Analysis of polymer electrolyte fuel cell performance by electrode polarization model

Yoshihiro Mugikura*, Koichi Asano

Central Research Institute of Electric Power Industry, 2-6-1 Nagasaka, Yokosuka-shi, Kanagawa-ken 240-0196, Japan

A B S T R A C T

For development of polymer electrolyte fuel cell (PEFC) lifetime estimation method, a high accuracy PEFC electrode polarization model is required. An electrode polarization model which was previously proposed was verified. However, accuracy of the electrode polarization model was not enough to estimate PEFC performance under various conditions. A new high accuracy PEFC electrode polarization model has been developed based on electrochemical consideration and data observed at elevated pressures. In the cathode polarization model, effects of O_2 diffusion and H_2O plugging have to be considered to obtain high accuracy for long-term operation. In addition, PEFC performance degradation was analyzed by the electrode polarization model. Main factors of PEFC performance degradation are OCV drop, the cathodic activation polarization, voltage drops by O_2 diffusion and H_2O plugging.

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1. Introduction

Polymer electrolyte fuel cell (PEFC) power systems have been developed in many countries since the total efficiencies of PEFC power systems are expected to be higher than that of combination of electric power from the gird and hot water by a boiler system for residential application, or that of the gas engine systems for automobile application. Cell technology of a PEFC is an essential element and is a key technology to achieve both of high efficiency and long lifetime at same time. The electrode polarization model is used for a PEFC power generation efficiency estimation and performance factor analysis. The electrode polarization model has been required to have a high accuracy. Authors have been developing electrode polarization models for molten carbonate fuel cell (MCFC) and solid oxide fuel cell (SOFC) [1–4]. These electrode polarization models have good accuracy under various conditions. Especially, in the cases of MCFC and SOFC, measured open circuit voltages (OCVs) have agreed with OCVs theoretically calculated by Nernst equation [1,4]. On the other hand, for PEFC, OCVs calculated by Nernst equation do not agree with measured OCVs [5]. Measured OCVs of PEFC are much lower than theoretical OCVs. OCV is a very important factor to estimate PEFC performance since OCV is the base line for cell performance estimation. Therefore, OCV compensation equation is needed to estimate PEFC performance accurately. Amphlett et al. have proposed an electrode polarization model [6,7]. Their

electrode polarization model was verified with Ballard stacks and had good accuracy. Therefore, their electrode polarization model was verified with authors' data at first. And a new electrode polarization model has been developed. In addition, PEFC performance degradation by long-term operation was analyzed by the electrode polarization model.

2. Experimental

PRIMEA® as membrane electrode assemblies (MEAs), which are manufactured by the Japan Gore-Tex Inc. was used for verification and development of PEFC electrode polarization model. The MEAs have Pt loadings with $0.4\,mg\,Pt\,cm^{-2}$ in the anode and cathode, respectively. The active electrode area is $25\,cm^2$. MEAs were sandwiched between two gas diffusion layers and were then assembled in JARI standard single cells [8].

A pressurized test stand with a pressure vessel was used to operate PEFC under various conditions. This test stand supplied the gas, which was humidified using a bubbler. The fuel gas and air, whose humidity was controlled using a dew-point meter, were supplied to the cell. The operating pressure was 0.3 MPa or less. The vessel pressure was adjusted according to the operating pressure, and the anode and cathode pressures were adjusted according to the operating pressure by controlling the differential pressure on the basis of the vessel pressure.

All measurements were performed using an As-510-4 fuel cell analyzer and an As-510-CVM potentiostat/galvanostat (NF Corporation, Japan). Polarization measurements were performed under different pressures (0.1 and 0.3 MPa). The *I–V* characteristics were

* Corresponding author. Tel.: +81 46 856 2121; fax: +81 46 856 3346.
  E-mail address: mugi@criepi.denken.or.jp (Y. Mugikura).

Table 1
Cell specifications and operating conditions.

Manufacture	Japan Gore-Tex Inc. (jGi)
Membrane thickness	30 μm
Anode catalyst	Pt/C
Cathode catalyst	Pt/C
Pressure	**0.1** and 0.3 MPa
Cell temperature	80 °C
Fuel	H_2 **100**, 90, 80, 70 and 60%
Oxidant	Air
Uf	60, **70**, 80 and 90%
U_{O_2}	20, 30, **40**, 50 and 60%
Anode dew point	65, 70, 75 and **77** °C
Cathode dew point	65, 70, 75 and **77** °C

Bold face indicates standard operating condition.

obtained by the As-510-4 fuel cell analyzer. The testing conditions included an operating temperature of 80 °C, anode and cathode dew points of 77 °C each, and gas flow rates of hydrogen and air that were fixed at 70% of the fuel utilization (Uf) and 40% of the oxygen utilization (U_{O_2}) at 0.25, 0.5 and 0.75 A cm^{-2}, respectively. The fuel utilization was changed from 60 to 100% as shown in Table 1. Oxygen utilization was changed from 20 to 60%. The anode gas composition was changed by adding N_2 to anode gas. Anode and cathode dew points were changed from 65 to 77 °C.

In addition, long-term operation test was performed to confirm lifetime limiting factors. During the operation, performance analysis test had been performed every thousand hours. In the performance analysis test, the anode and cathode gas conditions such as Uf, U_{O_2} and dew points were changed, and *I–V* characteristics were measured.

3. Result and discussion

Output voltage (*V* (V)) of a fuel cell is expressed by open circuit voltage (*E* (V)), Nernst loss (η_{NE} (V)), anode polarization(η_a (V)), cathode polarization (η_c (V)), voltage drop by internal resistance (η_{ir} (V)) as performance factors [1]:

$$V = E - \eta_{NE} - \eta_a - \eta_c - \eta_{ir} \tag{1}$$

Theoretical open circuit voltage (E_{th}) is calculated by following Nernst equation:

$$E_{th} = E_0 + \frac{RT}{2F} \ln(P_{H_2} P_{O_2}^{0.5}/P_{H_2O}) \tag{2}$$

where E_0 (V) is the standard potential, R (J mol^{-1} K^{-1}) is the gas constant, T (K) is the absolute temperature, F (C mol^{-1}) is the Faraday constant and P (atm) is the partial pressure.

Under no load, the anode and cathode gas compositions are constant in the cell. However, under the load, since the gas compositions are changed by the fuel and oxygen consumptions by the cell reactions and voltages calculated by Eq. (2) are changed. Voltage difference between OCVs under load and no load is called as Nernst loss. Internal resistance was measured by current interrupt method. Measured internal resistance of a PEFC was used to calculate η_{ir}.

Relationship between measured OCV and theoretical OCV was investigated as shown in Fig. 1. OCVs were measured under various conditions as shown in Table 1. Measured OCVs were obviously much lower than theoretical OCVs calculated by Eq. (2). Effects of several operating conditions such as the fuel utilization, the oxygen utilization, dew points of the anode and cathode gases, on OCV were examined. It has been found out that U_{O_2} affects measured OCV and higher oxygen utilization makes measured OCV lower as shown in Fig. 2. It seems that this is caused by low oxygen supplying to the cathode reaction site:

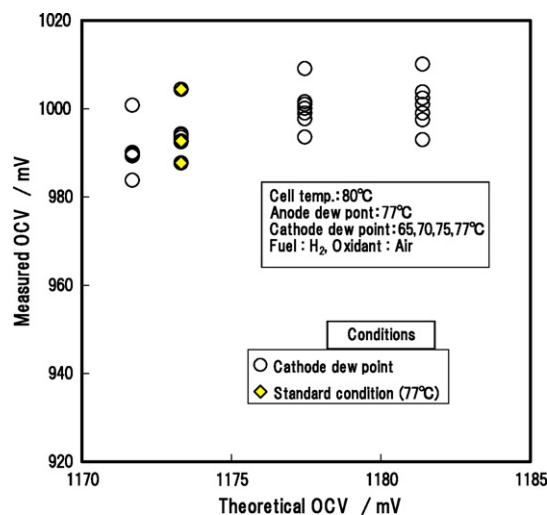$$E = E_{th} - 0.028 U_{O_2} - 0.018 \tag{3}$$

Fig. 1. Comparison between theoretical and measured OCV.

OCVs compensated by Eq. (3) were compared with measured OCVs as shown in Fig. 3. Compensated OCVs agree with measured OCVs.

Subsequently, the anode and cathode polarizations were investigated with measured data. At first, an electrode polarization model by Amphlett et al. was verified. Dependency of their anode electrode polarization model on current density is logarithm. However, the anode polarization is very small and is proportional to current density. As a result, for reformed LNG as a fuel, effect of hydrogen partial pressure (P_{H_2}) on the anode polarization was investigated and an equation has been electrochemically derived [9]:

$$\eta_a = A_1 i - A_2 \ln(P_{H_2}) \tag{4}$$

where i (A cm^{-2}) is the current density, and A_1 and A_2 are the parameters of anode polarization model.

For hydrogen as a fuel, the anode polarization does not depend on P_{H_2}. Following equations were derived [9]. A parameter in Eq. (5) has determined using experimental data:

$$\eta_a = 0.02i \tag{5}$$

The cathode polarization was investigated. A cathode polarization model which was proposed by Amphlett et al. as same as the anode
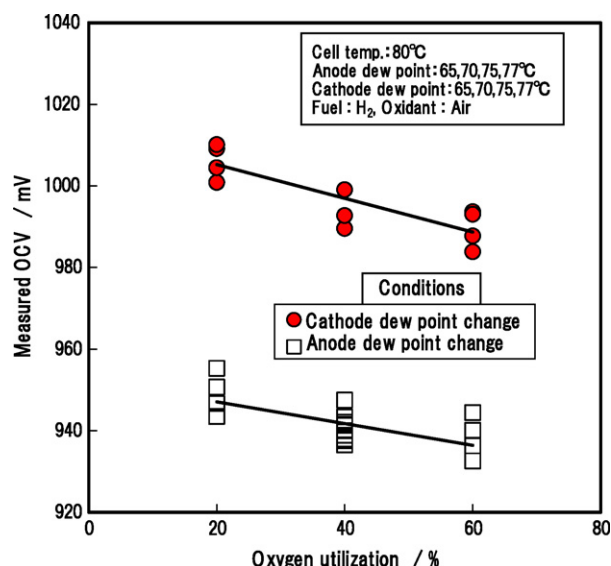

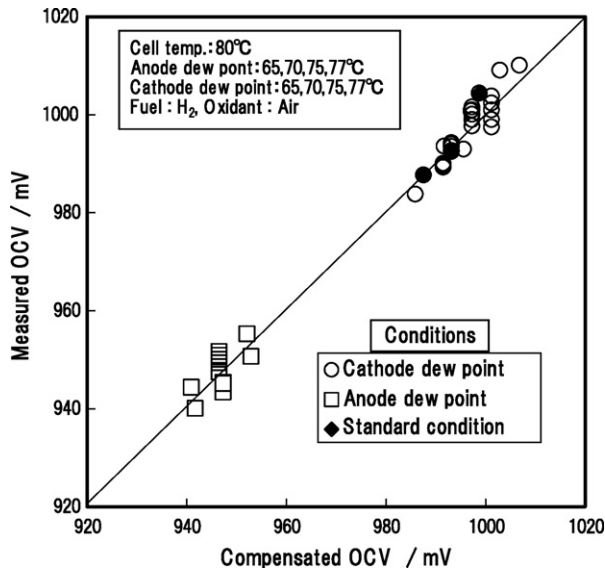**Fig. 2.** Relationship between measured OCV and U_{O_2}.

Fig. 3. Relationship between measured and estimated OCVs.

Fig. 4. Relationship between measured output voltages and output voltages estimated by Eq. (8).

polarization model is expressed by flowing equation [9]:

$$\eta_c = 0.943 - T \times 10^{-5}(354 - 15.3 \ln(232i))$$
$$- 7.8 \times 10^{-5}T \ln\left(\frac{\exp(498/T)P_{O_2}}{5.08 \times 10^6}\right) \tag{6}$$

This equation takes account in only electron transfer process and not gas diffusion process [6,7]. Effects of P_{O_2}, U_{O_2}, and cathode dew point on the cathode polarization were estimated by Eq. (6). Measured output voltage does not agree with output voltage estimated by Eq. (6) [9]. Therefore, a new cathode polarization model has been electrochemically investigated and Eq. (7) was derived. Parameters in Eq. (8) have determined using experimental data:

$$\eta_c = C_1 + C_2 \ln(i) + C_3 \exp\left(\frac{C_4}{T}\right) \ln(P_{O_2}P_{H_2O}^2) \tag{7}$$

$$\eta_c = 0.09 + 0.05 \ \ln(i) - 0.045 \ln(P_{O_2}P_{H_2O}^2) \tag{8}$$

In the right side of Eq. (8), the second and third terms correspond with the current density dependency and the cathodic activation polarization respectively. As the dependency of the exchange current density on gas composition in the third term, $P_{O_2}P_{H_2O}^2$ is applied instead of P_{O_2} which was applied by Amphlett et al. as Eq. (6).

As each partial pressure such as O_2 and H_2O in the cathode polarization model, mean partial pressure between inlet and outlet of a cell is generally used [1–4]. In a PEFC cathode gas stream, since O_2 is consumed and H_2O generates by the cell reactions, O_2 partial pressure and H_2O partial pressure change in the cathode gas stream. However, estimated output voltages by Eq. (8) using mean partial pressure do not agree with measured output voltages. Therefore, effects of partial pressures on accuracy of the cathode polarization model were evaluated. As a result, output voltages estimated from outlet partial pressures give better accuracy than those from mean partial pressures [9]. In the cathode gas stream, steam seemed to be saturated immediately with H_2O generated by the cell reaction and condense as water. It seems that steam condensation should occur near cell inlet and mean cathode partial pressure approaches to outlet partial pressure.

Consequently, I–V characteristics and pressure effect were evaluated as shown in Fig. 4. Output voltages were measured under different current densities and pressures. At 0.3 MPa, estimated output voltages were much higher than measured output voltages. According to consideration of pressure effect, the cathode polar-
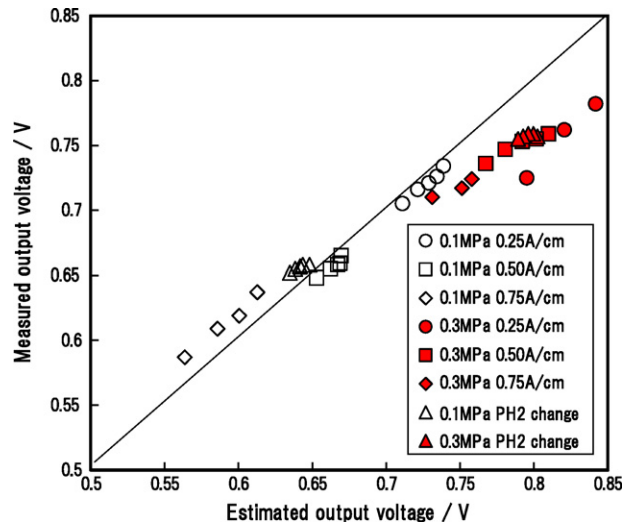
ization depends on mol fraction of oxygen (m_{O_2}) and not on P_{O_2} as following equation as shown in Fig. 5:

$$\eta_c = 0.09 + 0.05 \ln(i) - 0.045 \ln(m_{O_2}P_{H_2O}^2) \tag{9}$$

Oxygen concentration at the cathode surface would depend on oxygen diffusion coefficient and oxygen diffusion coefficient depends on the pressure. Effect of the pressure is cancelled by pressure dependency of oxygen diffusion coefficient. Same phenomenon is observed in MCFC cathode polarization model [3].

The average difference between measured output voltages and voltages estimated by Eqs. (3), (5) and (9) is lower than ±10 mV.

Subsequently, accuracy of developed electrode polarization model for long-term operation is verified. Therefore, a PEFC single cell was operated for 5000 h as shown in Fig. 6. Using data observed by the performance analysis test, electrode polarization model was verified and PEFC lifetime limiting factors were analyzed.

From Figs. 7–10, measured output voltages were compared with estimated voltages by the polarization model. Estimated output voltages agreed with measured output voltages until 2400 h as shown in Figs. 7 and 8. However, difference between estimated
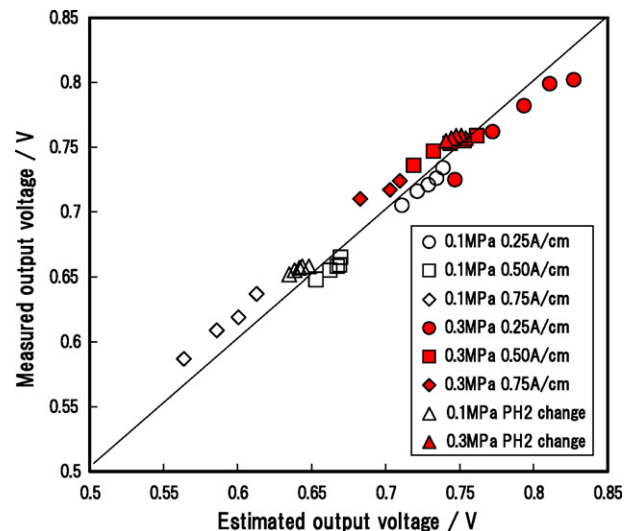

Fig. 5. Relationship between measured output voltages and output voltages estimated by Eq. (9).
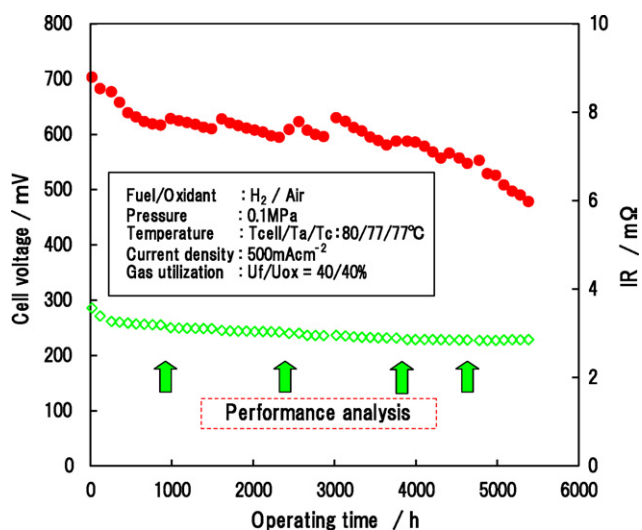
Fig. 6. A result of long-term operation of a PEFC single cell.

Fig. 8. Relationship between measured output voltages and output voltages estimated by Eqs. (3), (5) and (9) at 2400 h.

and measured output voltages became larger after 2400 h as shown in Fig. 9. Since difference between measured and estimated output voltages became larger especially at current densities higher than 0.5 A cm^{-1}, diffusion process would affect the cell performance and be considered to have high accuracy. At high current density, amount of mass transfer is greater than that at low current density. Therefore, effect of O_2 diffusion on the cathode polarization was evaluated. When O_2 concentration was lower than 10%, difference between estimated and measured output voltages became larger. The effect of O_2 diffusion would be appeared in low O_2 concentration. In addition, the term of O_2 diffusion is confirmed to check pressure dependency. Oxygen diffusion coefficient has pressure dependency as mentioned earlier. In the cathode polarization model, pressure dependency of the term of O_2 diffusion is cancelled by pressure dependency of O_2 diffusion coefficient as well as MCFC electrode performance model. At last, following equation has developed:

$$\eta_c = 0.09 + 0.05\ln(i) - 0.045\ln(m_{O_2}P_{H_2O}^2)$$
$$- 0.09(\ln(m_{O_2}) - \ln(0.1)) \tag{10}$$

In the right side of Eq. (10), the fourth term corresponds with the O_2 diffusion. The last term is necessary to compensate difference between Eqs. (9) and (10) since effect of O_2 diffusion appears at O_2 concentrations lower than 10%. Magnitude of the fourth term becomes larger when the effect of O_2 diffusion is significant. Relationships between measured and output voltages estimated by Eq. (10) at 3900 and 4750 h are compared as shown in Figs. 11 and 12, respectively. Output voltages estimated by Eqs. (3), (5), (9) and (10) were used. Output voltages estimated Eq. (10) agree with measured output voltages at 0.5 A cm^{-2}. However, for output voltages at 0.75 A cm^{-2}, accuracy of Eq. (10) is still not enough. The reason of low accuracy would be H_2O plugging which is caused by blocking of gas diffusion by condensed water. At high current density, steam generation by the cell reaction increases in proportional to current density. Removal of the steam from the cathode reaction site is not enough because of limitation of steam mass transfer. Mass balance of steam in the cathode gas stream was considered. Effect of H_2O plugging on the cathode performance is expressed by mass balance

Fig. 7. Relationship between measured output voltages and output voltages estimated by Eqs. (3), (5) and (9) at 900 h.
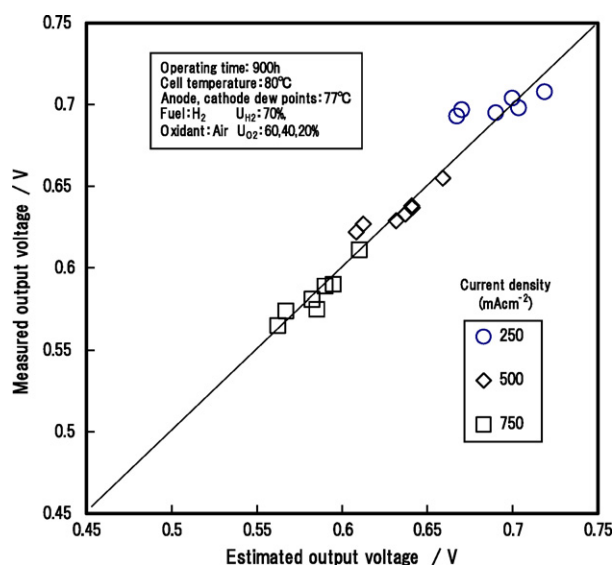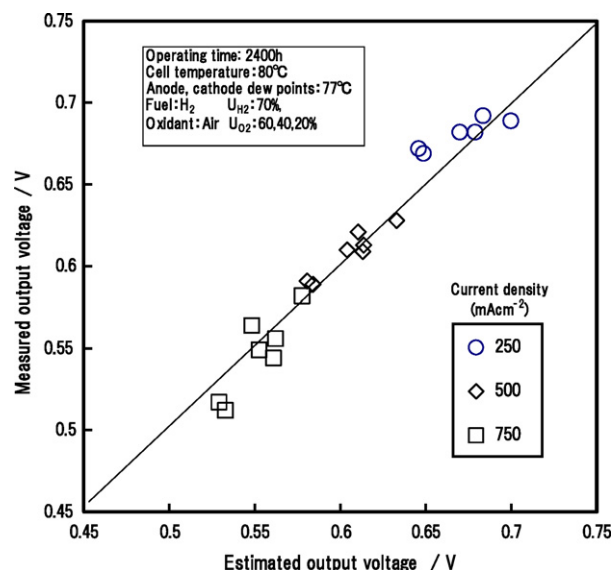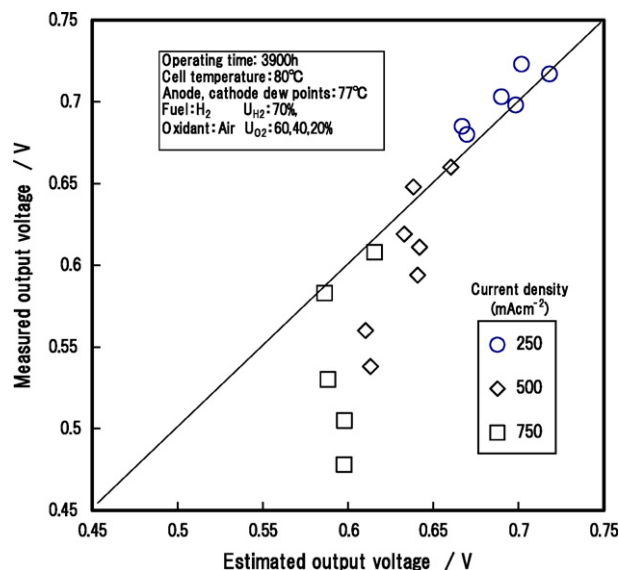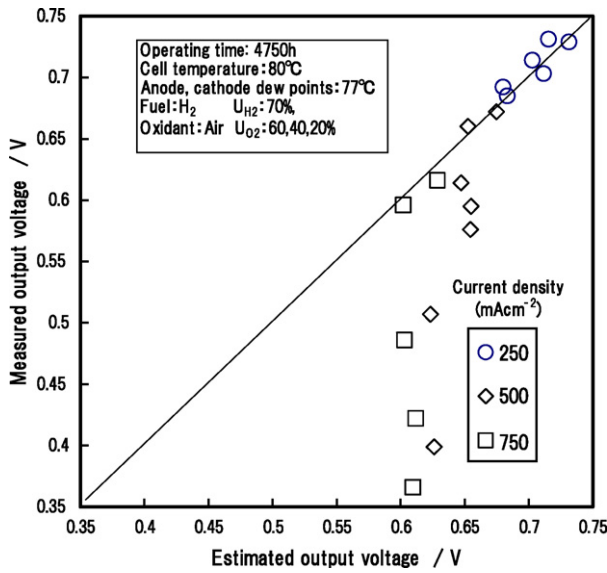

Fig. 9. Relationship between measured output voltages and output voltages estimated by Eqs. (3), (5) and (9) at 3900 h.

Fig. 10. Relationship between measured output voltages and output voltages estimated by Eqs. (3), (5) and (9) at 4750 h.
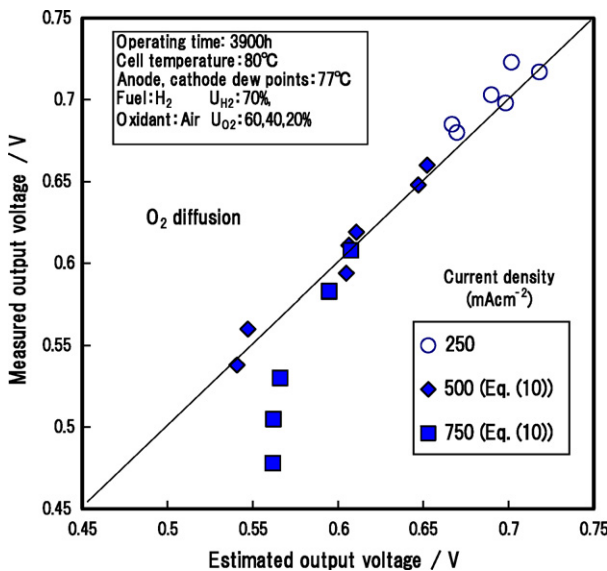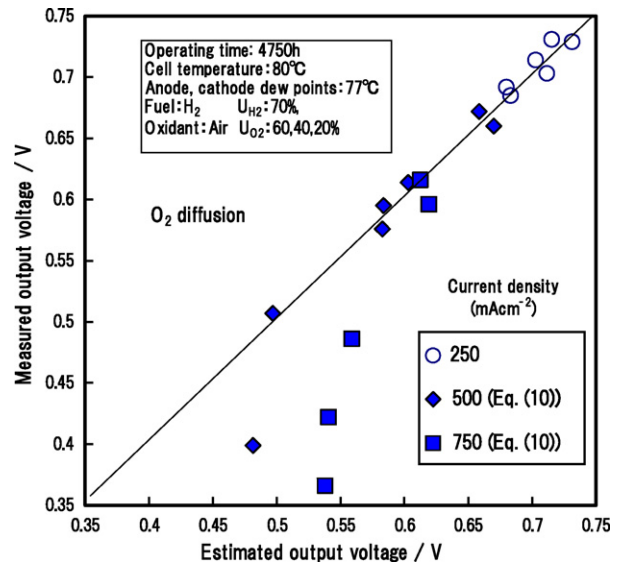

Fig. 12. Relationship between measured output voltages and output voltages estimated by Eqs. (3), (5), (9) and (10) which takes account in O_2 diffusion at 4750 h.

of H_2O generation, supply and removal in the cathode and anode gas streams.

Since the cathode gas supply and H_2O generation at same gas utilization are proportional to the current density, a term related to H_2O plugging is proportional to the current density. In consideration of H_2O removal from the cell, H_2O removal in the anode gas stream is taken account in as well as that in the cathode gas stream. Moreover, the fuel and oxygen utilizations are very important since the anode and cathode gas flow rates supplied to a PEFC are identified by these utilizations:

$$\eta_c = 0.09 + 0.05\ln(i) - 0.045\ln(m_{O_2}P_{H_2O}^2) - 0.09(\ln(m_{O_2})$$
$$- \ln(0.1) - i(2m_{O_2i} + m_{H_2Oi}/U_{O_2} - (m_{H_2O} - m_{H_2Oi})/U_{O_2}$$
$$- (m_{H_2Oa} - m_{H_2Oai})/U_{H_2})) \tag{11}$$

where m_{O_2i} is the cathode inlet O_2 mole fraction, m_{H_2O} is the cathode outlet H_2O mole fraction, m_{H_2Oi} is the cathode inlet H_2O mole fraction, m_{H_2Oa} is the anode outlet H_2O mole fraction and m_{H_2Oai} is the anode inlet H_2O mole fraction.

In the fourth term in the right side of Eq. (11), H_2O plugging has been recognized and terms of $2m_{O_2i}$ and m_{H_2Oi}/U_{O_2} in Eq. (11) correspond with amount of generation of H_2O and supply of H_2O to the cathode gas stream, respectively. These amounts are proportional to the current density. A term of $(m_{H_2O} - m_{H_2Oi})/U_{H_2}$ in Eq. (11) corresponds with steam removal in the cathode gas stream, is equal to difference between input steam and output of steam in the cathode gas stream. This term is proportional to the current density. As same as mass balance of the cathode steam, mass balance of the anode steam is expressed in Eq. (11). Parameter C_4 in Eq. (11) is the common parameter for O_2 diffusion and H_2O plugging. This result strongly suggests that limitation of O_2 diffusion and H_2O plugging are caused by same physical material degradation of the cathode.

Fig. 11. Relationship between measured output voltages and output voltages estimated by Eqs. (3), (5), (9) and (10) which takes account in O_2 diffusion at 3900 h.
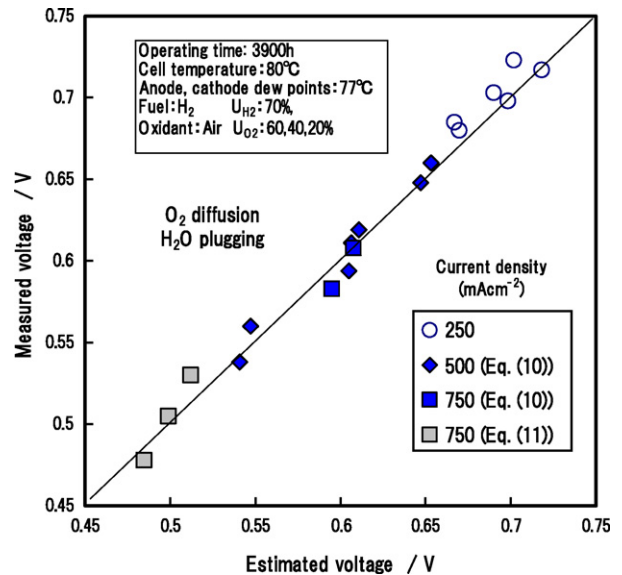

Fig. 13. Relationship between measured output voltages and output voltages estimated by Eqs. (3), (5) and (9)–(11) which takes account in O_2 diffusion and H_2O plugging at 3900 h.
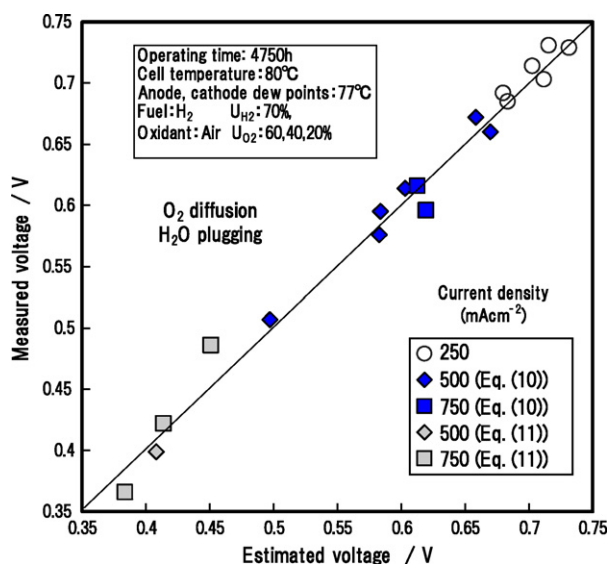
Fig. 14. Relationship between measured output voltages and output voltages estimated by Eqs. (3), (5) and (9)–(11) which takes account in O_2 diffusion and H_2O plugging at 4750 h.

Fig. 16. A result of performance factor analysis by the developed electrode polarization model at 0.75 A cm^{-2}.

Output voltages were estimated by Eqs. (3), (5), (9), (10) and (11). Relationships between measured and estimated output voltages at 3900 and 4750 h are compared as shown in Figs. 13 and 14, respectively. Eq. (11) has good accuracy for data obtained at high current density. Effects of O_2 diffusion and H_2O plugging in the cathode should be significant in long-term operation of PEFC.

Finally, PEFC performance degradation by long-term operation was analyzed by the developed electrode polarization model. A performance factor analysis has been performed. A result of performance factor analysis at 0.5 A cm^{-2} is shown in Fig. 15. Until 900 h, OCV drop and cathodic activation polarization increased. OCV drop is sum of the second and third terms of the right side in Eq. (3). The cathodic activation polarization corresponds with Eq. (9). After 2400 h, the cathodic activation polarization slightly increased. After 3900 h, the voltage drop by the cathode O_2 diffusion appeared and increased with time. The voltage drop by the cathode O_2 diffusion
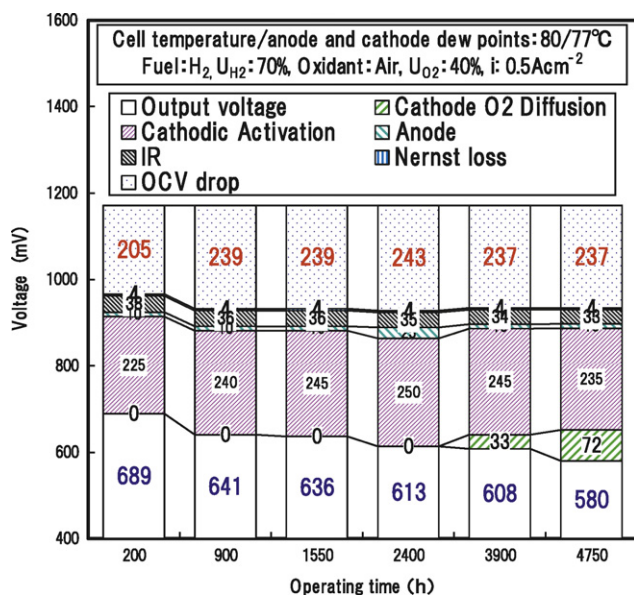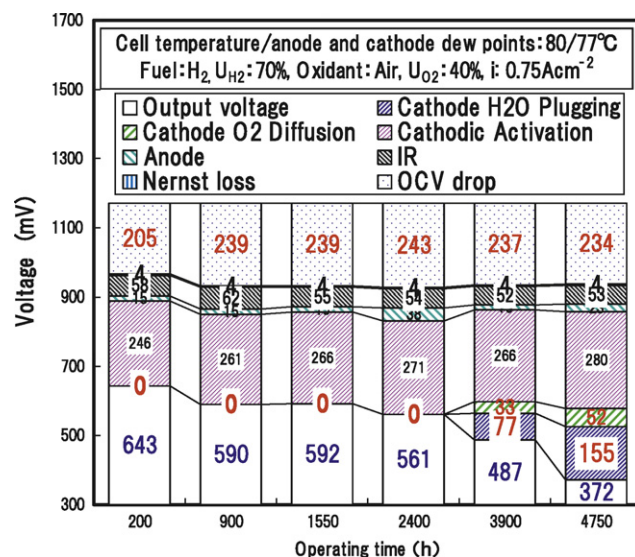
is the fourth term of the right side in Eq. (10). PEFC performance degradation at 0.5 A cm^{-1} was caused by OCV drop, the cathodic activation polarization and O_2 diffusion as shown in Fig. 15. Especially, the voltage drop by O_2 diffusion has increased after long-term operation at 0.5 A cm^{-2}.

A result of performance factor analysis at 0.75 A cm^{-2} is shown in Fig. 16. Until 3900 h, OCV drop and the cathodic activation polarization increased as mentioned above. Voltage drops by IR, the anode polarization and cathodic activation polarization were larger than those at 0.5 A cm^{-2} since these factors depend on current density. After 3900 h, effect of H_2O plugging appeared and increased with time. The effect of H_2O plugging is expressed by the last four terms of the right side in Eq. (11). PEFC performance degradation at 0.75 A cm^{-1} was caused by OCV drop, the cathodic activation polarization, O_2 diffusion and H_2O plugging as shown in Fig. 16. Effect of H_2O plugging has increased at high current density after long-term operation. Effects of O_2 diffusion and H_2O plugging should increase since water repellent performance of the cathode gas diffusion layer may be weakened.

4. Conclusions

Open circuit voltage compensation model, the anode polarization model and cathode polarization model have been newly developed. These polarization models would be available for performance estimation of PEFC at pressure range from 0.1 to 0.3 MPa. The effects of O_2 diffusion and H_2O plugging were considered as terms of the cathode polarization model. Only one parameter is necessary to express the effects of O_2 diffusion and H_2O plugging. This result strongly suggests that limitation of O_2 diffusion and H_2O plugging are caused by the same physical material degradation of the cathode. In addition, PEFC performance degradation by long-term operation was analyzed by the electrode polarization model. PEFC performance degradation by long-term operation was caused by OCV drop, the cathodic activation polarization and O_2 diffusion and H_2O plugging.

Acknowledgements

Fig. 15. A result of performance factor analysis by the developed electrode polarization model at 0.5 A cm^{-2}.

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