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Voltage–time behavior of a polymer electrolyte membrane fuel cell stack at constant current discharge

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Abstract

Empirical equations were developed to describe the voltage–time behavior of polymer electrolyte membrane fuel cell (PEMFC) stacks at constant current discharge. When either ambient temperature or discharge current is too high, the experimental voltage–time curves exhibit rapidly falling cell voltage within a short discharge time. Various experimental voltage–time curves have been fitted very well with empirical equations at different discharge currents and ambient temperatures. The effect of parameters of the empirical equations on the shape of voltage–time curve is also analyzed. Inadequate mass-transfer is likely a reason for the voltage falling down rapidly, and polymer electrolyte membrane dehydration is responsible for the inclination of the voltage–time curves. The empirical equations are helpful for forecasting and explaining the long-term discharge performance of the PEMFC stacks. Published by Elsevier Science B.V.

Keywords: Fuel cell stack; Discharge performance; PEMFC; Fuel cell modeling; Voltage–time behaviors

1. Introduction

In the pursuit of cleaner air and less emitted pollution, the fuel cell has been considered as one of the most promising source of energy for electric vehicles and for other portable electrical power applications. Among many kinds of fuel cells, the polymer electrolyte membrane fuel cell (PEMFC) has received much attention in the last two decades [1–14] because of its lightweight, compactness, high power and low cost. In order to understand and improve the performance of PEMFC, several models [8–13] have been developed to explain the behavior of voltage variation with discharge current for single cells and for fuel cell stacks. Kim et al. [8] have modeled the voltage–current curves for a single fuel cell using an empirical equation, accounting for processes including activation, Ohmic and mass-transfer. Amphlett et al. [9,10] have tried to describe the relationship of voltage and current of Ballard Mark IV fuel cell using mechanistic and empirical methods. Chu et al. [11–13] have described the voltage–current behaviors of PEMFC stacks as a function of electrode processes and mass-transfer. However, modeling the voltage–current behaviors of polymer electrolyte fuel cells in terms of electrode processes and mass transfer alone is not enough to evaluate the practical performance of fuel cells or fuel cell stacks, because practical fuel cells have to be working for long time at different ambient temperatures, since long-term operation the temperature of fuel cell stack may change with time. How to assess the effects of temperature and time changes on the performance of fuel cell stacks is considered when all electrode processes and mass-transfer are accounted for.

This research is to study the long-term performance of a PEMFC stack at constant current discharge, instead of describing the short-term voltage–current behaviors only.

2. Experimental

A bipolar PEMFC stack was used, which could provide about 50 W output power under optimum conditions. There were 42 cells in the stack and each cell had active electrode area of 18 cm^2. The open circuit voltage was about 42 V. The volume of the stack was about 250 cm^3. The stack was humidified with water steam, and initially run at 0.5 A for several hours to reach a stable performance before using it for generating data.

High purity hydrogen (99.99%) was used as fuel, and compressed air as oxidant. The ambient temperature was controlled with a Tenney Environment Chamber (Model no. BTRC), which was programmed through a computer with Linktenn II Software. An Arbin Battery Tester BT-2043 was used for programming controlled constant current discharge

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test. A Hewlett-Packard Electronic Load (Model no. 6050A) and a Hewlett-Packard Multimeter were used for measuring current and voltage when the stack voltage was greater than 35 V. A Matheson digital flow-meter (LFE 1000H) was used for hydrogen flow measurements. A hydrogen purger was used and set to a 10 s length per 5 min period for all measurements. The inlet hydrogen and air pressures were adjusted to 3 and 5 psi, respectively. An electric fan (ca. 10 W) was placed toward the stack during stack evaluation for heat dissipation. A thermocouple was used for stack temperature measurements.

3. Development of empirical equations

The voltage of a polymer electrolyte fuel cell stack sometimes is not constant in time, but sometimes drops steadily or rapidly. For example, when the discharge current is too high, the stack voltage is falls rapidly within a short time of starting the discharge. Fig. 1 shows the voltage–time curves of a 50 W bipolar fuel cell stack at ambient temperature of 20°C and at different discharge currents. When current is 1.0 or 1.5 A, the cell voltage drops only a little in time. However, when current is equal to or higher than 2.0 A, the stack voltage falls rapidly within about 35 min of starting the constant current discharge. Fig. 2 shows the voltage–time curves of a 50 W bipolar fuel cell stack at constant current (1.0 A) discharge and at different ambient temperatures. When temperature is equal to or higher than 30°C, the cell voltage drops slowly at first and then falls rapidly within about 40 min. The origin of the falling cell voltage versus time curves at constant current will be explored in this study. Apparently, the voltage–time behavior of the PEMFC stack is affected by the variations of stack temperature and discharge current. All the previous models [8–13] are unable to explain or describe this phenomenon. The following equations were developed to solve the problem.

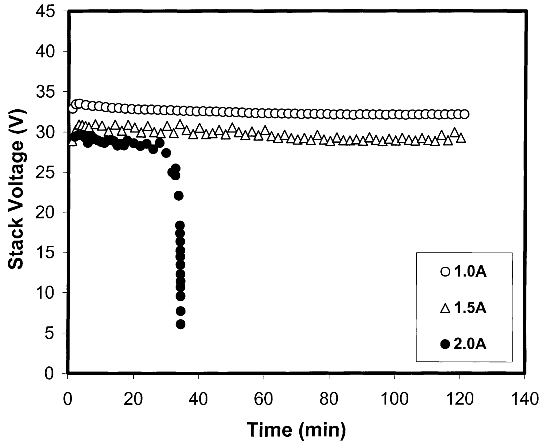

Fig. 1. Constant current discharge performance of a PEMFC stack (42 cells, area: 18 cm^2 per cell) at ambient temperature of 20°C and different discharge current.

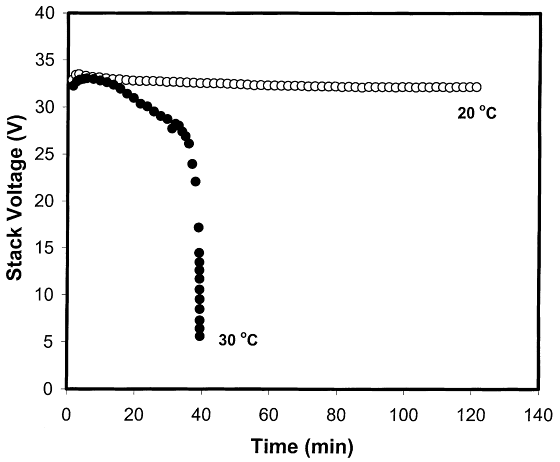

Fig. 2. Constant current (1.0 A) discharge performance of a PEMFC stack (42 cells, area: 18 cm^2 per cell) at different ambient temperatures.

For a fuel cell stack the stack voltage can be described as follows [11–13]:

$$E = E_o - E_{act} - E_{Ohmic} - E_{mass} \quad (1)$$

$$E = E_o - b\log(i) - (R + \Delta R)i - E_{mass} \quad (2)$$

Here, E_o (V) is the open circuit voltage of the stack, E_{Ohmic} (V) the Ohmic over voltage of the stack, which is equal to the sum of the Ohmic over voltages of all single cells linked in series, E_{mass} (V) the over voltage of the stack caused by mass-transfer, b value the sum of Tafel slopes of all single cells linked by series, R the sum of Ohmic resistances of all single cells linked by series and ΔR is the incremental value of R because of temperature and relative humidity changes.

At constant current discharge, the sum of E_o and activation over voltage can be considered as a constant if we neglect their variations with temperature. However, the value of R may change appreciably with time because the effects of stack temperature and polymer electrolyte membrane dehydration on stack Ohmic resistance are significant. The stack temperature may increase with time after starting the constant current discharge until reaching a steady state with the ambient. When stack temperature is too high, the fuel and air transfers may be blocked or unbalanced, causing mass-transfer over voltage. For simplification, Eq. (2) is rewritten as

$$E = E_a - i\Delta R - E_{mass} \quad (3)$$

Here, E_a (V) is the apparent voltage of the stack at a specific current value, which is equal to the voltage at the initial time of constant current discharge. By analyzing a large number of voltage–time curves of PEMFC stacks at constant current discharge and at different ambient temperatures and relative humidities, we found that the E_{mass} can be described as

$$E_{mass} = iA\exp\left[\frac{1}{T_m - T}\right] \quad (4)$$

Here, T_m (°C) is the stack temperature that is high enough to initiate mass-transfer over-voltage. T (°C) is the stack temperature at any time, and the term A (Ω) is a parameter, which affects the rate of stack impedance jump at high temperature because of mass transfer.

ΔR can be described as

$$i\Delta R = iB\exp\left[\frac{N(T-T_0)}{T_b-T_0}\right] \tag{5}$$

Here, T_b (°C) is stack temperature at a steady condition with ambient, T_0 (°C) is the ambient temperature, the term B (Ω) is a parameter, which affects the rate of Ohmic resistance change with stack temperature and N is a function parameter, which determines a curvature of selective function with a different value for each kind of polymer electrolyte stack.

Therefore, Eq. (3) can be rewritten as

$$E = E_a - iA\exp\left[\frac{1}{T_m-T}\right] \pm iB\exp\left[\frac{N(T-T_0)}{T_b-T_0}\right] \tag{6}$$

In Eq. (6), if an increase of stack temperature causes stack resistance to increase, such as polymer electrolyte dehydration at high temperature, the symbol of the term on the rightmost side should be minus; and vice versa. Moreover, the stack temperature (T) is a function of time. In order to obtain the voltage–time function of the stack, we need to find the stack temperature at specified times by experiments. Sometimes, we only know a few values of stack temperature from experiments for a long-term of constant current discharge, and this is not enough to describe the whole range of stack temperature. Therefore, we need to find a temperature–time function to calculate the voltage for the stack at all times.

Unfortunately, stack temperature variation is dependent on many factors, such as stack power, stack size, stack shape, stack cooling-styles, the value of discharge current and heat dissipation coefficient. It is difficult to obtain an analytical solution. However, an empirical equation to describe the stack temperature–time behavior is obtained for PEMFC stack.

$$T = \frac{T_0 + (T_b - T_0)t}{t+S}, \quad S > 0 \tag{7}$$

Here, T_0, T_b and T are described in Eq. (6), the term t (min) is discharge time, and S (min) is a time parameter, which affects the rate of stack temperature change. At the beginning of discharge the stack temperature change is the fastest. With increasing time, the stack temperature change becomes gradually slower.

Using Eqs. (6) and (7), we can calculate the voltage–time curves of PEMFC stacks for a given discharge current in terms of the time-dependent over-voltage for all electrode processes and mass-transfer.

4. Calculated results

In order to understand the physical meanings of the parameters described in Eqs. (6) and (7) more clearly, we have carried out a series of calculations by varying one parameter only and keeping other parameters constant. These calculated results are summarized as follows.

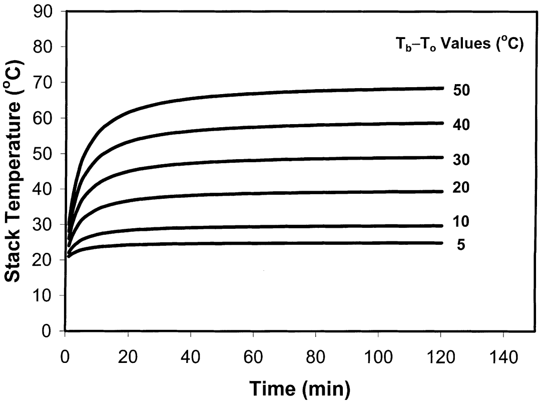

Fig. 3. Calculated curves of stack temperature vs. time for a PEMFC stack at constant current discharge using an empirical equation. Parameters used: $T_0 = 20$°C, $S = 4.0$ min and different $T_b - T_0$ values.

4.1. *Effect of* $T_b - T_0$

Fig. 3 shows the calculated data of stack temperature versus time using Eq. (7), which explains the effect of the term of ($T_b - T_0$) on the temperature–time curve at constant current discharge. The stack temperature grows quickly at the beginning time of discharge, especially over the first 20 min. Then the growth of it becomes slow and the temperature–time curve becomes flat gradually. By increasing the value of ($T_b - T_0$), the plateau of the temperature–time curve becomes higher.

4.2. *Effect of S number*

Fig. 4 shows the calculated stack temperature versus time using Eq. (7) and shows the effect of the term S on the temperature–time curve at constant current discharge. By

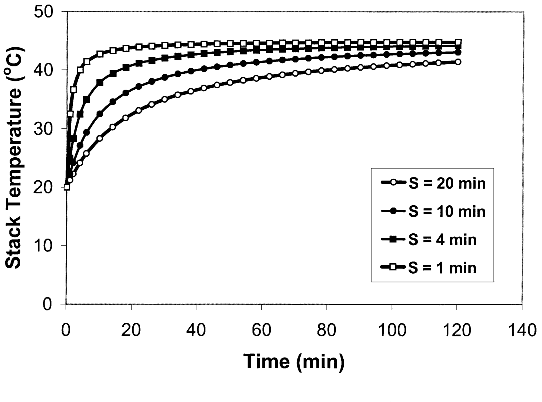

Fig. 4. Calculated curves of stack temperature vs. time for a PEMFC stack at constant current discharge using an empirical equation. Parameters used: $T_0 = 20$°C, $T_b - T_0 = 25$°C and different S values.

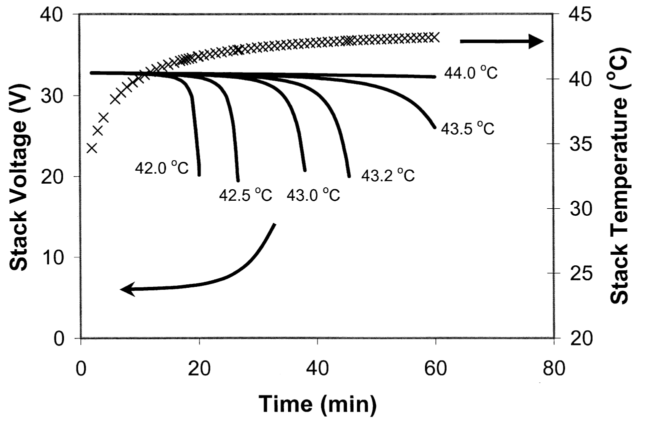

Fig. 5. Calculated curves of stack voltage vs. time (solid lines) for a PEMFC stack at constant current discharge using an empirical equation. Parameters used: $E_a = 33\,\mathrm{V}$, $A = 0.2$, $B = 0$, $i = 1.0\,\mathrm{A}$, $T_b - T_0 = 14.1°\mathrm{C}$, $S = 4.0\,\mathrm{min}$, $T_0 = 30°\mathrm{C}$ and varying T_m values. The top line is the curve of stack temperature vs. time.

increasing the value of S, the rate of stack temperature growth decreases but the plateau of the temperature–time curve changes only a little.

4.3. Effect of T_m value

Fig. 5 shows the calculated data of stack voltage versus time, which explains the effect of the T_m value on the behavior of voltage–time behavior. With increasing time the stack temperature gradually reaches the value of T_m, and the stack voltage begins to drop because of mass-transfer over-voltage occurrence. If stack temperature is smaller than the value of T_m, there is no mass-transfer over voltage and no voltage drop phenomenon. Because the maximum stack temperature is 43°C in Fig. 5 (see the top curve), the voltage–time curve drops only when the T_m value is equal to or smaller than 43°C.

4.4. Effect of parameter A

Fig. 6 shows the calculated data of stack voltage versus time, which explains the effect of parameter A on the behavior of voltage–time behavior. By increasing the value of parameter A, the rate of stack voltage drop becomes more significant.

4.5. Effect of parameter B

Fig. 7 shows the calculated data of stack voltage versus time, which explains the effect of parameter B. Here, the symbol of the term on the rightmost side in Eq. (6) is considered as minus. By increasing the value of parameter B, there is no apparent effect on the time to reach catastrophic failure. However, the plateau of the voltage–time curve becomes more downwardly inclined.

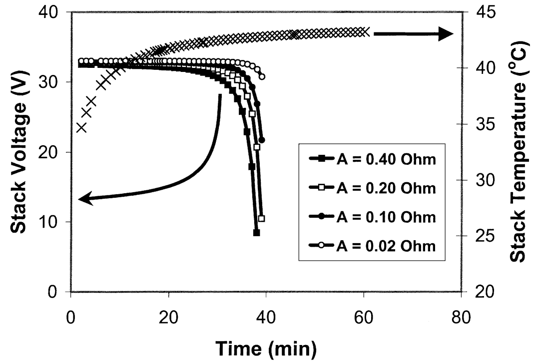

Fig. 6. Calculated curves of stack voltage vs. time (solid lines) for a PEMFC stack at constant current discharge using an empirical equation. Parameters used: $E_a = 33\,\mathrm{V}$, $T_m = 43°\mathrm{C}$, $B = 0$, $i = 1.0\,\mathrm{A}$, $T_b - T_0 = 14.1°\mathrm{C}$, $S = 4.0\,\mathrm{min}$, $T_0 = 30°\mathrm{C}$ and varying A values. The top line is the curve of stack temperature vs. time.

5. Experimental results

5.1. Temperature–time curve

The stack temperatures experimentally recorded are compared with the calculated data by Eq. (7). Fig. 8 shows the temperature–time curve obtained from a 50 W PEMFC stack at constant current discharge (1.5 A) and at ambient temperature of 20°C. The points were experimental data, and the line was obtained by calculation using Eq. (7) ($T_0 = 20°\mathrm{C}$, $T_b - T_0 = 19.5°\mathrm{C}$ and $S = 4.0\,\mathrm{min}$). As shown in the figure the calculated curve fits well with the experimental points. In the following calculations for stack voltage–time curves we keep the term S constant (4.0 min) and using different T_0 and $T_b - T_0$ values.

5.2. Voltage–time curves

5.2.1. Effect of discharge current

Fig. 9 shows a series of voltage–time curves at constant current discharge with different current values for a 50 W

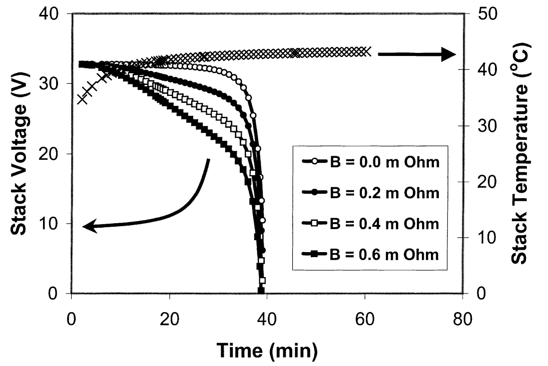

Fig. 7. Calculated curves of stack voltage vs. time (solid lines) for a PEMFC stack at constant current discharge using an empirical equation. Parameters used: $E_a = 33\,\mathrm{V}$, $T_m = 43°\mathrm{C}$, $A = 0.2\,\Omega$, $i = 1.0\,\mathrm{A}$, $T_b - T_0 = 14.1°\mathrm{C}$, $S = 4.0\,\mathrm{min}$, $T_0 = 30°\mathrm{C}$, $N = 11$ and varying B values. The top line is the curve of stack temperature vs. time.

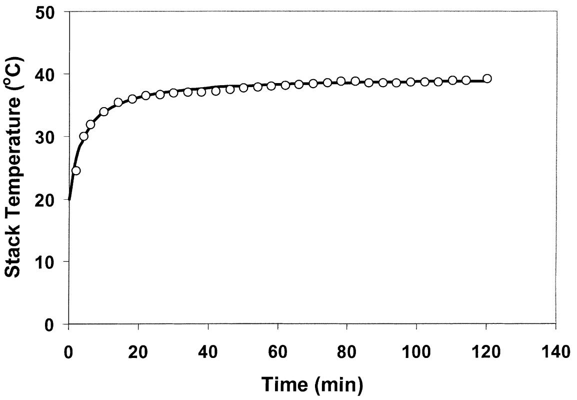

Fig. 8. Variation of stack temperature vs. time for a PEMFC stack at constant current (1.5 A) and ambient temperature of 20°C. The points and line were obtained from experimental and calculated data, respectively. Calculation parameters: $T_0 = 20$°C, $T_b - T_0 = 19.5$°C and $S = 4.0$ min.

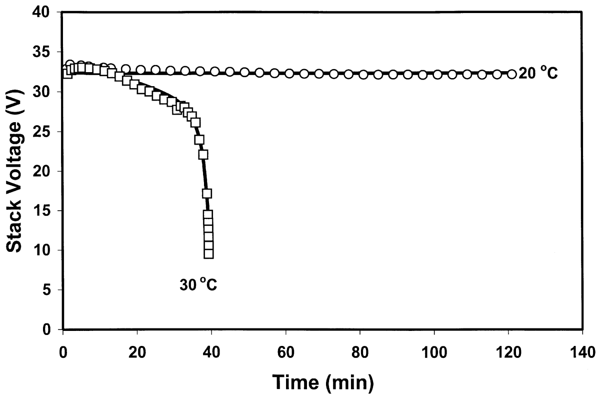

Fig. 10. Constant current discharge (1.0 A) performance of a PEMFC stack at different ambient temperatures. The points and lines were obtained from experimental and calculated data, respectively.

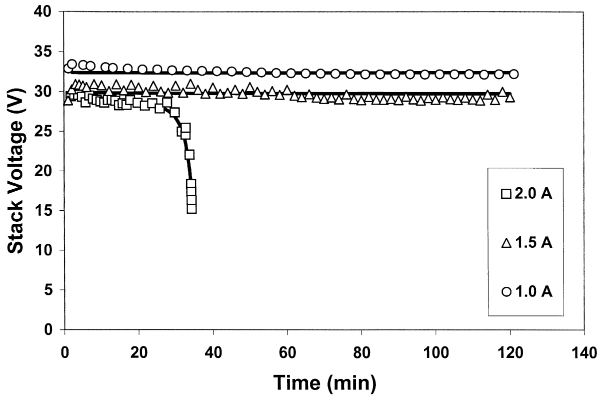

Fig. 9. Constant current discharge performance of a PEMFC stack at ambient temperature of 20°C. The points and lines were obtained from experimental and calculated data, respectively.

PEMFC stack. The points and lines were obtained from experiments and calculations, respectively. As shown in the figure all calculations fit with the experimental points very well. All the parameters used here for calculations are shown in Table 1. With increasing the discharge current, the difference of stack temperature at steady state (T_b) and ambient temperature (T_0) becomes larger, and the stack apparent voltage (E_a) becomes smaller. However, the stack temperature causing mass-transfer over-voltage occurrence (T_m) remains unchanged when ambient temperature is kept constant at 20°C.

Furthermore, at low value (1.0 A) of constant current discharge the voltage–time curve is relatively flat over 2 h. Increasing the discharge current value (1.5 A) the voltage–time curve becomes inclined. If the discharge current is too high (2.0 A), the voltage–time curve is downwardly inclined and falls down rapidly until reaching zero voltage in less than 40 min.

5.2.2. *Effect of ambient temperature*

Fig. 10 shows the effect of ambient temperature on the voltage–time behavior for a 50 W PEMFC stack. The points and lines were obtained from experiments and calculations, respectively. The parameters used here for calculations are shown in Table 1. Increasing the ambient temperature from 20 to 30°C, the values of E_a, T_m, and $T_b - T_0$ seemingly does not change significantly. However, the stack T_b value at ambient temperature of 30°C is about 10°C higher than that at ambient temperature of 20°C when they have the same value of discharge current (1.0 A). Therefore, at higher ambient temperature, the stack temperature reaches its T_m value (43°C) faster. As expected, at $T_0 = 20$°C the voltage–time curve is relatively flat, but at $T_0 = 30$°C it becomes inclined and falls down rapidly to zero voltage within about 40 min. The plateau of voltage–time curve is downwardly inclined slightly if the parameter B is not zero. Therefore, the

Table 1
Parameters used for calculations of the voltage–time curves for a 50 W PEMFC stack

T_0 (°C)	i (A)	E_a (V)	A (Ω)	B (mΩ)	T_m (°C)	$T_b - T_0$ (°C)	S (min)
20	1.0	33.0	0.6	0.0	44.0	14.0	4.0
20	1.5	31.0	0.7	0.0	44.0	20.0	4.0
20	2.0	30.0	0.4	0.0	44.0	26.4	4.0
30[a]	1.0	33.0	0.2	0.2	43.0	14.1	4.0
−5	3.0	24.5	0.1	0.0	38.0	53.6	4.0

[a] For this calculation the parameter $N = 11$.

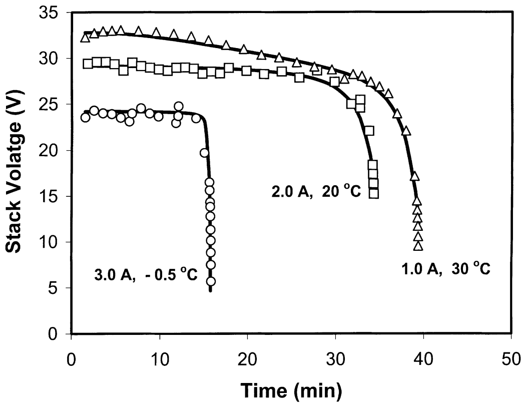

Fig. 11. Stack voltage dropping with time when either discharge current or ambient temperature was too high for a PEMFC stack at constant current discharge condition. The points and lines were obtained from experimental and calculated data, respectively.

parameter B gives a sign of whether the polymer electrolyte membrane is dehydrated or not.

5.2.3. Origin of voltage dropping

Fig. 11 shows a series of voltage–time curves at constant current discharge for a 50 W PEMFC stack. All these voltage–time curves are initially declining and their voltages are falling down to zero rapidly within different times. The points and lines in the figure were obtained from experiments and calculations, respectively. As shown in the figure, all calculations fit with the experimental points very well. All the parameters used here for calculations are shown in Table 1. At −5°C (ambient) and 3.0 A the discharge current is too high (3.0 A), leading to stack voltage dropping to 0 V in 15 min. At 30°C (ambient) and 1.0 A the ambient temperature is too high, causing stack voltage to drop to 0 V within 40 min. At 20°C (ambient) and 2.0 A the stack voltage drops to 0 V within 35 min because internal stack temperature is too high. Therefore, too high ambient temperature or discharge current will cause the fuel and air flows being blocked, interrupted or unbalanced. Too high stack internal temperature will cause a dehydration of the polymer electrolyte membrane. The factors of inadequate ambient temperature, discharge current and stack internal temperature are the origins of the gradual inclination and rapid drop of the voltage–time curves at constant current discharge for the PEMFC stack.

6. Conclusions

Several empirical equations were developed to describe the experimental stack temperature–time and the stack voltage–time curves for PEMFC stacks at constant current discharge. The experimental stack temperature–time curve is fitted very well with Eq. (7), which contains the parameters of ambient temperature (T_0), stack temperature at a steady state (T_b) and time factor (S). The experimental voltage–time curves at different discharge current and ambient temperatures are simulated with Eq. (6), which contains the parameters of stack internal temperature (T), stack mass-transfer temperature (T_m) and voltage decreasing rate factor (A). All experimental voltage–time curves are fitted very well with the empirical equations. When stack temperature reaches the value of T_m, a mass-transfer problem occurs, and the voltage–time curve shows the voltage drop rapidly. When either ambient temperature or discharge current is too high, the stack temperature will reach the T_m value and cause a mass-transfer problem. In addition, when stack internal temperature is too high, the polymer electrolyte membrane will dehydrate, causing a gradual inclination in the voltage–time curve.

The empirical equations (6) and (7) are helpful for stack design because they are useful for forecasting the stack long-term performance. We may conduct calculations by setting different parameters for the empirical equations. For example, we may calculate a series of stack temperature–time curves to determine how fast the stack temperature increase will be for obtaining a maximum stack power. Also we may calculate a series of the stack discharge voltage–time curves to decide what stack performance will be for a given ambient temperature or discharge current.

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