JOURNAL OF APPLIED ELECTROCHEMISTRY 26 (1996) 147–152

Effect of operational potential on performance decay rate in a phosphoric acid fuel cell

J. ARAGANE, H. URUSHIBATA,

Advanced Technology R&D Center, Mitsubishi Electric Corporation, 1-1, Tsukaguchi-Honmachi 8-Chome, Amagasaki, Hyogo, 661 Japan

T. MURAHASHI

Kobe Works, Mitsubishi Electric Corporation, 1-2, Wadasaki-cho, 1-chome, Hyogo-ku, Kobe, 652 Japan

Received 5 December 1994; revised 15 August 1995

The effect of operational potential on the cell voltage decay rate in a phosphoric acid fuel cell was estimated using the calculation of the platinum dissolution rate. The voltage loss, due to deterioration in activation polarization, was used in calculating the cell voltage decay rate. The voltage loss due to activation polarization was estimated using the relationship between the activation polarization and the platinum surface area. The change in the Pt surface area, arising from the dissolution of platinum, was obtained under accelerated open circuit voltage (o.c.v.) conditions. The study was focused on typical voltage decay rates from 0.1 to 10 mV per 1000 h. It was found that the cell voltage decay became significant even at low temperature during long-term operation (at o.c.v.) and that the cell had to be operated below 840 mV (*iR*-free) at 200 mA cm^{-2}, 200 °C for a decay rate of 1 mV per 1000 h. From the present estimation, operational conditions such as temperature, cathode potential, and holding time at a given potential, can be roughly determined for a given decay rate. It was concluded that the voltage loss due to platinum dissolution may be negligible at a rated power operation.

1. Introduction

Particle growth in platinum electrocatalysts used in phosphoric acid fuel cells (PAFC) has already been reported [1–4]. However, its effect on cell performance (cell terminal voltage) is less well known. In general, when a net current is drawn from a cell, fuel cell performance (terminal voltage) is influenced by activation polarization, concentration polarization and ohmic resistance [5]. In the literature, the cell performance was simulated based on the agglomerate model [6]. From this simulation, it was found that the voltage loss due to diffusion deterioration was not large at 200 mA cm^{-2}. In a real application, however, gas diffusion might become significantly hindered in long-term operation, causing gas partial pressure decrease at active sites. To cope with this problem, several modifications to the electrode structure and acid management have been implemented to improve cell performance stability to a commercially acceptable level. Improvements to the electrode structure include changes to the manufacturing process and the pore size distribution of cell components. Improvements to the acid management include adjusting the acid inventory in the cell by calculating the evaporation rate of the acid to give a cell life of around 40 000 h. In this context, further examination of the stability of the electrocatalyst is needed. In particular, the decrease in the activation polarization is a key factor for the expected reliability (i.e., 1 mV decay per 1000 h) of the PAFC. As a result of the change in the activation polarization, voltage loss may occur due to changes in the intrinsic platinum surface area and the effective platinum surface area [7].

It has been found that the effective metal surface area changed corresponding to the change in the platinum particle size after 100 h operation [8]. At under 100 h operation, the decrease in the effective surface area was larger than the decrease in the platinum surface area obtained by XRD (X-ray diffraction). Therefore, the platinum surface area is only considered in this paper as the effect of the effective surface area is negligible after 100 h operation. Thus, the performance loss of the catalyst is thought to be qualitatively explained in terms of the surface area (particle size). In this paper the activation polarization is examined and quantitatively estimated.

The platinum dissolution rate was experimentally determined at o.c.v. (open circuit voltage: ~1 V), By using data for platinum solubility in phosphoric acid [9] and the method of Ross [10] the platinum dissolution rate was calculated. By comparing the experimental and calculated data a formulation for platinum dissolution rate was obtained [11]. A relationship between the cell voltage decay rate and the platinum loading was also obtained [11]. From these relationships the effect of operational conditions on the cell voltage was determined.

0021-891X © 1996 Chapman & Hall

2. Experimental details

2.1. *Sample electrodes*

The cathodes used in this experiment were the backing paper type where catalyst layer was laminated on the carbon fibre paper on the one side, and PTFE was used as a hydrophobic agent. The PTFE content in the catalyst layer was 45% in weight. The sintering temperature in the electrode manufacturing process was 350 °C. The anode was of the same type and the PTFE content in the catalyst layer was 35%. The sintering temperature of the anode was 340 °C. The sintering time was 20 min for both cathode and anode.

2.2. *Instrumentation and fuel cells*

Single cells with an active area of 100 cm^2 were used. The operating conditions were 190 °C and 200 mA cm^{-2}. When examining the dependence of potential on platinum behaviour (dissolution etc.), the current density was adjusted to obtain a given potential. After the cell had been held at o.c.v. for a given time, the cell performance was measured at 200 mA cm^{-2} and the cell was disassembled for analysis. Reformed gas (hydrogen: 80%, CO_2: 20%) and air were used as the fuel and the oxidant, respectively. The gas utilizations were 85% on fuel and 75% on air.

The electrodes were removed from cells which had operated for a given period. The phosphoric acid was leached from the electrodes in hot water for instrumental analyses (XRD and EPMA, electron probe microanalysis).

2.3. *Analysis*

The platinum particle size was measured by XRD. The particle size can be obtained using Scherrer's equation [12].

$$t = \frac{0.09\lambda}{B\cos\theta} \tag{1}$$

where t is the platinum particle size in nanometre, λ is the X-ray wavelength (nm) and B is the half width at full maximum of the measured peak. A copper anode was used, therefore the value of λ was 0.1540 nm ($CuK\alpha_1$). A platinum crystallite has several peaks in the diffraction pattern, and the Pt(2 2 0) peak was selected, because it has no background carbon effect.

The specific surface area of the platinum particles were calculated using,

$$s = \frac{6 \times 10^4}{\rho R} \tag{2}$$

where s is the platinum relative surface area in $m^2\,g^{-1}$, ρ is the platinum density ($g\,cm^{-3}$), and R is the diameter of the particles (Å). An instrumental correction term has been proposed [13] to obtain an accurate particle size; however, in this experiment the term was omitted because its effect is small.

In addition, the following assumptions were made in the calculations of the effects of operational conditions on the cell decay rate:

(i) The change in activation polarization only is considered (as mentioned above).
(ii) The acid concentration is constant during cell operation. Therefore the solubility, and the diffusion coefficient, of platinum ions are constant.
(iii) The gas utilization and current density are constant during cell operation. Therefore, the gas partial pressures are constant.
(iv) The mechanisms of platinum dissolution and particle growth are potential-independent and time-independent.

3. Results and discussion

3.1. *Performance decay during open circuit voltage*

The cell voltage decay was examined with the cells maintained at o.c.v. The cell voltages were measured before and after o.c.v. The o.c.v. conditions were 190 °C, RG/air, 1 V. These results were reported previously [11]. It was found that the cell voltage decayed by 114 mV after 1400 min at o.c.v. It was also found that the iR-free voltage (H_2/O_2) decreased by 78 mV. The value of oxygen gain (potential difference between on oxygen and air used) increased by 36 mV after 1400 min. This indicates the deterioration of gas diffusibility, increase in overvoltage for oxygen to diffuse from a gas stream to active sites on the cathode.

These results show that maintaining o.c.v. brought about a deterioration of gas mass transfer as well as a decrease in the catalytic activity. The gas mass transfer in the electrode has a significant role in the PAFC. Previous experimental results [7] show the isolated platinum from the carbon support after single cell operation. The isolated platinum cannot be used in an electrode reaction, so that the platinum utilization (effective metal surface area) was decreased together with the deteriorated mass transfer due to the corrosion reaction of phosphoric acid. Further examination is necessary to quantitatively combine the cell performance with the gas mass transfer brought about by the electrode structure. As mentioned above, in this paper the voltage loss due to the diffusion polarization is not considered.

3.2. *Change in platinum loading and surface area during open circuit voltage*

The change in the platinum loading in the active component has been reported earlier [11] with cells maintained at o.c.v. for a given time. It was found that the amount of platinum in the cathode decreased and the amount in the matrix increased. The amount of platinum in the anode did not change. As for the platinum loading, the decrease in the cathode was equal to the increase in the matrix. The platinum particles at a

high potential (e.g., o.c.v.) dissolve and decrease to around 20% of nominal loading during 1400 min. This change was estimated to be $0.045\,mg\,cm^{-2}\,h^{-1}$. Figure 1 shows the distribution of platinum in the matrix after 180 min. It was found that the platinum was deposited and the deposited area looked like a straight band. The position of the deposition did not change with the o.c.v. holding time. The position was around 10 to 20 μm from the matrix. However,

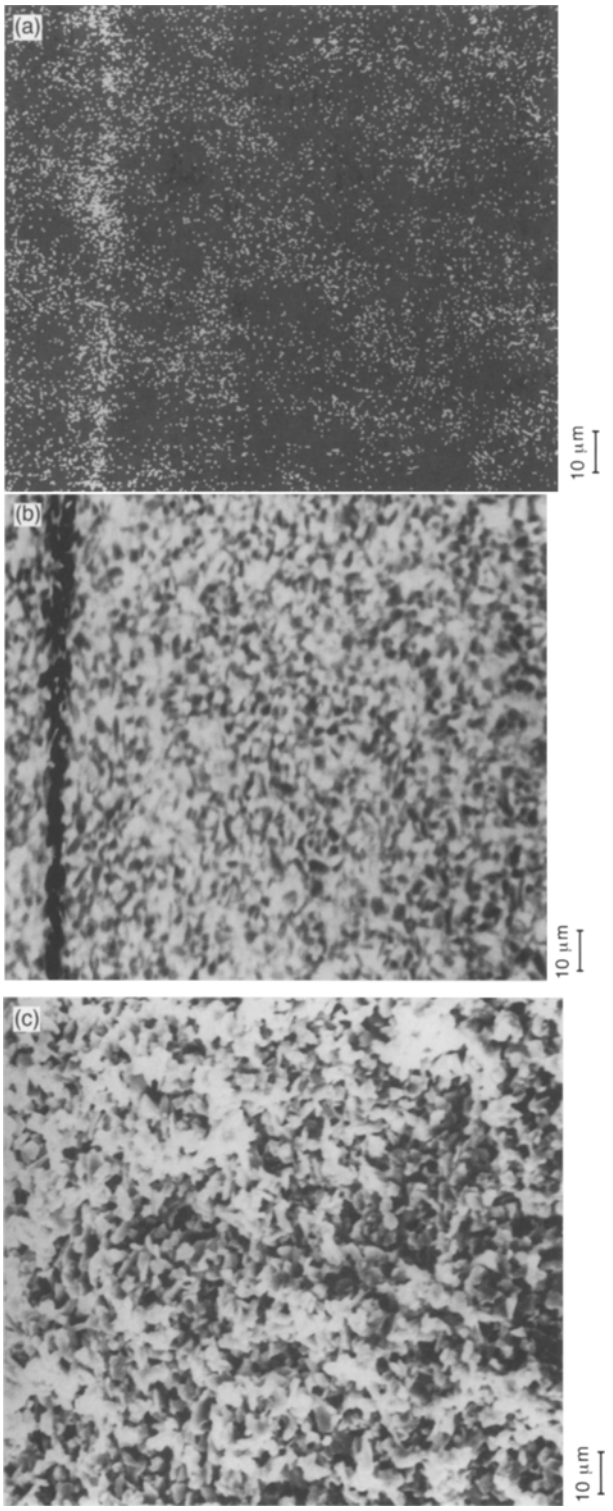

Fig. 1. Pt dissolution, migration and deposition in the matrix during o.c.v. conditions: 190 °C; 180 min; SRG/Air. (a) SEI; (b) BEI; (c) Pt$L\alpha$.

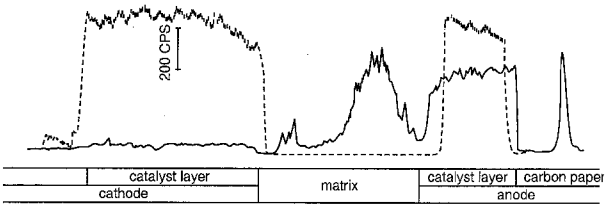

Fig. 2. Pt distribution in the active components of PAFC after operation. Key: (- - -) virgin; (——) 700 h (50 mA cm^{-2}) + 5h (o.c.v.).

the deposition position depends on the cell operation mode. Although the details have not yet been made clear, the position shifted towards the anode at o.c.v. after a loaded operation of 700 h. Figures 2 and 3 show examples of the experimental results. The cells were operated at given current densities (50 mA cm^{-2}, 300 mA cm^{-2}) for 700 h, and then maintained at o.c.v. for 5 h. Compared with the previous data [1] and Fig. 1 in the present paper, these figures show that much more platinum was dissolved and moved from the cathode. The EPMA mapping clearly shows that maintaining the o.c.v. led to the reduced amount of platinum in the cathode and the loaded mode accelerated the transport of the platinum. The o.c.v. operation accelerated the reduction in the cathode platinum loading. Platinum ions may be considered to be in equilibrium with the platinum catalyst; however, they are chemically reduced by hydrogen from the anode. The more hydrogen that diffuses to the matrix and other components from the anode, the more platinum is deposited and the more platinum is dissolved from the cathode. This phenomenon depends on the acid occupation in the matrix. Hydrogen mass transfer is changed with the acid occupation. The acid occupation varies with the current density. This suggests that operation at o.c.v. accelerates platinum migration and deposition in the matrix through improved mass transfer of hydrogen due to the drying up of the phosphoric acid. It is considered that after a cell operation of 700 h, the volume of the phosphoric acid is so expanded due to the water produced that hydrogen mass transfer from the anode is reduced. This leads the shifting of platinum to the anode as can be seen in Figs 2 and 3.

Furthermore, the higher the potential, the less the remaining amount of platinum in the cathode. This shows that the higher potential produced more platinum ions which were transported from the cathode.

The change in platinum surface area during o.c.v. holding has also been reported [11]. It was found that the platinum surface area decreased from around $50\,m^2\,g^{-1}$ to around $30\,m^2\,g^{-1}$.

3.3. *Evaluation of activation polarization*

From the decrease in the surface area and the platinum loading, an increase in activation polarization is predicted. Activation polarization is given by [14].

$$\eta_{act} = \frac{RT}{F}\ln\left(\frac{i}{i_0(SA)(CL)(CU)}\right) \qquad (3)$$

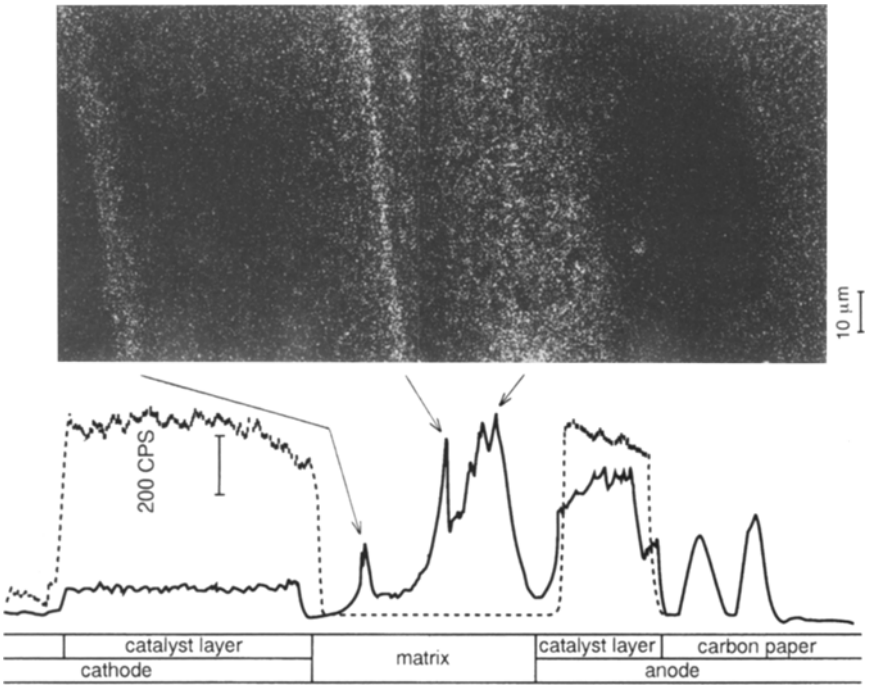

Fig. 3. Pt distribution in the active components of PAFC after operation. Key: (- - -) virgin; (——) 700 h (300 mA cm^{-2}) + 5 h (o.c.v.).

where i_0 is the exchange current density, and SA is the surface area of the platinum particles, CL is the amount of platinum in the electrode, and CU is the platinum utilization in an electrode reaction. F, R and T have their usual meanings. Figure 4 was obtained using Equation 3 from the data from our previous work [11]. Figure 4 shows the change in the activation polarization against the change in platinum loading for two different cases. In one case, the change in platinum loading is only estimated (circles). In the other case, the change in platinum loading and Pt surface area are both calculated (triangles). This Figure shows that the increase in the activation polarization (triangles) after 1400 min was around 85 mV, while the loss of iR-free voltage (H_2/O_2) was around 80 mV at that time. This means that the voltage loss appearing as the change in iR-free voltage (H_2O_2) can be almost completely explained in terms of activation polarization using the change in platinum loading and platinum surface area.

3.4. *Potential and temperature dependence on platinum dissolution rate*

A quantitative investigation was conducted to obtain a correlation between the potential and platinum dissolution rate, and between the temperature and the dissolution rate. By combining an operating condition, such as potential and temperature, with the platinum

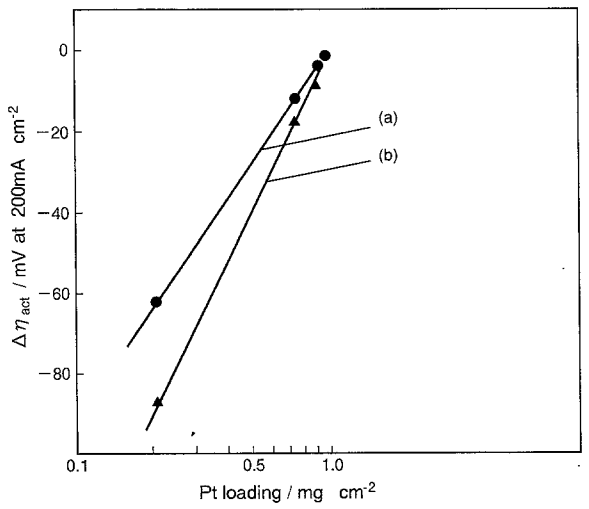

Fig. 4. Relation between Pt loading and activation polarization: Equation 3 (from [11]). Key: (●) using the change of Pt loading; (▲) using the change of Pt loading and surface area. (a) 92 mV decade^{-1}; (b) 130 mV decade^{-1}.

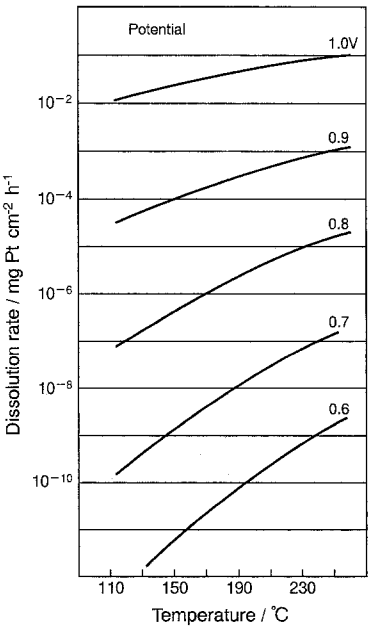

Fig. 5. Dependence of temperature on Pt dissolution rate as a function of potential (from [11]).

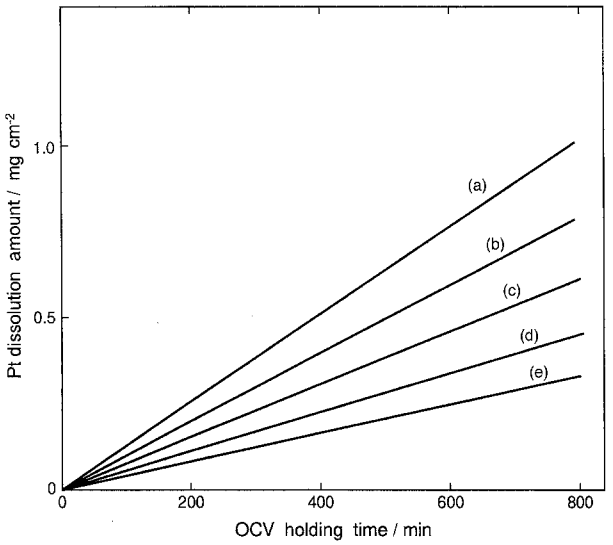

Fig. 6. Relationship between Pt dissolution amount and o.c.v. holding time as a function of temperature (calculated). T: (a) 230, (b) 210, (c) 190, (d) 170 and (2) 150 °C.

dissolution rate and the cell voltage, the effect of the operating conditions on cell voltage was examined.

The relationship between the potential and the platinum concentration was obtained using Bindra's data [9] and the following equation was obtained.

$$E = 1.129 + \frac{RT}{2F}\ln(C) \qquad (4)$$

When the o.c.v. is 1.0 V, this equation gives a platinum concentration of 1.53×10^{-3} M at 190 °C. Assuming that the diffusion of platinum ions is the rate determining step in the platinum dissolution-migration process [6], the diffusion rate of platinum ions from the cathode can be obtained using Fick's first law. The calculated result is 1.49×10^{-4} mg cm^{-2} s^{-1}. This result does not agree with the data ($v = 1.25 \times 10^{-5}$ mg cm^{-2} s^{-1}) in [11]. This difference may arise from the difference between the samples. Bindra used a bulk platinum sample, while a gas diffusion electrode was used in the present experiment. To reconcile the two sets of data, a coefficient was introduced. The coefficient was obtained at a temperature of 190 °C assuming both temperature dependencies on the dissolution rate were the same. Thus, the following equation was obtained:

$$v = 8.2 \times 10^{-3}\exp\left(\frac{E - 1.129}{RT/2F}\right) \qquad (5)$$

Figure 5 shows the calculated results of the relationship between the platinum dissolution rate and the cell temperature as a function of potential. This Figure indicates the platinum dissolution rate under operational conditions. Furthermore, the platinum loading can be obtained from this dissolution rate after a given time, and the performance loss due to the decrease in the platinum loading can be estimated using the data in Fig. 4.

Using Equation 5 and the data shown in Fig. 4, the order estimation of cell voltage decay rate can be made when the cell was operated under a given condition. In a PAFC application the cell might be held at a high potential (e.g. o.c.v.) at startup and in an emergency stop. Therefore, the range of tolerance for o.c.v. should be estimated for the system design.

Figure 6 shows the amount of platinum dissolution at o.c.v. as a function of temperature. It was found that 0.4 mg cm^{-2} of platinum dissolves in 500 min at o.c.v., 190 °C. Figure 7 shows the relationship between time and temperature, which shows a decay rate of 5 mV and 10 mV per 1000 hours. Figure 7 shows that it takes around 360 min at 100 °C and around 2000 min at room temperature for a decay of 5 mV per 1000 h. These results show that the cell voltage is degradated through irreversible decay (dissolution) of the platinum catalyst at a low temperature when air and fuel gas are fed to the cell. Figure 8 shows the relationship between time and the cathode

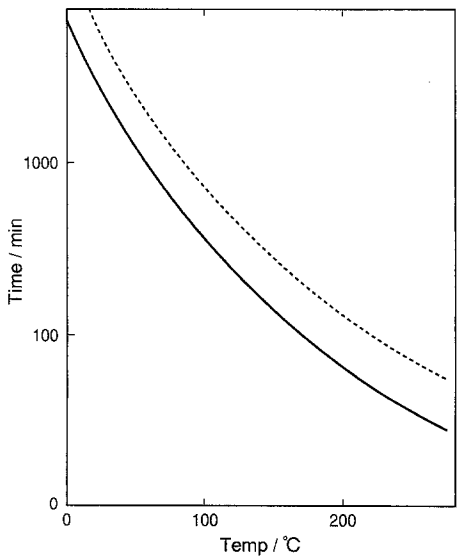

Fig. 7. Relationship between time and temperature, showing 5 (——) and 10 mV (- - -) decay per 1000 h at 1.0 V (o.c.v.).

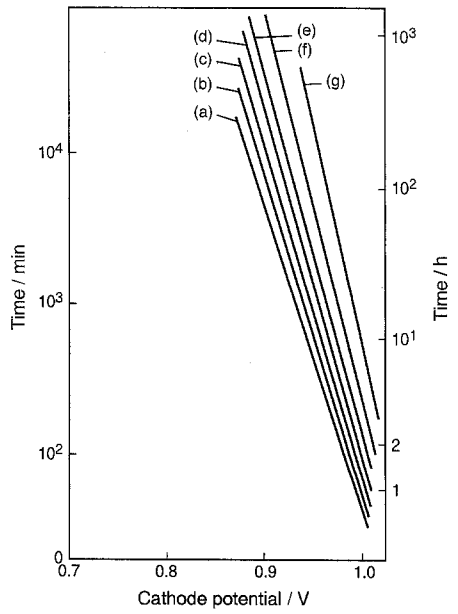

Fig. 8. Relationship between time and cathode potential as a function of temperature, showing 5 mV decay per 1000 h. T: (a) 230, (b) 210, (c) 190, (d) 170, (e) 150, (f) 120 and (g) 80 °C.

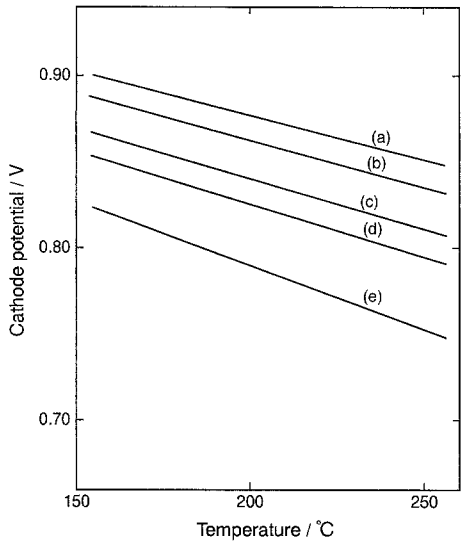

Fig. 9. Relationship between cathode potential and temperature which shows typical decay rates. Curves: (a) $E = 1.129 - 5.30 \times 10^{-4}\,T$ (10 mV/1000 h); (b) $E = 1.129 - 5.65 \times 10^{-4}\,T$ (5 mV/1000 h); (c) $E = 1.129 - 6.12 \times 10^{-4}\,T$ (1 mV/1000 h); (d) $E = 1.129 - 6.48 \times 10^{-4}\,T$ (0.5 mV/1000 h); (e) $E = 1.129 - 7.17 \times 10^{-4}\,T$ (0.1 mV/1000 h).

potential, which shows the 5 mV decay as a function of temperature.

In these calculations, the solubility of platinum ions at high temperature was extrapolated to low temperature and so an estimation error was introduced. However, the platinum dissolution rate decreases at lower temperatures. Furthermore, the platinum diffusion rate also decreases due to the increase in viscosity of the phosphoric acid at lower temperature. In this context the calculated results, which were obtained using the data at the higher temperature, shows a larger value than in the real case. Therefore, these calculated results may be used as a safety index in system design.

From these Figures, the following results were obtained. At o.c.v. the performance decay is negligible over short times, such as several tens of minutes; it is not negligible, however, even at room temperature, for longer holding times. A decay of 5 mV was calculated at conditions of 80 °C for 600 min, and room temperature for 2000 min.

The potential dependence of the performance decay rate at a rated power operation was estimated. Assuming that the cell is operated at a constant voltage, the relationship between the cathode potential and a temperature which provides a given decay rate is obtained. Figure 9 shows relationships giving decay rates of 0.1, 0.5, 1, 2, 5 and 10 mV per 1000 h. These estimations indicate that the performance decay due to platinum dissolution can be neglected under normal operational conditions and that the cell has to be maintained under operational conditions milder than 200 °C, 840 mV (*iR*-free) to obtain the decay rate of 1 mV per 1000 h.

In a real cell, the cathode potential (*iR*-free) is maintained below 800 mV. Therefore, at a rated power operation, the performance decay due to platinum dissolution should be negligible.

4. Conclusion

The stability of platinum catalyst in a PAFC was studied. The platinum dissolution–redeposition and migration in the cell depended on the operation mode. The dissolution rate from the cathode was measured using an accelerated mode of o.c.v. At the o.c.v., the platinum loading in the cathode decreased to 20% of the nominal loading after 1400 min. At that time, the performance loss was 114 mV. This value includes not only the catalytic activity, but also the diffusion loss caused by the corrosion reaction at the high potential.

The dissolution rate of platinum catalyst was estimated as a function of potential and of temperature, assuming that the diffusion of platinum ions in the electrolyte is the rate determining process. The present results show the influence of potential and temperature on the stability of the platinum catalyst and the cell performance in a phosphoric acid fuel cell. It was found that the performance decay due to platinum dissolution can be neglected under normal operational conditions and that the cell has to be maintained under operational conditions milder than 200 °C, 840 mV (*iR*-free) to obtain a decay rate of 1 mV per 1000 h.

References

[1] J. Aragane, T. Murahashi and T. Odaka, *J. Electrochem. Soc.*, **135** (1988) 844.
[2] *Idem, ibid.*, references [1–9] cited therein.
[3] M. T. Paffett, W. Hutchinson, J. D. Farr, P. Papin, J. G. Beery and S. Gottesfeld, *J. Power Sources* **36** (1991) 137.
[4] S. Mukerjee and S. Srinivasan, *J. Electroanal. Chem.* **357** (1993) 201.
[5] R. P. Iczkowski and M. B. Cutlip, *J. Electrochem. Soc.* **127** (1980) 1433.
[6] J. Giner and C. Hunter, *ibid.* **116** (1969) 1124.
[7] J. Aragane, H. Urushibata and T. Murahashi, *ibid.* **141** (1994) 1804.
[8] J. Aragane, H. Urushibata and T. Murahashi, *J. Electrochem. Soc. of Japan* **63** (1995) 642.
[9] P. Bindra, S. J. Clouser and E. Yeager, *J. Electrochem. Soc.* **126** (1979) 163.
[10] P. N. Ross, Lawrence Berkeley Laboratory, Report LBL-19766-REV (1985).
[11] J. Aragane and T. Murahashi, *Nippon Kagaku Kaishi*, no. 10, (1988) 1670.
[12] P. Scherrer, *Göttinger Nach.* **2** (1918) 98, from B. D. Cullity, 'Elements of X-Ray Diffraction', Addison-Wesley Reading MA (1956) p. 99.
[13] K. Kinoshita and P. Stonehart, 'Modern Aspect of Electrochemistry', vol 12, p. 236, Plenum, New York (1977).
[14] D. N. Patel, H. C. Maru, M. Farooque and C. H. Ware, *J. Electrochem. Soc.* **131** (1984) 275.