fuel cell system analysis. We introduce this Amphlett's model-based voltage degradation model for low-pressure PEMFC stack into our fuel cell bus. We first derive the oxygen concentration term from the PEMFC output voltage equation and introduce the concept of oxygen concentration resistance coefficient, then use a 5 kW low-pressure PEMFC stack module for the study. Two sets of the similar tests are carried out before the driving cycle test and after the stack operating in the driving cycle for 640 h. Then the model coefficients changing with time are obtained from the experimental data. Finally, the degradation model is used to analyze the losses of the fuel cell stack. By comparing the model simulation results with the test data from the fuel cell bus running for 30,000 km, the degradation of the stack used in our fuel cell bus is evaluated.

2. Development of PEMFC model

The output voltage of the fuel cell is defined as the function of the thermodynamic potential, the activation overvoltage, and the ohmic overvoltage, as shown by the following Eq. (1)

$$V = E + V_{\rm act} + V_{\rm ohm} \tag{1}$$

where V, V_{act} , V_{ohm} and E are the fuel cell output voltage, the activation overvoltage, the ohmic overvoltage, and the thermodynamic potential, respectively. E can be described via Nernst equation as

$$E = 1.229 - 0.85 \times 10^{-3} (T - 298.15) + 4.309 \times 10^{-5} T$$
$$\times \left[\ln(p_{\text{H}_2, \text{interface}}) + \frac{1}{2} \ln(p_{\text{O}_2, \text{interface}}) \right]$$
(2)

Eq. (2) can be reformed as

$$E = E' + 2.15425 \times 10^{-5} T \ln(p_{O_2, \text{interface}})$$
(3)

$$E' = 1.229 - 0.85 \times 10^{-3} (T - 298.15) + 4.309$$
$$\times 10^{-5} T \ln(p_{\text{H}_2,\text{interface}})$$
(3a)

where T is the fuel cell operating temperature. $p_{O_2,interface}$ is the oxygen partial pressure in the reactive interface. $p_{\rm H_2,interface}$, the hydrogen partial pressure in the reactive interface can be expressed as

$$p_{\rm H_2,interface} = p_{\rm anode,channel} - p_{\rm H_2O,anode}$$
 (3b)

where $p_{\text{anode, channel}}$ is the total pressure in the anode gas channel. The partial pressure of water vapor in the flow channels, $p_{\rm H_2O,anode}$ can be defined as following Eq. [6]

$$p_{\rm H_2O,anode} = 0.5 p_{\rm anode, H_2O}^{\rm sat}$$
(3c)

where $p_{\text{anode},\text{H}_2\text{O}}^{\text{sat}}$ is the water saturated pressure in the anode at the fuel cell operating temperature.

Activation overvoltage can be given as the following Eq. [6]

$$V_{\text{act}} = \xi_1 + \xi_2 T + \xi_3 T[\ln(c_{\text{O}_2,\text{interface}})] + \xi_4 T[\ln(i+i_n)] \quad (4)$$

where $c_{O_2,interface}$ is the concentration of dissolved oxygen at the gas/liquid interface, which can be defined by Henry's law expression of the form [6]

$$c_{\mathrm{O}_2,\mathrm{interface}} \approx \frac{p_{\mathrm{O}_2,\mathrm{interface}}}{5.08 \times 10^6 \mathrm{exp}(-498/T)}$$
 (4a)

 $\xi_1, \xi_2, \xi_3, \xi_4$ are constants. $i + i_n$ is the total current density. *i* is the output current density, and i_n is the internal and fuel crossover equivalent current density [15].

Substituting Eq. (4a) into Eq. (4), it can obtain:

$$V_{\text{act}} = \zeta_1 + \zeta_2 T + \zeta_3 T[\ln(p_{\text{O}_2,\text{interface}})] + \zeta_4 T[\ln(i+i_n)]$$

$$V_{\text{act}} = V'_{\text{act}} + \zeta_3 T[\ln(p_{\text{O}_2,\text{interface}})]$$
(5)

where $\zeta_1, \zeta_2, \zeta_3, \zeta_4$ are constants.

$$V'_{\rm act} = \zeta_1 + \zeta_2 T + \zeta_4 T[\ln(i+i_{\rm n})]$$
(5a)

Ohmic overvoltage can be described as

$$V_{\rm ohm} = -Ri \tag{6}$$

where R is the internal electric resistance.

Combining Eqs. (6), (5), (3) and (1) yields

$$V = E' + V'_{act} + V_{ohm} + 2.154 \times 10^{-5} T \ln(p_{O_2, interface}) + \zeta_3 T \ln(p_{O_2, interface})$$
(7)

This equation can be simplified to:

$$V = E' + V'_{\text{act}} + V_{\text{ohm}} + \psi T \ln(p_{\text{O}_2,\text{interface}})$$
(8)

where

$$\psi = 2.154 \times 10^{-5} + \zeta_3 \tag{8a}$$

Assume the oxygen partial pressure in the bipolar channel as $p_{O_2,channel}$, and assume the oxygen partial pressure in the reaction interface as

$$p_{O_2,\text{interface}} = p_{O_2,\text{channel}} - C_r i \tag{9}$$

where C_r is defined as the oxygen concentration resistance coefficient, which is influenced by the structure of gas distribution layer (GDL) and the liquid water contained in the GDL.

Substituting Eq. (9) into Eq. (8) gives:

$$V = E' + V'_{\text{act}} + V_{\text{ohm}} + \psi T \ln(p_{\text{O}_2,\text{channel}} - C_r i)$$
(10)

Table 1

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The basic parameters of the PEMFC stack
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Supposing each cell performance in the stack is the same, the output voltage of the stack can be expressed as

$$V_{\text{stack}} = nV = n[E' + V'_{\text{act}} + V_{\text{ohm}} + \psi T \ln(p_{\text{O}_2,\text{channel}} - C_{\text{r}}i)]$$
(11)

where *n* is the cell number in series in the stack. The fourth term in the right side of Eq. (11) is defined as oxygen concentration different term. In Eq. (11), E', V'_{act} , and V_{ohm} do not relate to oxygen partial pressure. In the following section, tests are elaborately designed to obtain each of the constants in the above equations.

3. Experimental

Tests are carried out on the test station FCATS G700 manufactured by GREENLIGHT power technologies company. Air is from the air station, and hydrogen is from the compressed hydrogen cylinders.

A 5 kW low-pressure PEMFC stack module is used for the study. The same kind of PEMFC is also used in our fuel cell buses (one of our fuel cell bus PEMFC stack is about 72 kW). The 5 kW stack consists of 80 cells in series. The active area of the PEMFC is 280 cm^2 , and the membrane is Nafion®112. The basic parameters of the stack are listed in Table 1.

3.1. Tests before the driving cycle test

Before the driving cycle test, a set of tests are designed to distinguish the empirical coefficients from the equations in Section 2.

3.1.1. Ohmic resistances tests

The ohmic resistances are determined by using the current interrupt method [15]. The electronic load is adjusted until the desired test current is stable, then the load current is switched off rapidly. The changed voltage is recorded to the storage oscilloscope. The internal ohmic resistance can be obtained by dividing the changed voltage with the current.

The test results of the reference [16] show that the internal resistances of very thin membranes do not change with the current density if the reactive gases are well humidified. As

Cells number in series	Active area (cm ²)) Oxidant	Fuel	Rated power (kW)	Rated operating current (A)
80	280	Air	Pure hydrogen	5	90
Rated operating temperature (°C)	Rated operating pressure	Cathode rated air stoichiometric ratio	Anode rated stoichiometric ratio	Operating temperature (°C)	Operating pressure (kPa)
60	Atmospheric pressure	2.5	1.5	Room temperature to 65	Atmospheric pressure to 50
Operating relative humidity (%)	Cathode stoichiometric ratio	Anode stoichiometic ratio	Max allowable different pressure between anode and cathode (kPa)	t Max allowable continuous operatin current (A)	g The allowable minimum start temperature (°C)
60–100	2.1–2.7	1.3–1.5	30	168	5



Fig. 1. The internal resistances of the stack in different current density and air dew point temperatures.

Nafion 112 is used in the 5 kW low-pressure PEMFC stack, the hydrogen is always humidified around 90%, and the humidity of the air is always around 60–100%. We design an experiment to confirm the relationship between the stack internal resistance and the current density. The stack operating temperature is kept at 60 °C. The reactive gases pressure is atmosphere pressure. The air stoichiometric ratio is 2.3. The hydrogen stoichiometry is 1.3, and the dew point temperature of the hydrogen is 55 °C. The test results show that if the dew point of the air is kept between 50 °C and 60 °C, the internal resistances of the stack change very little with the current density, especially under high current density as shown in Fig. 1.

Other experiment results show that under good humidity condition the stack internal resistances do not change with the air stoichiometric ratio below 2.5. We also carried out the experiment to find the relationship of the stack internal resistances to the stack operating temperatures. In the experiment, the operating pressure is atmosphere pressure, the air stoichiometric ratio is 2.3, the hydrogen stoichiometric ratio is 1.3, reactants are both saturated. The results are shown in Fig. 2. The changed voltages are linear to the interrupted currents, and the slopes of these lines are greater as the stack operating temperatures reduces. These mean that the internal resistances of the stack have little relation with the currents and become higher as the stack operating temperature is lower. The relationship of the internal resistance to the stack operating temperature is a conic as shown in Fig. 3.



Fig. 2. The changed voltages with different interrupted currents in different stack operating temperatures.



Fig. 3. The relationship of the stack internal resistances with the stack operating temperatures.

The stack resistance can be expressed as Eq. (12)

$$Rn = 5.61 \times 10^{-6} \times T^2 - 3.7248 \times 10^{-3} \times T + 0.655$$
(12)

So the ohmic overvoltage can be expressed as

$$V_{\text{ohm}} = (7.013 \times 10^{-8} \times T^2 - 4.656 \times 10^{-5} \times T + 8.188 \times 10^{-3}) \times I$$
(13)

3.1.2. The air concentration term tests

The concentration term can be easily separated from the stack output voltage by the following method.

The air stoichiometric ratio changes from λ_1 to λ_2 , while the other operating parameters kept unchanged. Then based on the Eq. (10), we have the following equations:

$$V_1 = E' + V'_{\text{act}} + V_{\text{ohm}} + \psi T \ln(p_{\text{O}_2,\text{channel},\lambda_1} - C_r i)$$
(14)

$$V_{2} = E' + V'_{act} + V_{ohm} + \psi T \ln(p_{O_{2}, channel, \lambda_{2}} - C_{r}i)$$
(15)

Subtracting these two equations gives

$$\Delta V = \psi T\{\ln(p_{O_2, \text{channel}, \lambda_2} - C_r i) - \ln(p_{O_2, \text{channel}, \lambda_1} - C_r i)\}$$
(16)

where ΔV is the voltage difference of the PEMFC output voltage under the air stoichiometric ratio λ_1 and λ_2 . $p_{O_2,channel,\lambda_1}$ and $p_{O_2,channel,\lambda_2}$ are the oxygen partial pressure in the bipolar channel under stoichiometric ratio λ_1 and λ_2 , respectively.

Under good humidity condition, the oxygen partial pressure in the bipolar channel can be expressed as Eq. (17)

$$p_{\text{O}_2,\text{channel},\lambda} = (p_{\text{ca}} - p_{\text{ca},\text{H}_2\text{O}}^{\text{sat}}) \times 0.21 \times \left[1 - \frac{(\lambda - 1)/\lambda}{(1 - 0.21/\lambda)}\right]$$
$$/\ln\left[\frac{1 - 0.21/\lambda}{(\lambda - 1)/\lambda}\right] \tag{17}$$

where λ is the air stoichiometric ratio. p_{ca,H_2O}^{sat} is the water saturation partial pressure in cathode. p_{ca} is the cathode operating pressure.

The constants ψ and C_r can be easily obtained by the following designed experiments. The stack operating temperatures are kept at 30 °C, 40 °C, 50 °C, 60 °C, respectively, and the air stoichiometric ratios are changed with $\lambda = 1.9, 2.1, 2.3, 2.5$, and 2.7, respectively. The results V–I curves under the 60 °C are shown in Fig. 4. The stack output voltage differences $n\Delta V$ of



Fig. 4. The stack V-I curves under different air stoichiometric ratios.

the experiments are shown in Figs. 5 and 6. Then, the constants ψ and C_r can be derived by the genetic arithmetic method [17]. The genetic arithmetic method is used to process the difference voltages of the PEMFC stack. The results are shown in following:

When T = 333.15 K, then $\psi = 2.0 \times 10^{-4}$, $C_r = 1.800 \times 10^{-4}$. When T = 323.15 K, then $\psi = 2.0 \times 10^{-4}$, $C_r = 2.007 \times 10^{-4}$. When T = 313.15 K, then $\psi = 2.0 \times 10^{-4}$, $C_r = 2.100 \times 10^{-4}$.



Fig. 5. The stack voltage differences under different air stoichiometric ratios (1).



Fig. 6. The stack voltage differences under different air stoichiometric ratios (2).

When
$$T = 303.15$$
 K, then $\psi = 2.0 \times 10^{-4}$, $C_r = 2.168 \times 10^{-4}$.

So the constant ψ changes very little with the operating temperature. Substituting ψ into Eq. (8a), it gives $\zeta_3 = 1.78 \times 10^{-4}$. The thermodynamic potential is not sensitive to oxygen concentration by comparing 2.154×10^{-5} with ζ_3 . The oxygen concentration resistance coefficient C_r increases a little as the operating temperature decreases, which is due to more liquid water in the GDL at low operating temperature. According to the test data, C_r can be expressed as:

$$C_{\rm r} = -3.2 \times 10^{-8} \times T^2 + 1.92 \times 10^{-5} \times T - 2.663 \times 10^{-4}$$
(18)

3.1.3. Activation overvoltage calculation

As E', V_{ohm} , $\psi T \ln(p_{O_2,channel} - C_r i)$ and the PEMFC output voltages V in Eq. (10) have been obtained, the constants in V'_{act} can be also obtained by using the same genetic arithmetic method. The results show that ζ_1 and ζ_2 are little sensitive to the operating temperature. $\zeta_1 = 0$, $\zeta_2 = 3.273 \times 10^{-4}$, while ζ_4 and i_n are strongly affected by the operating temperature. For example, when T = 333.15 K, 323.15 K, 313.15 K, 303.15 K, the related two parameters are $\zeta_4 = 8.106 \times 10^{-5}$, 9.748×10^{-5} , 1.145×10^{-4} , 1.316×10^{-4} , and $i_n = 0.99$, 1.603, 2.314, 3.324. Constants ζ_4 and the internal and fuel crossover equivalent current density i_n increase a little as the operating temperature decreases (i_n is typically in the range of 1-5 mA cm⁻² [18]). They can be expressed as following:

$$\zeta_4 = -1.686 \times 10^{-6} \times T + 6.427 \times 10^{-4} \tag{19}$$

$$i_{\rm n} = 9.93 \times 10^{-4} \times T^2 - 0.709 \times T + 127 \tag{20}$$

Substituting them into the Eq. (10) gets

$$V'_{\text{act}} = 3.2725 \times 10^{-4} \times T + (-1.6864 \times 10^{-6} \times T + 6.427 \times 10^{-4}) \times T \ln[i + (9.93 \times 10^{-4} \times T^2 - 0.709T + 127)]$$
(21)

3.2. Tests after 640 h driving cycle test

The testing driving cycle is shown in Fig. 7 [19]. This driving cycle was derived from the hybrid fuel cell bus simulation model based on the Chinese typical bus driving cycle. There are two phases (phase I and phase II) in the Fig. 7. The driving cycle consists of four phase I and one phase II. The 5 kW low-pressure PEMFC stack has been tested under the driving cycle for 640 h. The stack output voltage history under the current 100 A is shown in Fig. 8. The degradation of the stack output voltage is roughly linear. The degraded rate is about 5.8 mV h^{-1} , and the average cell output voltage's degraded rate is about $72.5 \mu \text{V h}^{-1}$, which is worse than those presented in other literatures [14,20]. The stack V–I curves before and after 640 h driving cycle test are compared in Fig. 9. The voltage has dropped about 4 V after 640 h driving cycle test under the current 100 A, which means that the stack voltage has degraded about 6.9%.



Fig. 7. The PEMFC stack test driving cycle.



Fig. 8. The stack output voltage degradation curve under the current 100 A.

In order to compare the losses of the stack before and after the driving cycle test, the similar tests listed in Section 3.1 are carried out after 640 h driving cycle test.

The results of the internal resistances tests under the operating temperature 333.15 K are shown in Fig. 10. After 640 h of driving cycle test, the internal resistance rose from $3.6956 \times 10^{-2} \Omega$ to $4.98 \times 10^{-2} \Omega$ by 34.7%. The increasing rate is about $2.006 \times 10^{-5} \Omega h^{-1}$. The increasing rate for converted average cell internal resistance is $2.508 \times 10^{-7} \Omega h^{-1}$. Assuming



Fig. 9. Comparison of the V-I curves before and after 640 h driving cycle test.



Fig. 10. The changed voltages in different interrupted currents after 640 h driving cycle test.

the increase of the internal resistance is linear, we find the ohmic loss

$$V_{\text{ohm}} = (7.013 \times 10^{-8} \times T^2 - 4.656 \times 10^{-5} \times T + 8.188 \times 10^{-3} + 2.508 \times 10^{-7} t) \times I$$
(22)

where *t* is the stack operating time under the driving cycle test.

The concentration term tests shown that after 640 h running of driving cycle test, the coefficients of the air concentration term changed little. And under the operating temperature 333.15 K, $\psi = 2.0 \times 10^{-4}$, $C_r = 1.810 \times 10^{-4}$.

Using the similar method listed in Section 3.1.3 gets $\zeta_1 = 0$, $\zeta_2 = 3.253 \times 10^{-4}$, $\zeta_4 = 9.882 \times 10^{-5}$, $i_n = 4.676$ under the operating temperature of 333.15 K. Compared to those before driving cycle test, ζ_1 and ζ_2 have changed very little, and the internal and fuel crossover equivalent current density i_n have risen about four times, which means that there are may be some hot pinholes in the membrane. Assuming the increase of internal and fuel crossover equivalent current density i_n is linear, it gives

$$V'_{act} = 3.2725 \times 10^{-4} \times T + (-1.6864 \times 10^{-6} \times T + 6.427 \times 10^{-4} + 2.775 \times 10^{-8}t) \times T \ln[i + (9.93 \times 10^{-4} \times T^2 - 0.709T + 127 + 0.00576t)]$$
(23)



Fig. 11. Comparison of the model calculation to the experimental value (the operating pressure is 1.0-1.2 atmosphere pressure. The operating temperature is 303.15-333.15 K. The relative humidity of anode/cathode is 80-100%/60-100%. The stoichiometric ratio of anode/cathode is 1.1-1.5/1.7-2.9).

4. Model validation

The correlation of the model to 20 actual experimental data under different operating temperatures and air stoichiometric ratios is shown in Fig. 11. The comparison of the model average cell V–I to actual cell V–I curves is shown in Fig. 12. The model voltage degradation rate under 100 A current is about 7.15%, while the actual voltage degradation rate is about 6.9% as shown in Section 3.2. The precision of the model is about 5%, which means the above modeling method is feasible. In the next section we will use the model to predict and analyze the degradation of the stack.

5. Model simulation and analysis

The V–I curves and the output powers of the stack changed with time are shown in Figs. 13 and 14, respectively. The test conditions are shown in following: the operating temperature:



Fig. 12. Comparison of the model V–I curves to the experimental V–I curves (the operating pressure is atmosphere pressure. The dew point of anode/cathode is 330.15 K/325.15 K. The stoichiometric ratio of anode/cathode is 1.2/2.3).



Fig. 13. The simulation V-I curves of the fuel cell stack in different age.

T = 333.15 K, H₂ and air stoichiometric ratios: $\lambda = 1.5$ and 2.5, respectively.

In order to analyze the losses of the stack conveniently, the concentration loss is defined as the following equation

$$V_{\rm con} = -[\psi T \ln(p_{\rm O_2, channel}) - \psi T \ln(p_{\rm O_2, channel} - C_{\rm r} i)] \quad (24)$$

Substituting this Eq. (24) into Eq. (10) gives

$$V = E'' + V''_{act} + V_{ohm} + V_{con}$$
(25)

where E'' is defined as normal thermodynamic potential

$$E'' = E' + 2.15425 \times 10^{-5} T \ln(p_{O_2, \text{channel}})$$
(25a)

 $V_{\rm act}''$ is activation loss

$$V_{\rm act}'' = V_{\rm act}' + \zeta_3 T \ln(p_{\rm O_2, channel})$$
(25b)

Under the rated current 90 A defined by the manufacturer, the losses of the stack with aging are shown in Table 2.

At the beginning of the driving cycle, the normal thermodynamic potential is 94.73 V, and the output voltage of the stack is 58.21 V. The ohmic loss is 3.31 V. The activation loss is 30.39 V, and the concentration loss is 2.80 V, the efficiency of the stack is $\eta = 61.45\%$.



Fig. 14. The simulation output powers of the fuel cell stack in different age.

Table 2	
The performance of the stack with age under the rated current 90 A	

Age (h)	Output voltage (V)	Stack efficiency (%)	Activation loss (V)	Ohmic loss (V)	Concentration loss (V)	Total loss (V)
BOL	58.21	61.45	30.39	3.31	2.80	36.5
500	55.15	58.22	32.55	4.22	2.80	39.57
1000	52.08	54.98	34.71	5.12	2.80	42.63
1500	49.00	51.73	36.88	6.02	2.80	45.7
2000	45.93	48.48	39.06	6.93	2.80	48.79
2500	42.84	45.22	41.24	7.83	2.80	51.87

After 2500 h driving cycle-test, the output voltage of the stack becomes 42.84 V. The ohmic loss is 7.83 V. The activation loss is 41.24 V. The concentration loss is still 2.80 V, and the efficiency of the stack is $\eta = 45.22\%$.

The activation loss dominates the total losses in the stack with almost 80%. The ohmic loss is the second largest loss. The concentration loss is the mildest and does not change with aging in the driving cycle condition. After 2500 h driving cycle test, the total losses change from 36.5 V to 51.87 V with 42.1%, the activation loss changes from 30.39 V to 41.24 V, increasing about 35.7%, the ohmic loss changes from 3.31 V to 7.83 V, increasing about 136.6%.

In the fuel cell bus power-train, there is low voltage protection function in the DC/DC converter to protect the fuel cell stack. The protection average cell voltage is about 0.65 V (because under the cell voltage lower than 0.65 V, some cells can not work properly, especially in the large stack with many cells in series.). So for the 5 kW low-pressure PEMFC stack, the output power at the operating voltage 52 V was selected for evaluating the performance of the stack. Table 3 shows the performances of the stack with aging under the protection voltage (52 V).

At the beginning of the driving cycle test, the output power of the stack under the voltage of 52 V is 7630 W, and the current density is 524.4 mA cm⁻².

After 2500 h driving cycle operation, the output power of the stack under the voltage of 52 V drops to 2066.3 W, and the current density is 142.2 mA cm^{-2} . The output power degraded 72.9%.

So under the driving cycle test rated current 135 A (current density is 482.14 mA cm⁻²), the stack average cell voltage will be lower than 0.65 V after 500 h operation. In the actual tests, it did happen that the test station shut down occasionally because of one of the cell voltage of the stack lower than the protected voltage of 0.4 V after 500 h driving cycle test. If the driving cycle test rated current is 90 A, then the output voltage of the

Table 3 The performance of the stack with age under the protection voltage (52 V)

Age (h)	Current density (mA cm ⁻²)	Stack output power (W)	Power degradation (%)
BOL	524.4	7630	_
500	417.5	6073	20.4
1000	323.7	4706	38.3
1500	247.5	3410	55.3
2000	188.3	2735.5	64.1
2500	142.2	2066.3	72.9



Fig. 15. The Stack Voltage Degradation of The Fuel Cell Bus with Kilometer.

stack will be lower than 52 V after 1000 h operation. The rated power of the stack must be reduced if the stack will be operated continuously.

In order to use this model to evaluate the performances of the stack in the fuel cell bus, the data of the fuel cell bus stack are compared with the results of the model. The stack voltage degradation related to distance is almost linear as shown in Fig. 15. A set of stable tests is carried out in lab before the real route test and after 30,000 km (about 824 h, statistically, the average speed of the bus in the route is about 36.4 km h^{-1}) test. The average cell V–I curves of the fuel cell bus stack are shown in Fig. 16. The average cell voltage dropped from 0.741 V to 0.665 V under the rated current 90 A after 30,000 km test. This corresponds to 820 h driving cycle tested in the test station very well. It can be calculated that after the bus operating 36,000 km (about 989 h), the average cell voltage will be lower than 0.65 V under the rated



Fig. 16. Comparison of the bus V–I curves before and after 30,000 km route test.

current 90 A. This means that the output power of the stack will not meet the request of the bus and the rated power must be reduced if the bus will be operated continuously.

6. Summary and conclusions

A semi-experimental voltage degradation model for a lowpressure PEMFC stack is introduced in this paper. The concentration term has been extracted from the PEMFC output voltage, and the concentration resistance coefficient has been defined. The constants of the model have been derived from the elaborately designed tests carried out in a 5 kW low-pressure PEMFC stack. Analysis of the model shows that the activation overvoltage dominates the total losses with almost 80% followed by the ohmic loss, and the concentration loss is the mildest and does not change with aging in the driving cycle condition (the concentration loss might have only been insignificant due to their relatively low current density where mass transport would not play a major role). The comparison of the simulation of the degradation model with the actual test data of the PEMFC bus running for 30,000 km shows that the bus PEMFC stack rated power or rated current must be reduced after 36,000 km. This degradation model can be used for optimal configurations, optimal control of the fuel cell system, and the fuel cell hybrid power-train system.

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